ABSTRACT

NA, JEONG-SEOK. Nanoscale Assembly for Molecular Electronics and In Situ Characterization during Atomic Layer Deposition. (Under the direction of Dr. Gregory N. Parsons.)

The work in this dissertation consists of a two-part study concerning molecular-based electronics and atomic layer deposition (ALD). As conventional “top-down” silicon-based technology approaches its expected physical and technical limits, researchers have paid considerable attention to “bottom-up” approaches including molecular-based electronics that self assembles molecular components and ALD techniques that deposit thin films with atomic layer control.

Reliable fabrication of molecular-based devices and a lack of understanding of the conduction mechanisms through individual molecules still remain critical issues in molecular-based electronics. Nanoparticle/molecule(s)/nanoparticle assemblies of “dimers” and “trimers”, consisting of two and three nanoparticles bridged by oligomeric ethynylene phenylene molecules (OPEs), respectively, are successfully synthesized by coworkers and applied to contact nanogap electrodes (< 70 nm) fabricated by an angled metal evaporation technique. We demonstrate successful trapping of nanoparticle dimers across nanogap electrodes by dielectrophoresis at 2 VAC, 1 MHz, and 60 s. The structures can be maintained electrically connected for long periods of time, enabling time- and temperature-dependent current–voltage (I–V) characterization. Conduction mechanisms through independent molecules are investigated by temperature dependent I–V measurements. An Arrhenius plot of log (I) versus 1/T exhibits a change of slope at ~1.5 V, indicating the transition from direct tunneling to Fowler–Nordheim tunneling. Monitoring of the conductance is also performed in real-time during trapping as well as during other modification and exposure sequences.
after trapping over short-term and long-term time scales. The real-time monitoring of conductance through dimer structures during trapping offers immediate detection of a specific fault which is ascribed to a loss of active molecules and fusing of the nanoparticles in the junction occurring mostly at a high applied voltage (≥3 VAC). After successful trapping, the sample exposure to air reveals a small rapid decrease in current, followed by a slower exponential increase, and eventual current saturation.

This work also reports on the dependence of electron transport on molecular length (2 to 4.7 nm) and structure (linear-type in dimers and Y-type in trimers). The extracted electronic decay constant of ~0.12 Å⁻¹ and effective contact resistance of ~4 MΩ indicate a strong electronic coupling between the chain ends, facilitating electron transport over long distances. A three terminal molecular transistor is also demonstrated with trimers trapped across nanogap electrodes. The source-drain current is modulated within a factor of 2 with a gate bias voltage of −2 to +2 V. A subthreshold slope of ~110 mV/decade is obtained.

Finally, we report on both fundamental understanding and application of atomic layer deposition. First, in situ analysis tools such as quartz crystal microbalance and electrical conductance measurements are combined to reveal direct links between surface reactions, charge transfer, and dopant incorporation during ZnO and ZnO:Al ALD. Second, the ability of ALD to form uniform and conformal coating onto complex nanostructures is explored to improve the ambient stability of single molecules/nanoparticle assemblies using Al₂O₃ ALD as an encapsulation layer. In addition, the ability to shield the surface polarity of ZnO nanostructures using Al₂O₃ + ZnO ALD, leading to hierarchical morphology evolution from one-dimensional ZnO nanorods to three-dimensional ZnO nanosheets with branched nanorods during hydrothermal growth is investigated.
DEDICATION

This dissertation is dedicated to my wife, Sung Kyung Song,

my parents, Il Song Na and Im Soon Song,

and my parents-in-law, Eun Geun Song and Sun Hee Won

for their love, sacrifice and prayer.
BIOGRAPHY

Jeong-Seok Na was born in the small town of Soonchang in South Korea in 1973. Then he and his family moved to Kwangju where he was raised until 1992. During that period, he graduated from Korea High School in 1992 and was accepted into the Chemical Engineering at Hanyang University, Seoul. After receiving his Bachelor Degree in 1999, he continued studying at Pohang University of Science and Technology (POSTECH) to earn his Master’s Degree in which his research focused on the metalorganic chemical vapor deposition and characterization of high dielectrics ZrO$_2$ and TiO$_2$ thin films using novel precursors for application in an alternative of SiO$_2$ gate dielectrics of a transistor. After graduation in 2001, he joined the central research and development center, Samsung Electro-Mechanics Company in the city of Suwon, South Korea. After working in industry as a senior researcher for three and a half years, he decided to pursue an advanced doctoral degree in Chemical Engineering at North Carolina State University, Raleigh in the fall of 2004. Under the excellent guidance of Dr. Gregory Parsons, he focused on the fundamental research related to the nanoscale assembly and charge transport measurements in molecular-based electronics as well as the real-time analysis during atomic layer deposition.
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Chapter 1

Objective and introduction
1.1 Objective of this work

The primary objective of this thesis work is to gain a fundamental understanding of charge transport characteristics through single, independent molecules as well as correlations between surface reactions and charge transport during ALD processing.

For the molecular-based electronics portion of this thesis, the first goal is to fabricate the nanogap electrodes, assemble the nanoparticle structures that consist of two nanoparticles bridged by independent linear-type molecules of interest across the nanogap electrodes, and investigate the conduction mechanisms through the molecules/nanoparticle junctions. The second goal is real time monitoring of the dielectrophoretic trapping process and the electrical stability of molecular junctions upon exposure to various gas environments. The final goal is to demonstrate three-terminal molecular devices using nanoparticle structures consisting of three nanoparticles bridged by a Y-type single molecule.

In the atomic layer deposition section of this thesis work, the first goal is to reveal other important factors as well as the surface chemistry to influence the surface reactions during ZnO:Al ALD. The second goal is to explore correlations between the surface deposition reactions, charge transport and dopant activation that occurs during ZnO and Al-doped ZnO (ZnO:Al) ALD by utilizing in situ quartz crystal microbalance and electrical conductance measurements. The final goal is to explore the Al₂O₃ and Al₂O₃+ZnO ALD to improve the ambient stability of the nanoparticle/molecule junctions as an encapsulation layer, and to shield the surface polarity of ZnO nanorods leading to hierarchical morphology evolution from nanorods to nanosheets, respectively.
1.2 Background of Molecular-based Electronics

1.2.1 Charge Transport Properties of Organic Molecules

Since it is suggested that a single molecule with a donor–spacer–acceptor (d–s–a) structure between two electrodes behaves as a molecular rectifier by Aviram and Ratner, various molecules have been reported as described in Figure 1.1, showing different applications such as molecular wires, switches, rectifiers, storage, and mono-molecular electronics depending on molecular structures between two electrodes. Charge transport properties through molecules are affected by intrinsic factors such as molecular length, conformation, highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) gap, and also by the type of molecule-electrode contact, and the electrode work function. Molecular wires have been studied intensively, which can be divided into two categories as shown in Table 1.1.

One is saturated alkane chains chemisorbed on Au or Hg via S atoms, which have high HOMO-LUMO gap of ~7 eV and exhibit relatively insulating properties. The other is π-conjugated molecules with relatively smaller HOMO–LUMO gap of 3–5 eV. Recently, it is reported the existence of molecule-electrode chemical bond plays a crucial role on the junction behavior. For alkanethiol based junctions, the current difference between physical and chemical contacts can be up to three orders of magnitude, indicating the absence of a chemical bond gives rise to an additional barrier. For π-conjugated molecules, however, the contact effects appear much less important than for saturated ones because the π-orbitals of
the molecule overlap with the metal, causing a relatively higher tunneling efficiency even without chemical bonds.

Figure 1.1  The molecules described in the text. (a) Wires; (b) hybrid molecular electronic (HME) switches; (c) HME rectifiers; (d) storage; and (e) two molecules showing promise for mono-molecular electronics.¹
Table 1.1  Electronic transports between saturated alkane chains and π-bonded molecules.

<table>
<thead>
<tr>
<th>Items</th>
<th>Classification</th>
<th>Saturated alkane chains</th>
<th>Conjugated π-bonded molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Molecular properties</strong></td>
<td>Structure</td>
<td>$(\text{CH}_2)_n$</td>
<td>$(\text{C}_6\text{H}_5)_n$</td>
</tr>
<tr>
<td></td>
<td>HOMO-LUMO gap</td>
<td>$\sim7$ eV</td>
<td>$\sim3.5$ eV (oligo-phenylene ethylene) $\sim5$ eV (phenyl group)</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (tunneling decay parameter)</td>
<td>$0.6 \sim 1.0$ Å⁻¹</td>
<td>$0.2 \sim 0.6$ Å⁻¹</td>
</tr>
<tr>
<td></td>
<td>Conformation effect</td>
<td>-</td>
<td>transport efficiency: planar (delocalized) $&gt;$ perpendicular (localized)</td>
</tr>
<tr>
<td></td>
<td>Substituted molecule effect</td>
<td>-</td>
<td>Negative differential resistance, HOMO-LUMO gap decrease</td>
</tr>
<tr>
<td><strong>Metal-molecule contact</strong></td>
<td>Chemicontact (orphysicontact) effect</td>
<td>Up to 3 orders of magnitude</td>
<td>Only an order of magnitude - chemicontact: much less important - relatively high tunneling efficiency even without chemicontact</td>
</tr>
<tr>
<td><strong>Overall current properties</strong></td>
<td>Current</td>
<td>-</td>
<td>1-1.5 orders of magnitude higher than saturated (σ-bonded) molecules</td>
</tr>
<tr>
<td></td>
<td>Current transport</td>
<td>tunneling</td>
<td>Tunneling + hopping (?)</td>
</tr>
</tbody>
</table>

Possible conduction mechanisms through organic molecules can be deduced based on temperature-dependent current-voltage (I–V) characteristics as described in Table 1.2. According to the thermal dependence of the device, conduction mechanism can be divided into two categories. One is thermionic or hopping conduction, which has temperature dependent I–V characteristics. The other is direct tunneling ($V < \Phi_B/e$) or Fowler-Nordheim tunneling ($V > \Phi_B/e$), which does not have temperature dependent I–V characteristics.
Table 1.2 Possible conduction mechanisms.

<table>
<thead>
<tr>
<th>Conduction mechanism</th>
<th>Characteristic behavior</th>
<th>Temperature dependence</th>
<th>Voltage dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct tunneling</td>
<td>$J \approx V \exp\left(-\frac{2d}{\hbar}\sqrt{2m\Phi}\right)$</td>
<td>none</td>
<td>$J \approx V$</td>
</tr>
<tr>
<td>Fowler-Nordheim tunneling</td>
<td>$J \approx V^2 \exp\left(-\frac{4d\sqrt{2m\Phi^{3/2}}}{3q\hbar V}\right)$</td>
<td>none</td>
<td>$\ln\left(\frac{J}{V^2}\right) \approx \frac{1}{V}$</td>
</tr>
<tr>
<td>Thermionic emission</td>
<td>$J \approx T^2 \exp\left(-\frac{\Phi - q\sqrt{qV/4\pi\alpha d}}{k_B T}\right)$</td>
<td>$\ln\left(\frac{J}{T^2}\right) \approx \frac{1}{T}$</td>
<td>$\ln(J) \approx V^{1/2}$</td>
</tr>
<tr>
<td>Hopping conduction</td>
<td>$J \approx V \exp\left(-\frac{\Phi}{k_B T}\right)$</td>
<td>$\ln\left(\frac{J}{V}\right) \approx \frac{1}{T}$</td>
<td>$J \approx V$</td>
</tr>
</tbody>
</table>

These two tunneling mechanisms can be distinguished by voltage dependencies. When the Fermi level of the metal is aligned closely to one energy level (HOMO or LUMO), the Simmons model is a good approximation method, which can be utilized to obtain the tunneling current density through a barrier in the voltage range of $V < \Phi_B/e$ given by

$$I = \left(\frac{q}{4\pi^2 \hbar^2}\right)\left\{\left(\Phi_B - \frac{qV}{2}\right) \cdot e^{-\frac{2(2m)^{1/2}}{\hbar} \alpha(\Phi_B + \frac{qV}{2})^{1/2}} - \left(\Phi_B + \frac{qV}{2}\right) \cdot e^{\frac{2(2m)^{1/2}}{\hbar} \alpha(\Phi_B + \frac{qV}{2})^{1/2}}\right\}$$

where $\hbar$ is the reduced Plank’s constant, $\Phi_B$ is the effective barrier height in the metal-insulator interface, $\alpha$ is a dimensionless adjustable parameter and $m$ is the mass of electron. The adjustable parameter ($\alpha$) is used to correct the simple rectangular barrier model to account for the effective mass of the electron. By using the nonlinear least square fitting, the values of $\Phi_B$ and $\alpha$ can be calculated.
1.2.2 Fabrication and Characterization of Metal-Molecule-Metal Junctions

Considerable attention has been paid to the electrical characterization of individual molecules during the last decade to realize the molecule-based electronics. However, there are many obstacles to impede further progress in the field of nanometer-scale electron transport, one of which is the lack of reliable methods to bridge a chemically synthesized nanostructure to macroscopic electronic circuits. Recently, many different approaches have been proposed to resolve this problem. They can be broadly divided into three categories. First is defining a nanometer-sized electrode gap through fabrication methods. Second is utilizing scanning probe microscope such as conducting probe atomic force microscopy or scanning tunneling microscopy. The final is assembling nanoparticles between the electrode gaps.

*Crossed wire tunnel junction*: Crossed-wire junction junctions were pioneered by Gregory\(^6\) and have been used to measure the inelastic electron tunneling spectra of the molecular adsorbates\(^6\) as well as to study Coulomb blockade.\(^7\) Kushmerick *et al.* performed the first measurements of electron transport across organic monolayers with a crossed-wire tunnel junction.\(^8\)-\(^10\) A schematic representation of a crossed wire tunnel junction is shown in Figure 1.2. The 10 µm diameter wires, one modified with a self-assembled monolayer of interest, are mounted to a custom built test stage so that the wires are in a crossed geometry with one wire perpendicular to the applied magnetic field (B). The junction separation is controlled by deflecting this wire with Lorentz force generated from a small dc current (<5
mA). This deflection current is slowly increased to bring the wires gently together, making a junction at the contact point.

![Schematic showing the crossed-wire tunnel junction.](image)

**Figure 1.2** Schematic showing the crossed-wire tunnel junction.

All measurements are acquired in the low applied force region with constant junction resistance. However, above a certain threshold force, the drop in resistance occurs due to the monolayer distortion. Crossed-wire tunnel junction is considered to contain ~10³ molecules. Since a direct comparison between the measured tunneling current in the crossed-wire tunnel junction and the tunneling current from a single molecule measured by STM shows a factor of 10³ difference, it has been suggested that the overall conductance of a set of parallel conjugated molecules is a linear superposition of the individual conductances.

*Thermally evaporated top contact through nanopore:* Electronic measurements can be performed in a nanostructure that has a metal top contact, a self-assembled monolayer (SAM) active region, and a metal bottom contact as shown in Figure 1.3. The essential feature of this fabrication process is the use of a nanoscale device area, which gives rise to a small number of self-assembled molecules (~1000) and also eliminates pinhole and other
defect mechanisms that hamper through-monolayer electronic transport measurements.

Figure 1.3  Schematics of a nanometer-scale device with a nanometer-scale pore etched through a suspended silicon nitride membrane showing a Au-SAM-Au junction formed in the pore area.\textsuperscript{12}

The starting substrate for the device fabrication is a 250-\textmu m-thick double-side polished silicon (100) wafer, on which 50 nm of low-stress Si\textsubscript{3}N\textsubscript{4} is deposited by low pressure chemical vapor deposition. On the back surface, the nitride is removed in a square 400 \textmu m by 400 \textmu m by optical lithography and reactive ion etching (RIE). The exposed silicon is etched in an orientation-dependent anisotropic etchant (at 85 °C in a 35 % KOH solution) through to the top surface to leave a suspended silicon nitride membrane 40 \textmu m by 40 \textmu m. And then 1000 Å of SiO\textsubscript{2} is thermally grown on the Si sidewalls to improve electrical insulation. A single hole with 30 to 50 nm in diameter is made through the membrane by electron beam lithography and RIE, producing the bowl-shaped geometry of the cross section.
Au contact of 200 nm thickness is evaporated onto the top side of the membrane, filling the pore with Au. The sample is then immediately transferred into a solution to self-assemble. As soon as the SAM layers are formed, the sample are quickly loaded into a vacuum chamber, and mounted onto a liquid nitrogen cooling stage to evaporate the bottom Au electrode, in which 200 nm of Au is evaporated at 77 K at a rate of less than 1 Å/s. Negative differential resistance (NDR) behavior was observed using a molecule containing a nitroamine redox center as the active self-assembled monolayer in the nanopore device.\textsuperscript{11,12}

Since the temperature dependent current-voltage measurements were possible using the nanopore device, the intrinsic conduction mechanisms were investigated and inelastic electron tunneling (IET) spectra were observed and analyzed.\textsuperscript{5}

\textit{Mercury drops:} Electron tunneling experiments were performed using Hg-SAM/SAM-Hg or Hg-SAM/SAM-M′ junctions,\textsuperscript{14-17} where M′ is a flat metal surface. Since mercury is a liquid metal with high affinity for thiols, these junctions have several advantages: (i) They are relatively easy to assemble and mechanically stable. (ii) They allow statistically large numbers of measurements. (iii) They measure the currents over small but significant areas (~1 mm\textsuperscript{2}, or ~10\textsuperscript{12} molecules) of contact. (iv) The junctions can be extended to either systems other than thiols or electrodes with different metals (Ag, Au, Cu, Hg) and alloys. There are disadvantages of these junctions as well: (i) They do not provide the molecular level resolution compared to STM and break junctions. (ii) They do not support the temperature-dependent current-voltage characterization. (iii) They probably cannot be developed into practically useful microelectronic components.
Mechanically controlled break junction (MCB): Measurements of electronic transport through a single molecule (or at most very few) were carried out using lithographically fabricated mechanically controlled break junction (MCB)\textsuperscript{18-20} to provide an electrode pair with tunable distance as shown in Figure 1.4.

![Figure 1.4](image)

Figure 1.4 Scanning electron microscope image of the lithographically fabricated break junction.\textsuperscript{18}

To obtain a contact to a single molecule from both electrodes, an electrode pair with a distance matching exactly this length is required. This setup is mounted in a three-point bending mechanism driven by a threaded rod. The substrate is bent to elongate the bridge and finally broken. Then the two open ends form an electrode gap which can be adjusted mechanically with subangstrom precision. The molecules with acetyl protection groups at the ends are dissolved in THF. A droplet of this solution is put on top of the opened MCB. When the molecules approach the surface of any of the gold electrodes, one of the acetyl protection groups splits off and a stable chemical bond between the sulfur atom and the gold surface is established. The opposite side of the molecule remains protected at this stage. After the solvent is evaporated, the whole setup is mounted in an electromagnetically
shielded box under a pressure of $10^{-7}$–$10^{-6}$ mbar. While the electrodes are approaching each other from large distances, the resistance decreases exponentially with distance and then at a certain distance, the system suddenly locks into a stable behavior indicating a metal-molecule-metal junction. In this system, however, different types of current-voltage characteristics, that is, symmetry or asymmetry in the I-Vs, can be observed with the same molecule even though all contacts are chemically stable.\textsuperscript{18}

Electromigration-induced break junction: A simple yet highly reproducible method to generate two metallic electrodes with a nanometer-sized gap has been presented. The fabrication is based on the breakage of metallic nanowires using electromigration of metal atoms as shown in Figure 1.5.\textsuperscript{21-27} Electromigration refers to the atomic motion in a conductor subject to large current density. The breaking process consistently produces two metallic electrodes whose typical separation is about 1nm. The electrode fabrication process begins with the generation of gold nanowires using conventional electron-beam lithography and shadow evaporation. Electron-beam lithography on a PMMA/P(MMA–MAA) bilayer resist is used to make a 200-nm-wide resist bridge suspended 400 nm above a SiO$_2$ substrate. Metallic nanowires are formed by evaporating 35-Å-thick chromium and 100-Å-thick gold at $\pm$ 15$^\circ$ angles relative to substrate normal. Finally, 35-Å-thick chromium and 800-Å-thick gold are deposited straight down through the resist bridge to ensure the reliable bonding between the nanowires and the gold bonding pads. Nanometer-sized gap is formed by ramping a voltage across the wires until a sudden drop in their conductivity occurs as a result of their breaking. The breakage of a nanowire is typically observed to occur near the region where two angle-evaporated electrodes overlap due to the high resistance associated with the
region. Using this break junction, the measurements of electron transport through a nanocrystal with SAM formed on gold electrodes, a small ensemble of a few OPE molecules with nitro moiety, and single C60 molecules have been performed.

**Figure 1.5** Field-emission scanning electron micrographs of a representative gold nanowire (a) before and (b) after the breaking procedure. The nanowire consists of thin (~10 nm) and thick (~90 nm) gold regions.

Conducting Probe Atomic Force Microscopy (CP-AFM): Metal-molecule-metal junctions are formed by using conducting probe atomic force microscopy (CP–AFM), where a junction is fabricated by placing a conducting AFM tip in contact with a metal-supported molecular film such as self-assembled monolayer (SAM) on Au as shown in Figure 1.6. The normal force feedback circuit of the AFM controls the mechanical load on the microcontact while the current-voltage characteristics are monitored. The ability to control the load on the microcontact is the unusual characteristics of this type of junction. The load-dependent tip-SAM contact area in these junctions is small (or order 10 nm²). This means the junction properties are mainly from a small number of molecules, typically less
than 100 for a 50 nm radius probe.

Figure 1.6  Scheme of the conducting probe atomic force microscopy experiment. Voltages are applied to the tip; the substrate is kept at ground. Measurements are performed in air.

A key advantage of CP-AFM for junction formation is that no micro- or nanofabrication processes are necessary and also molecules may be contacted by any conducting film that can be coated onto an AFM tip, providing flexibility for investigating the role of contacts on the junction $I-V$ behavior. Compared to STM, CP-AFM allows the probe to be controllably positioned just in contact in with the monolayer using an independent feedback signal, namely normal force. The load and length dependence of electron tunneling through a SAM of interest have been investigated.$^{28-30,33}$

**Scanning Tunneling Microscopy (STM):** The ability to probe individual molecules with atomic precision makes the STM an ideal tool for studying molecular electronics.$^{38-42}$ However, there exist some differences between the CP-AFM method and STM for characterizing molecular junctions. In STM, current, not force, is used to control tip-
positioning. If the STM tip is not in contact with the monolayer, the electron tunneling properties through the junction are determined by the molecules and the vacuum (or air) gap between the molecules and the tip. If the tip penetrates the monolayer, it is difficult to figure out how far it has penetrated and thus what portions of the molecules contribute to the current. The electron tunneling properties of a single-molecular junction can be measured using STM when isolated single molecules are formed in the SAM matrix. Because there exists the change in the STM heights caused by the thermal motion of molecules at room temperature, STM is used after cooling down the sample to prevent the thermal motion.

Nanoparticle/Molecule/Nanoparticle Assemblies between the electrodes: Although various methods have been reported to measure the conductance of molecular junctions, there still remain some difficulties, which include the uncertainty about the number of molecules in the junction and the lack of information about the shape and structure of the metal-molecule contacts. Recently, the dimer-based contact method is presented to measure the conductance of single conjugated molecules and provide several advantages as reported by Dadosh et al.\textsuperscript{43} (1) metal-single molecule contact can be fabricated with high certainty. (2) The need to fabricate nanometer-sized gaps can be avoided. (3) The temperature dependent current-voltage characteristics can be allowed over periods of hours and even days. Preparation method of molecularly bridged metal nanoparticles has been reported by several groups.\textsuperscript{21,22,43-46} The electrodes are fabricated on an electron beam defined pattern, consisting of Au/Ni layers. Electrostatic trapping method can be utilized as one of the techniques to assemble the synthesized nanoparticle/molecule/nanoparticle assemblies “dimer” between the nanoscale electrode gaps. The electrostatic trapping is reported to achieve relatively high
success rate of 50% and show stable contact properties even over a period of a few hours.\textsuperscript{43,47,48}

1.2.3 Assembly of Particles between the Electrodes

To obtain electron transport characteristics through metal-molecule junctions, nanoparticles (or molecularly bridged nanoparticles) can be assembled onto the electrode gaps with (or without) functionalized SAMs using various trapping methods driven by (i) radiation force from photon momentum change, (ii) dragging force of withdrawing meniscus water, (iii) magnetic field gradients, and (iv) electric field gradient.

\textit{Optical trapping:} The optical trapping/manipulation of single microparticles was first demonstrated by Ashkin in 1970.\textsuperscript{49} Optical trapping/manipulation is sometimes referred to as laser trapping/manipulation or optical/laser tweezers.\textsuperscript{50-56} A basic principle of optical trapping of a single microparticle is the refraction of a focused laser beam through the particle, as shown schematically in Figure 1.7.

\textbf{Figure 1.7} The principle of optical trapping of a single particle by a focused laser beam.\textsuperscript{54}
The refraction of light induces a photon momentum change, since the propagation direction and the wavelength of light vary in media with different refractive indices. The change in the light momentum, $\Delta P = P_1 - P_2$ where $P_1$ and $P_2$ are the momentum before and after refraction, respectively, should be conserved, so that a force is exerted on the particle with a direction opposite to that of the momentum change: $-\Delta P$. When the refractive index of the particle ($n_p$) is larger than that of the surrounding medium ($n_m$), the net force generated by the laser beam is directed to the focal point of the beam: $f$ in Figure 1.7. This force is called “radiation force” or “radiation pressure”, and acts as the driving force for optical trapping. Under the condition $n_p < n_m$, however, a particle experience the repulsive force from the laser beam. One technical method to trap such particles is the scanning laser micromanipulation, which is fast and repetitive circular scans of a focused laser beam around a particle to be trapped (or “encaged”). In addition to particles with $n_p < n_m$, metal particles with high reflection and/or absorption coefficient at the wavelength of the incident light also experience repulsive forces from it. Metal particles such Au, Ag, and Cu can be trapped optically by a TEM$_{01}$-mode laser beam with an intensity minimum on the beam axis as well as the scanning method.

*Receding meniscus:* The effort to precisely position (bio)molecules onto microstructured substrates has been made using a receding meniscus generated by a drying droplet. Receding meniscus method allows DNA molecules to be aligned and also avoids the possible damage during fabrication (e.g., metallization prior to electrical measurement). Chu et al. in our group assembled the nanoparticles onto a SAM-functionalized nanoscale electrode gap. Nanoparticle solution drop forms a meniscus near the probe needle and a few nanoparticles enter into the electrode gaps due to the dragging
force of withdrawing meniscus water. Therefore, the electron transport measurements of the molecules of interest are possible using SAM-nanoparticles-SAM bridge structure between the electrode gaps.

*Magnetic directed assembly:* A magnetic directed-assembly technique was reported to make molecular junctions based on magnetically susceptible and electrically conductive microspheres\(^4\) and also to fabricate carbon nanotube field-effect transistors\(^6\) between magnetic source/drain electrodes. Magnetic directed assembly utilizes localized magnetic fields within a ferromagnetic array to direct magnetically susceptible species to the high-field region between micro-scale electrodes. Magnetic directed assembly has several desirable properties in terms of device fabrication such as high yield, accurate placement, and predictable orientation for assembled species. Fabrication procedure is shown in Figure 1.8.

![Illustration and SEM image of magnetic assembly](image)

**Figure 1.8** (a) Illustration showing the fabrication of hemispherically metallized silica microspheres and their magnetic controlled assembly onto SAM-functionalized electrodes. (b) SEM image showing such a microsphere junction.\(^5\)
The assembly efficiency shows that approximately 60% of junctions exhibit single bead, 20-30% show two to three beads, and 10-20% remain empty.\(^\text{46}\) In terms of contact stability, it is found that the I–V characteristics are reproducible over several days and also are able to stand up to applied bias of 2 V. Magnetic-directed assembly is suggested to provide a simple method for the parallel fabrication of molecular junctions.

**Electrostatic trapping:** The movement of polarizable particles in non-uniform fields, termed dielectrophoresis by Pohl\(^\text{62}\) has been utilized as a useful non-invasive, non-destructive tool for separation of micro-organisms\(^\text{62,63}\) and trapping of nanoparticles\(^\text{43,44,64-77}\) and carbon nanotubes.\(^\text{78-84}\) The basic principle of dielectrophoresis is that when placed in a non-uniform alternating current (AC) electric field, polarized particles experiences a variable translational force, depending on the field frequency. For a homogeneous dielectric particle suspended in an aqueous medium, the time-averaged DEP force can be expressed as

\[
F(\omega) = 2\pi\varepsilon_m r^3 \text{Re}(f_{CM}) |\nabla E_{rms}|^2
\]

where \(\omega\) is the angular field frequency, \(r\) is the particle’s radius, \(f_{CM}\) is the Clausis-Mossoti factor given by

\[
f_{CM} = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*}
\]

where \(\varepsilon_p^*\) and \(\varepsilon_m^*\) is the complex permittivities of the particle and the medium, respectively.

For a real dielectric, the complex permittivity is

\[
\varepsilon^* = \varepsilon - j\frac{\sigma}{\omega}
\]
where \( j = \sqrt{-1} \), \( \varepsilon \) is the permittivity and \( \sigma \) is the conductivity of the dielectric. From equation (1), the absolute value of DEP force depends on the term \( V|E_{rms}|^2 \), (a factor related to the geometry of the electric field) and on the real part of \( f_{CM} \), the in-phase component of the particle’s effective polarizability. The real part of \( f_{CM} \) is bounded by the limits \( 1 < \text{Re}(f_{CM}) < -\frac{1}{2} \) and varies with the frequency of the applied field and the complex permittivity of the medium. Positive DEP occurs when \( \text{Re}(f_{CM}) > 0 \), the force is towards regions of highest field strength. However, when \( \text{Re}(f_{CM}) < 0 \), the force is towards decreasing field strength and the particles are repelled from the electrode edges. The direction of DEP force is shifted at the crossover frequency at which the Clausis-Mossotti factor crosses from positive to negative. Dielectric constants of various materials are given in the table 1.3 below.

**Table 1.3**  
**Dielectric constants of various materials.**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Water</th>
<th>Cyclohexane</th>
<th>Acetone</th>
<th>Ethanol</th>
<th>Polystyrene</th>
<th>Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>80</td>
<td>2.03</td>
<td>21</td>
<td>26</td>
<td>2.55</td>
<td>( \infty )</td>
</tr>
</tbody>
</table>

In case of metal nanoparticles in aqueous medium, \( \text{Re}(f_{CM}) \sim 1 \), indicating that positive DEP always occurs independent of the frequency of the applied field.
1.3 Background of Atomic Layer Deposition (ALD) Process

Atomic layer deposition (ALD) was first introduced as atomic layer epitaxy (ALE) in the late 1970s by Suntola and co-workers as a means of depositing amorphous and polycrystalline films for application to thin film electroluminescent displays. After successful introduction of ALD, many efforts were made to grow III–V compound semiconductors via ALD. Since the mid 1990s, there have been considerable interests in exploiting the ALD technology in the silicon-based microelectronics industry. These rapid interests result from the needs for continuous miniaturization of device dimensions and conformal coating in the trench regions with higher aspect ratio in integrated circuits (IC).

ALD technique is based on the sequential self-limiting gas-solid reactions and consists of repeating the following four steps: (i) A self-terminating reaction of the first reactant (reactant A), (ii) A purge or evacuation to remove the nonreacted reactants and the gaseous reaction by-products, (iii) A self-terminating reaction of the second reactant (reactant B), (iv) A purge or evacuation. Steps (i)–(iv) form one reaction cycle, as shown in Figure 1.9. Here the self-limiting growth implies that the amount of the film deposited during each cycle is the same and is governed only by the density of the chemisorption or reaction sites at the surface. In an ALD process, a plot of growth rate versus substrate temperature exhibits a plateau or inflection region, where self-limiting ALD reaction occurs, as depicted in Figure 1.10. This temperature range is often called the “ALD process window”. At lower temperatures than this range, excess reactant condensation typically leads to a larger growth rate, whereas insufficient activation energy for chemisorption or reaction results in reduced growth rate. At higher temperatures, film growth rate may be increased by thermal
decomposition of reactants or decreased by desorption of desired products of reactants. Insufficient dosing of reactants or purging results in gas-phase mixing and reaction of alternate reactants, which can prevent a process from being ideal self-limiting within the ALD temperature window.

Figure 1.9  Schematic illustration of one ALD reaction cycle.
Here, Al₂O₃ ALD is chosen as a sample case because Al₂O₃ is one of the most widely studied materials grown by ALD and can be deposited even at low temperatures (<100 °C). This results in the utilization of Al₂O₃ for encapsulation of organic devices without degradation. It is well known that ALD process provides densely packed, continuous, and highly conformal coatings. There are three different approaches for ALD of Al₂O₃: (i) Trimethylaluminum (TMA) + water, (ii) TMA + O₃, and (iii) TMA + oxygen radicals obtained from remote plasma discharge.
**ALD using $H_2O$.** The $Al_2O_3$ film growth is performed according to two self-limiting surface reactions exposed to TMA and water, which can be described in the following two reactions.

(a) $Al\text{-}OH^* + Al(CH_3)_3 \rightarrow Al\text{-}O\text{-}Al(CH_3)_2^* + CH_4$

(b) $Al\text{-}CH_3^* + H_2O \rightarrow Al\text{-}OH^* + CH_4$

where asterisks (*) denote the surface species. Groner et al. pointed that the major problems of low temperature $Al_2O_3$ ALD are high hydrogen concentrations caused by the Al-OH surface species and very long H$_2$O purge times. However, $Al_2O_3$ ALD still shows good properties such as smooth surface (RMS < 4 Å) and reduced gas permeability. The barrier properties can be improved by using two pairs of double layer such as SiN$_x$/AlO$_x$ or parylene/AlO$_x$. In addition, ultrathin and conformal $Al_2O_3$ films can be deposited on nanoparticles using ALD.

**ALD using ozone ($O_3$).** When $Al_2O_3$ films are grown by ALD using TMA and O$_3$, the process time for the chemical reaction and purge out of the excessively adsorbed species can be shorter than that of ALD using $H_2O$ oxidant. This is due to the high chemical reactivity between TMA and O$_3$ and the less sticky nature of O$_3$ compared to $H_2O$, especially at low growth temperature range (<100 °C). $Al_2O_3$ is formed using TMA and O$_3$ as an active oxidant like this:

$$2Al(CH_3)_3 + O_3 \rightarrow Al_2O_3 + 3C_2H_6$$
Al₂O₃ films using O₃ as oxidant showed higher residual OH and C impurity concentrations compared to those using H₂O as oxidant. Since O₃ gas, although reactive, is separated from the organic layers by the cathode and has no energetic particles, superior OLED encapsulation properties of Al₂O₃ films using TMA and O₃ have been reported.⁹⁵

Plasma-enhanced ALD (PEALD).⁹⁶-⁹⁸ Plasma-enhanced ALD can be utilized for depositing oxide films at very low temperatures because O₂ is used as oxidant instead of water. The possible plasma damage to an OLED can be minimized since PEALD uses pulsed plasma with a short pulse time.⁹⁶ Compared to ALD Al₂O₃ using H₂O as oxidant, PEALD shows higher growth rate and lower etch rate, indicating denser film and thus better insulating characteristics.⁹⁸

1.4 Experimental Approach

1.4.1 Physical and Chemical Characterization

Ellipsometry. Ellipsometry can be used to determine the thickness of films as well as optical constants by measuring the change in polarization state of light reflected from the surface of a sample. The measured values are expressed as Ψ and Δ, which are related to the ratio of Fresnel reflection coefficient, Rₚ and Rₛ for p and s-polarized light, respectively.

\[ \tan(\Psi)e^{i\Delta} = \frac{R_p}{R_s} \]

Because ellipsometry measures the ratio of two values, it can be highly accurate and very reproducible. Ψ and Δ are typically obtained versus wavelength and incident angle and then
unknown parameters in optical model such as film thickness or optical constants or both are varied to find a best fit to experimental data. Ellipsometry can be used to measure the film thickness of ALD-grown Al₂O₃ on Si substrate.

**Atomic Force Microscopy (AFM).** The basic principle of the operation of AFM is to measure the atomic level forces between a sharp probing tip (which is attached to a cantilever spring) and a sample surface. Images are obtained by scanning the sample and measuring the deflection of the cantilever as a function of lateral position. Typical forces between tip and sample range from $1 \times 10^{-10}$ to $1 \times 10^{-5}$ N. The two main classes of interaction are contact mode and tapping mode. In contact mode, the tip and sample become in close contact as the scanning proceeds, corresponding to the repulsive regime of the intermolecular force curve. In tapping mode, the cantilever is oscillated at its resonant frequency (several hundreds of kilohertz) and positioned above the surface and thus taps the surface only for a small fraction of its oscillation period, strongly reducing the lateral “dragging” force. This research utilizes Digital Instrument DI3 model AFM with Supersharp Veeco probe tips (typically 2 nm radius of curvature). The AFM images of gold nanoparticles trapped in the nanoscale electrode gaps was obtained in tapping mode.

**Auger Electron Spectroscopy (AES).** Incident electrons with energy 3-20 keV cause core electrons from atoms in the sample to be ejected, resulting in a photoelectron and an atom with a core hole. Then the atom relaxes via electrons with a lower binding energy dropping into the core hole. The energy thus relaxed can emit an electron, which is called Auger electron. The energy of the Auger electron is characteristic of the element used to
identify the element in the sample. AES is known as a surface-sensitive technique (typically 5-50 Å) due to the short inelastic mean free path (IMFP) of Auger electrons in solids. However, AES cannot detect hydrogen or helium, but sensitive to all other elements and most sensitive to the low atomic number elements.

Secondary Ion Mass Spectrometry (SIMS). SIMS is a characterization technique used for the compositional analysis of small samples. In a SIMS instrument, a high energy primary ion beam is directed at an area of the sample. The interaction of the primary ions with the sample surface has three main effects: (1) It leads to a mixing of the upper layers of the sample and thus an amorphization of the surface; (2) Atoms from the primary ion beam are implanted in the sample; (3) Some secondary particles (atoms and small molecules) are ejected from sample. Among the ejected particles are electrically neutral, positively, and negatively charged species. Charged particles of one polarity (“secondary ions”) can be extracted from the sputtering area and accelerated to a mass spectrometer through an electric field between the sample and an extraction lens. Then the secondary ions are sorted by mass (and energy) and finally counted in an ion detector (i.e., electron multiplier or a Faraday cup). SIMS can be used for practically all elements of the periodic table including hydrogen. In addition, SIMS allows the routine measurement of many trace elements at very low concentration (ppb level). For our research, SIMS depth profiling was carried out to monitor the mass spectrum of Al, Zn and O in the Al-doped ZnO thin films at each depth using CAMECA IMS 6F.
Fourier Transform Infrared Spectroscopy (FT-IR). To complement the AES and SIMS, FT-IR is used for fast characterization of the chemical states of impurities present in the deposited films. This technique operates by exposing the sample to an IR beam and recording the frequencies absorbed by the sample, which correspond to the specific molecular vibrational frequencies of the chemical species present. Using the Berreman effect, FT-IR can be utilized to understand the change and distribution of specific metal oxide bonding states in ionic oxide films for our research. The Berreman effect was first explained in the early 1960s, which describes the emergence of absorption bands at the frequencies of bulk crystal longitudinal optical (LO) phonon modes in off-normal transmission and reflection IR spectra for finite size ionic oxide crystals, including thin films and freestanding slabs. Thus LO modes can be detected using the Berreman effect in ionic oxide films (i.e., Al$_2$O$_3$ and ZnO) on metallic, semiconducting, or insulating supports and in freestanding slabs. For a specific system with aluminum-doped ZnO thin films coated by atomic layer deposition on silicon substrates with different doping ratios, the LO peaks associated with Zn–O, Al–O, and Zn–O–Al bonding exhibit a noticeable change at an incident angle of 60° with respect to the normal to the sample. This approach reveals the distribution of various metal oxide bonding states within the thin films. A transmission FT-IR spectroscopy (Thermo Nicolet Magna 750) with a detection limit of about 1 at% and detectable wavenumbers of 400 to 4000 cm$^{-1}$ was used for this research.

Transmission Electron Microscopy (TEM). Transmission electron microscopy (TEM) provides extremely high resolution, approaching 1.5 Å. Since the incident electron beam must pass entirely through the section, which needs to be prepared only ten to hundreds of
nanometers thick, the sample preparation is a real challenge. The three primary imaging modes are bright-field, dark-field and high-resolution microscopy. In particular, high resolution TEM (HRTEM) gives structural information on the atomic size level and has become very important for interface analysis. Physical thickness, presence of interface layers or smoothness of an interface and crystallinity of a film can be obtained from TEM. Electron energy loss spectroscopy (EELS) is the analysis of the distribution of electron energies for electrons transmitted through the film. EELS is very sensitive to low-Z (Z=atomic number) elements (Z \leq 10). It is mainly used to micro-analytical and structural information approaching the very high resolution of the electron beam.

1.4.2 Electrical Characterization

*Low temperature I–V measurements.* The charge transport measurements through organic molecules are performed in the probe station under vacuum of \( \sim 5 \times 10^{-4} \) Torr using a Keithley 2602 system. The sample temperature can be cooled down from 298 to 80 K (or 4 K) by flowing liquid nitrogen (or liquid helium) into the cryostat in the probe station and controlled by a temperature controller (ST–100–2PROB, Janis). Temperature-dependent current-voltage characteristics are required to understand the conduction mechanisms through the molecules of interest.

*Inelastic Electron Tunneling Spectroscopy (IETS).* Inelastic electron tunneling spectroscopy (IETS) was developed in the 1960s to study the vibrational spectrum of molecules included at a metal-oxide interface\(^{100}\) and has since become a powerful
spectroscopic tool for molecular identification and chemical bonding investigation.\textsuperscript{5,101-107}

The basic concept is that the small, sharp increases in the AC tunneling conductance, dI/dV, are observed when the energy of the tunneling electrons reach the energy of a vibrational mode of molecules in the junction, i.e., \( eV = \hbar v \), where \( \hbar \) is Planck’s constant, \( v \) is the frequency of a molecular vibration, and \( e \) is the electron charge. The voltage (V) is converted to the wave number by the relation of 1 meV = 8.065 cm\(^{-1}\). IETS has an orientational preference: an oscillating dipole moment perpendicular to the oxide surface generally couples to tunneling electron more strongly than that parallel to the surface. Samples are placed into cryostat for electrical characterizations in the temperature range of 300 to 4 K. Cryogenic temperatures are necessary to minimize the thermal broadening of electrons at the Fermi level of the metal electrode to enable resolution of molecular vibrations.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure11.png}
\caption{Schematic representations of the current-voltage, the conductance-voltage, and the second derivative of the current with respect to voltage for a tunneling junction. The latter is an “inelastic electron tunneling spectrum”.\textsuperscript{105}}
\end{figure}
Inelastic electron tunneling (IET) spectra are obtained via a standard lock-in second-
harmonic measurement technique as shown in Figure 1.11. A synthesized function
generator is used to provide both the modulation and the lock-in reference signal. Then
second-harmonic signal (proportional to $d^2I/dV^2$) is directly measured using lock-in amplifier.
In table 1.4, the major vibrational modes are summarized for the several molecular
junctions.

Table 1.4 Vibrational mode assignments for the molecular junctions investigated.

<table>
<thead>
<tr>
<th>molecule</th>
<th>peak position</th>
<th>mode</th>
<th>activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mV</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>C11</td>
<td>95</td>
<td>766</td>
<td>CH$_2$ rocking</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>1081</td>
<td>$\nu$(C-C)</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1371</td>
<td>CH$_2$ wag</td>
</tr>
<tr>
<td></td>
<td>362</td>
<td>2920</td>
<td>$\nu$(C-H)</td>
</tr>
<tr>
<td>OPE</td>
<td>57</td>
<td>463</td>
<td>Aryl C-H ip</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>1074</td>
<td>$\nu$(18a)</td>
</tr>
<tr>
<td></td>
<td>138</td>
<td>1114</td>
<td>$\nu$(8a)</td>
</tr>
<tr>
<td></td>
<td>274</td>
<td>2211</td>
<td>$\nu$(C≡C)</td>
</tr>
<tr>
<td>OPV</td>
<td>96</td>
<td>777</td>
<td>Aryl C-H op</td>
</tr>
<tr>
<td></td>
<td>134</td>
<td>1078</td>
<td>$\nu$(18a)</td>
</tr>
<tr>
<td></td>
<td>144</td>
<td>1163</td>
<td>$\nu$(18a)</td>
</tr>
<tr>
<td></td>
<td>174</td>
<td>1403</td>
<td>$\nu$(15)</td>
</tr>
<tr>
<td></td>
<td>195</td>
<td>1573</td>
<td>$\nu$(8a) &amp; $\nu$(C≡C)</td>
</tr>
</tbody>
</table>

1.4.3 In situ characterization during atomic layer deposition

In situ quartz crystal microbalance (QCM). The quartz crystal microbalance has
emerged a powerful means to measure relative mass changes in real time during ALD as
shown in Figure 1.12. QCM measurements are carried out according to the Sauerbrey
equation, which relates the change in resonant frequency of a quartz crystal ($\Delta f$) to the change in mass due to adsorption on the crystal ($\Delta m$):

$$\Delta f = -\frac{2 f_0^2}{A \sqrt{\rho_q \mu_q}} \Delta m$$

where $f_0$ is the resonant frequency of the unloaded crystal, $A$ is the active area of the crystal between the electrodes, $\rho_q$ is the density of quartz and $\mu_q$ is the shear modulus of quartz.

Most of previous QCM sensors are calibrated to measure thin films grown during physical vapor deposition (i.e., evaporation) with line-of-sight deposition only on the front surface. These constraints give rise to two challenges for operating a QCM in an ALD reactor. First, ALD coating occurs on both front and back surface of the QCM sensor. Thus deposition on the back surface of the QCM sensor hinders mass measurements during the growth of conducting materials, resulting in electrical shorts and failure in crystal oscillation. To prevent deposition of the back surface of the QCM sensor, modifications are made to allow a purge gas to be introduced to the back side of crystal holder. Second, the QCM must be operated at deposition temperatures of 100-400 °C. At these high temperatures, small temperature fluctuations in the QCM sensor produce large apparent mass fluctuations. So extremely stable control of temperature should be achieved using active feedback control of heaters. These modifications enable accurate, calibrated mass measurement in real time during ALD.
**Figure 1.12**  (a) Schematic view of *in situ* QCM measurement attached to an ALD reactor. (b) Schematic view of *in situ* QCM with Ar purge on the back side of quartz crystal.

*In situ electrical conductance measurement.* The in situ conductance measurement provides an easy and excellent method for probing conductance changes during thin film growth. The electrical conductivity of thin films is determined by bulk and surface effects. For our research, the in situ conductance measurement tool is attached to the ALD reactor as shown in Figure 1.13. The current is measured in real time at an applied bias voltage of 0.1 V in the middle of Ar purge after each precursor exposure during ALD. Insulating spacers are used to electrically isolate two wires, which are connected to the I-V measurement tool.
1.5 Outline of this Dissertation

This dissertation has been focused on two major nanoscale research areas. The first part is molecule-based electronics. To gain the fundamental understanding of charge transport through independent single molecules, nanoparticle structures that consist of two (or three) nanoparticles bridged by independent molecules of interest were assembled onto the nanogap electrodes. The charge transport through the nanoparticle/molecule(s)/nanoparticle junctions was investigated with variation in molecular length and structure. In addition, research was conducted on the intricacies of atomic layer deposition (ALD), which is a key technique for depositing thin films with atomic layer control. New correlations between surface deposition reactions, charge transport and dopant activation that proceeds during ZnO and Al-doped ZnO (ZnO:Al) ALD were revealed by utilizing in situ analysis.
tools such as quartz crystal microbalance and electrical conductance measurements. Also the influence of varying Al doping sequences on the surface reactions during ZnO:Al ALD was investigated and compared with the ex situ film properties (i.e., film thickness, chemical composition, current-voltage characteristics). Al\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}+ZnO ALD were explored to improve the ambient stability of the nanoparticle/molecule junctions as an encapsulation layer, and to shield the surface polarity of ZnO nanorods leading to hierarchical morphology evolution from nanorods to nanosheets, respectively.

Chapter 2 shows the summary of key challenge and findings in the molecule-based electronics using nanoparticle/molecules/nanoparticle assemblies.

Chapter 3 presents the summary of key challenge and findings in the atomic layer deposition of Al\textsubscript{2}O\textsubscript{3}, ZnO and ZnO:Al films.

Chapter 4 describes the successful trapping of nanoparticle/molecule(s)/nanoparticle dimer assemblies via dielectrophoresis across nanogap electrodes fabricated by angled metal evaporation and the conduction mechanisms through independent molecules within dimer assemblies using temperature dependent current–voltage measurements (300–80 K). An Arrhenius plot of log (I) versus 1/T exhibits a distinct change of slope at \~1.5 V, indicating the transition from direct tunneling to Fowler-Nordheim tunneling.

Chapter 5 demonstrates the real-time monitoring of conductance through single molecule junctions which consist of nanoparticle/molecule(s)/nanoparticle units between nanoscale planar electrodes during dielectrophoretic directed self assembly. After successful assembly, the conductance through the junction is also monitored in real-time during other modification and exposure sequences over short-term and long-term time scales.
Chapter 6 presents the dependence of molecular length and structure on electron transport through nanoparticle/molecules(s)/nanoparticle junctions. The synthesized molecular length ranges from 2 nm to 4.7 nm, showing strong electronic coupling between the chain ends, facilitating electron transport over long distances. The electron transport through the linear–type (in dimers) and Y–type (in trimers) molecular structures has been also compared, showing no significant dependence of electron transport on molecular structures.

Chapter 7 demonstrates the extension of two terminal molecular wires using dimers to a possible three terminal molecular transistor using trimers, consisting of three ~15 nm gold nanoparticles bridged by a Y–type molecule, trapped in a planar nanogap electrodes (<30 nm). The current versus voltage characteristics shows a weak gate control with the modulation of source-drain current by a factor of ~2 over a gate bias of −2 to +2 V.

Chapter 8 addresses a significant challenge in molecular electronic junctions regarding both understanding and control of the stability of molecule/nanoparticle nanostructures under ambient exposure. Atomic layer deposition of aluminum oxide thin films at low temperatures (30–50 °C) is utilized to gently encapsulate and stabilize molecular electronic junctions. The presence of the molecule junction after encapsulation is confirmed by the observed transition from direct tunneling to Fowler–Nordheim tunneling and analysis of junction breakdown at high fields.

Chapter 9 describes the surface reactions occurring during ALD of ZnO and ZnO:Al films using in situ quartz crystal microbalance and electrical conductance analysis. It is observed that chemical interactions between Zn– and Al– species during ZnO:Al ALD
depend on the doping cycle ratio, the order of metal precursor exposure, and the surface chemistry. Results from the *in situ* analysis is consistent with those from the post–deposition characterization including the film thickness, chemical bonding features, chemical composition, and I–V characteristics.

Chapter 10 presents new relations between surface deposition reactions, charge transfer, and dopant activation that proceed during low temperature ALD of transparent conducting ZnO and ZnO:Al films using a systematic combination of *in situ* quartz crystal microbalance and electrical conductance measurements. Conductance oscillations follow the ZnO ALD mass uptake cycle as the surface alternates between zinc hydroxide and zinc–alkyl termination. Full dopant activation is found to proceed only after dopant atoms assimilate into the film bulk, several nanometers below the growing ZnO surface.

Chapter 11 reports the controlled shielding of inherent surface polarity nature and resulting morphology evolution of ZnO nanostructures by combining Al₂O₃+ZnO ALD and subsequent ZnO hydrothermal growth. The surface polarity of ZnO nanorods is maintained after ZnO coating, but is screened by coating of amorphous Al₂O₃. Zinc oxide morphologies are observed to transition from one-dimensional nanorods to two-dimensional nanosheets on the surface of Al₂O₃ + ZnO ALD coated nanorods during hydrothermal growth, with increasing thickness of intermediate Al₂O₃ film. Possible growth mechanisms and practical “phase space” diagram are also proposed in terms of the dependence of morphology transition on both surface polarity shielding and substrate feature spacings. Furthermore, three-dimensional nanorods/nanosheets/nanorods structures are demonstrated.
1.6 References


Chapter 2

Key advances in molecular electronics developed in this work
Understanding the charge transport through independent molecules is still critical issues. Previously, electron beam lithography was used to fabricate the nanoscale electrode gap for trapping the nanoparticle dimers. Here, angled metal evaporation technique is developed and applied to the initial microscale electrode gap (5 µm), resulting in the nanogap electrodes (~70 nm). Then synthesized nanoparticle/molecules/nanoparticle structures ‘dimers’ have been successfully utilized to contact across the nanoscale metal electrodes via dielectrophoretic trapping. The best trapping results are observed at 2 VAC, 1MHz and 60s in our system. The real time monitoring of conductance through dimer structures during dielectrophoretic trapping provides immediate detection of a specific fault ascribed to loss of the active molecule and fusing of the nanoparticles in the junction, mostly at higher applied voltage (3 VAC, 100 kHz). The electric field distribution in the electrode geometry is simulated using FEMLAB software. The simulation suggests that one nanoparticle of the dimer first contacts the right electrode edge with the highest electric field gradient and then the other nanoparticle of the dimer contacts the left electrode. These simulation results are in good agreement with the AFM line profile of a dimer experimentally trapped between the nanogap electrodes.

Investigation of the conduction mechanisms using temperature dependent current versus voltage (I–V) measurements. Nanoparticle dimers contacted across nanoscale metal electrodes are attractive because the structures can be maintained electrically connected for long period of time (days and weeks), enabling time- and temperature-dependent I–V characterization. Temperature-dependent I–V characteristics (I (V, T)) are measured between
290 and 80K through single oligomeric phenylene ethynylene molecules (OPEs)–linked gold nanoparticle dimer. From an Arrhenius plot of \( \ln (I) \) versus \( 1/T \), a marked change of slope is observed at \( \sim 1.5 \) V, indicating transition from direct tunneling to Fowler–Nordheim tunneling.

**Ambient stability of nanoparticle dimers over short-term and long-term time scales.** In molecular electronic junctions, the electronic contacts and transport mechanisms can be highly sensitive to sample history and ambient exposure. Here, after successful junction formation with nanoparticle dimers trapped across nanogap electrodes, the current is monitored at a continuous bias of 0.5 V under various ambient conditions in real time over short-term and also long-term scales. Upon alternate exposure to inert argon gas, vacuum, and ambient air as a function of time, the current rapidly decreases within a few minutes only after exposure to ambient air. Evacuating the system results in reversible recovery of the current to its original value. To investigate the long-term stability of nanoparticle/molecule junctions, samples are stored in air with no bias. When a sample is kept in vacuum over many days, there is no significant current change. However, upon exposure to air, a small rapid decrease in current is followed by a slower exponential increase and eventual saturation. Initial rapid decrease in current is ascribed to reversible oxidation of gold–thiol contacts upon exposure to ambient water vapor, and for longer times water vapor accumulating in the junction region may lead to additional current pathways and net increase in current.

**Dependence of molecular length and structure on electron transport.** The electron transport properties of organic molecules depends not only on device geometry and
metal–molecule contact properties, but also on the chemical and electronic structure of molecules in junctions including molecular length, substitution (i.e., redox molecules) and extent of conjugation. Many studies have mainly focused on molecules with relative short molecular length (typically less than 2 nm lengths) as well as only one thiol bound to the electrode. The current strategies of chemical synthesis for molecular wires continuously place an emphasis on the molecular length for practical applications. Only few studies have recently addressed the weak length dependence of resistance in conjugated molecules. Here we investigate the dependence of charge transport on molecular length of a series of single OPE dithiol molecules (up to 4.7 nm between two sulfur atoms) with covalently bound to gold nanoparticles. We extract the electronic decay constant (β) of ~ 0.12 Å⁻¹ and effective contact resistance of ~4 MΩ using the dimer structures. The chemical bonding of gold-thiol in metal-molecule junctions is considered to enhance strong electronic coupling between the chain ends, facilitating electron transport over long distance. The dependence of different molecular structures such as linear-type (in dimer) and Y-type (in trimer) with similar molecular length on the electron transport is observed not significant although a little larger current flow was observed at 1 V for the trimers.

Demonstration of three-terminal molecular devices using nanoparticle/Y-type molecule/nanoparticle trimeric structures. The control of electron transport via a third electrode is highly desired and can be used as a field effect transistor (FET)–like device in addition to providing the clear signs for the presence of molecules inside the gap. Here three-terminal molecular devices are demonstrated with three gold nanoparticles bridged by a
Y-type OPE molecule ‘trimers’, in which two gold nanoparticles were contacted to two metal electrodes and the third gold nanoparticle closely contacted to the heavily doped Si back gate with a dry etched SiO$_2$ layer. The gold nanoparticle trimers are trapped in the nanogap electrodes using dielectrophoresis. The source-drain current is changed within a factor of 2 with a gate bias of −2 to +2 V, showing a weak gate effect in our device. The subthreshold slope is obtained ~110 mV/decade from the log–scale source-drain current vs a gate bias (0 to -2.5V). This is the first experimental demonstration of a three-terminal device, consisting of three molecular arms bridged by gold nanoparticles.
Chapter 3

Key advances in atomic layer deposition developed in this work
Revealing additional factors to influence surface reactions during atomic layer deposition (ALD). As described in chapter 1, atomic layer deposition (ALD) technique is based on self-limiting gas-solid reactions. Al₂O₃ and ZnO ALD are performed using separate TMA and H₂O exposures, and DEZ and H₂O exposures, respectively, as follows:

\[
\begin{align*}
\text{ZnO:} & \quad \text{ZnOH}^* + \text{Zn(C₂H₅)₂} \rightarrow \text{ZnOZnC}_2\text{H}_5^* + \text{C}_2\text{H}_6 \quad \text{(DEZ pulse)} \\
& \quad \text{ZnOZnC}_2\text{H}_5^* + \text{H}_2\text{O} \rightarrow \text{ZnOZnOH}^* + \text{C}_2\text{H}_6 \quad \text{(H}_2\text{O pulse)} \\
\text{Al}_2\text{O}_3: & \quad \text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{AlOAl(CH}_3)_2^* + \text{CH}_4 \quad \text{(TMA pulse)} \\
& \quad \text{AlOAl(CH}_3)_2^* + \text{H}_2\text{O} \rightarrow \text{AlOAlOH}^* + \text{CH}_4 \quad \text{(H}_2\text{O pulse)}
\end{align*}
\]

ALD reaction is well known to depend on the surface end-functional groups as shown above. For example, DEZ precursor is only reactive on the –OH terminated surface, but not on the hydrophobic –CH₃ terminated surface. However, in situ quartz crystal microbalance (QCM) measurements during aluminum-doped ZnO (ZnO:Al) ALD reveal that the chemical reaction depends on other factors as well as the surface chemistry shown above. For instance, aluminum-doped ZnO ALD with three different doping sequences was performed at the doping ratio of 1/19, where each 20th DEZ pulse is replaced with one TMA pulse. For case 1, the TMA/H₂O exposure cycle results in a mass uptake of ~40 ng/cm², similar to the value during Al₂O₃ ALD (Figure 3c), indicative of TMA reacting with available –OH groups. For case 2, the TMA/DEZ/H₂O cycle shows QCM response that is very similar to the case 1 data, with evidence for DEZ physisorption and desorption during the Ar purge. The QCM response in case 2 suggests that the O–Al(CH₃)₂⁺ surface remains relatively stable under DEZ exposure, consistent with the expected stronger bonding energy of Al–O relative to Zn–
O species. For case 3 with DEZ/TMA/H₂O cycle, however, a different trend is observed in the QCM results. The mass increases during DEZ exposure, then decreases upon introduction of TMA, indicative of etching. The net mass uptake during the doping step in case 3 is 69 ± 5.5 ng/cm², which is larger than the ~40 ng/cm² measured after the doping sequence for cases 1 and 2. The mass uptake trend for case 3 doping is related to the relative stability of the Al and Zn related precursors, surface adsorbates, and metal oxides. This observed phenomenon results from the different bonding energy (512.1 kJ/mol and 284.1 kJ/mol for Al-O and Zn-O, respectively) as well as the different ionic radius (0.05 nm and 0.074 nm for Al³⁺ and Zn²⁺, respectively).

**Unveiling correlation between surface reaction and charge transfer at the monolayer scale during ZnO ALD.** Previously, several researchers used *in situ* QCM and conductance measurements independently to study steady state ZnO and ZnO:Al ALD. However, *in situ* QCM and conductance analysis have rarely been combined. We show that their combination provides a powerful means to observe direct links between surface reactions and charge transfer. This has been considered very difficult in conventional chemical vapor deposition process, which involves simultaneous supply of reactant gases to a reactor. The surface of zinc oxide is known to be an active heterogeneous basic catalyst, with an isoelectric point (IEP) in water of ~8.1 – 9.8. Upon water exposure during ALD, surface basic sites, including surface hydroxyls or lattice oxygen, can bind a proton which will release charge to the film bulk, resulting in charge accumulation and surface band bending. For example, OH groups can bond to metal Lewis acid site through lone–pair donation, leaving a hydrogen atom to bond to lattice oxygen, promoting charge donation to the film bulk. After the water exposure
step in the ALD ZnO process, the subsequent DEZ exposure will revert the surface basic sites back to a more neutral ethyl termination, decreasing net conductance. In addition, the number of charge carriers needed to produce the observed change in conductance during each water exposure step can be estimated using Ohm’s law, and conductivity equation of $\sigma = ne\mu$ (where $n$ is the volume density of charge carriers, $e$ is the fundamental charge and $\mu$ is carrier mobility). Assuming a reasonable mobility value ($\mu$) of 1 cm$^2$/Vs for ALD ZnO thin film transistors, the charge transfer density is estimated $\sim 6.4 \times 10^{14}$ charges/cm$^2$. This value is in the same order of magnitude as the density of surface growth sites, $\sim 8.6 \times 10^{14}$ cm$^{-2}$, obtained from mass uptake results, and the estimated OH group density, $1.06 \times 10^{15}$ cm$^{-2}$, on the ZnO ALD surface at low temperature in the literature. This correlation indicates that a significant fraction of the reaction sites involved in deposition are also engaged in charge transfer between the surface and film bulk.

*Proposing the dopant activation mechanism in the ZnO:Al ALD.* To date, there has been no report on how incorporated dopants activate within the growing films during ALD of ZnO:Al (or other doped materials). So it was expected that the substitution of Al$^{3+}$ into Zn$^{2+}$ sites in wurtzite ZnO could result in charge donation and an immediate increase in the conductance. However, unexpected but interesting phenomenon is observed using *in situ* conductance measurements. The Al–doping process shows a reproducible characteristic variation upon introduction of the TMA and H$_2$O during ZnO:Al ALD. The conductance trend over 4 macro cycles (where 1 macro cycle consists of 1 TMA/H$_2$O + 19 DEZ/H$_2$O cycles) is obtained during steady–state growth. Three regimes are identified: (I) conductance
decrease (~ up to 4th DEZ/H2O cycle), (II) small conductance increase (from 4th to 11th cycle), and (III) more enhanced conductance increase (~11th to 19th cycle). As the Al-O layer near the surface becomes buried in the depositing ZnO, it will interact less with the surface. When the thickness of the ZnO layer over the thin buried Al–O region exceeds the Debye length (~2–3 nm), the trap layer will be effectively screened, and the surface will resume its previous charge transfer and conduction oscillation characteristics. This 2–3 nm thickness corresponds well with the ZnO film thickness deposited within regions I and II in the conductance oscillation plots. Within region III, the rapid increase in conductance then corresponds to fully buried Al–O regions, with full contribution from Al bulk doping, and minimal contribution from surface Fermi level pinning.

Identifying the distribution of Al dopants and chemical bonding (Al-O, Zn-O, Al-O-Zn) in the ZnO:Al films. Atomic layer deposition can easily control the film properties of ZnO:Al by changing the precursor cycle ratio. However, the Al-O doping layer is incorporated between thick ZnO layers at the monolayer scale. Therefore, it is challenging to identify the presence and distribution of the doping layer in ZnO:Al films. Secondary ion mass spectroscopy (SIMS) measurements are performed to investigate the doping profile for ZnO:Al films, identifying the spatial positions of the TMA/H2O cycles within the ZnO layer. The ²⁷Al signal in the SIMS data shows peak intensity corresponding to the points of TMA/H2O exposure, and oscillating signal pattern demonstrates that the Al dopants are non–uniformly distributed through the ZnO film. Furthermore, angled Fourier transform infrared spectrometry (FTIR) is first utilized to study the distribution of chemical bondings such as Zn-O, Al-O, and Zn-O-Al in the ZnO:Al films. Especially the longitudinal optical phonon
(LO) peaks are observed only at an angled incidence of IR beam to samples, not at a normal incidence, which is known as Berreman effect. Both transverse optical (TO) and LO phonon peaks related to Zn-O bonding become decreased as the doping ratio increases and then disappear at the doping ratio of 1/4, in which, however, a new peak associated with Zn-O-Al bonding occurs instead. This suggests that the aluminum species readily mix with the ZnO over the thickness associated with 4 cycles of ZnO deposition. This is consistent with the QCM results that show that TMA affects the subsequent DEZ/H₂O mass uptake for ~4 ALD cycles.

Nanoencapsulating the single molecules/nanoparticle nanoassemblies using low temperature Al₂O₃ ALD. One significant challenge in engineered molecular systems is to understand and control the stability of the molecular structures under ambient exposure. This problem is particularly acute in the field of molecular electronic junctions, where electronic contacts and transport mechanisms can be highly sensitive to sample history and ambient exposure. However, the stability of charge transport through isolated molecular junctions during extended ambient exposure is less widely characterized, and methods to protect the junctions from the environment have been only briefly discussed. Nanoparticle/molecule/nanoparticle structures, consisting of ~40 nm gold nanoparticles linked by a single (or small number of) oligomeric phenylene ethynylene molecules (OPEs), are synthesized and electrically bridged across planar nanoscale electrode gaps. Results show that the junction conductance is not significantly modified by the deposition process itself upon exposing molecular junctions to atomic layer deposition processes at low temperatures (≤ 50 °C) to form Al₂O₃ encapsulating layers around the molecule junctions. Moreover, junctions coated
at low temperature show significantly improved long-term stability, where the molecular conductance does not change during storage for more than 20 days in laboratory air.

Surface polarity shielding and hierarchical morphology evolution of ZnO nanostructures by sequential hydrothermal crystal synthesis and atomic layer deposition of Al$_2$O$_3$+ZnO. To date, only a few studies have been reported on the formation of two-dimensional (2D) ZnO nanostructures using solution-based hydrothermal method. Two-dimensional ZnO nanostructures are prepared by varying growth conditions such as pH, precursor concentration and temperature during hydrothermal growth. However, controlled synthesis of 2D ZnO nanostructures in solution still remains challenging due to the inherent structural polarity (i.e., thermodynamic restriction) of ZnO, leading to the anisotropic crystal growth along the c-axis orientation. We have achieved the controlled shielding of surface polarity of one-dimensional (1D) ZnO nanorods (NRs) and resulting morphology evolution of 1D NRs to 2D ZnO nanowalls (NWs) by sequential hydrothermal crystal synthesis and ALD of Al$_2$O$_3$ + ZnO bi-layer. We employ multi-step synthesis using ALD and hydrothermal methods. First, ZnO NRs are synthesized on the ZnO ALD-coated Si substrate. Second, the film coating through ALD of ZnO or Al$_2$O$_3$ + ZnO is performed on the 1$^{st}$ ZnO NRs, followed by hydrothermal growth. ZnO NRs maintain their surface polarity after only ZnO ALD, but lose it after insertion of amorphous Al$_2$O$_3$ coating layer. During subsequent hydrothermal growth, ZnO morphology is dramatically changed from 1D NRs to 2D NWs with increasing thickness of Al$_2$O$_3$ layer on the surface of 1$^{st}$ ZnO NRs. Moreover, the surface geometry influences the ZnO morphology with varying gap distance between ALD-coated ZnO NRs. Possible growth mechanisms and practical “phase space” diagram are
proposed on the basis of the surface polarity- and geometry dependent morphology transition of ZnO nanostructures. As a further demonstration of the versatility of the ALD process to control surface polarity, samples with ZnO nanosheets were treated to another Al₂O₃ + ZnO ALD and subsequent hydrothermal growth, resulting in hierarchical nanorod/nanosheet/nanorod structures.
Chapter 4

Conduction mechanisms and stability of single molecule nanoparticle/molecule/nanoparticle junctions*

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*My contributions to this work include developing the nanoscale electrodes, process and conditions of the dimer assembly onto the electrodes as well as performing all the electrical characterization and analysis of electrical results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. The design of experiments was done primarily by Dr. Gregory Parsons, Dr. Christopher Gorman, Jennifer Ayres and me. The synthesis and assembly of the molecule into the dimers were performed by the Gorman research group including co-authors, Dr. Christopher Gorman, Jennifer Ayres and Kusum Chandra.
4.1 Abstract

Nanoparticle/molecule/nanoparticle dimer assemblies have been successfully trapped by dielectrophoresis across nano-gap electrodes, enabling temperature dependent charge transport measurements through an oligomeric phenylene ethynylene molecule, and transition from direct tunneling to Fowler-Nordheim tunneling is observed at ~1.5 V. Samples formed by dielectrophoresis show better contact stability than those by receding meniscus. The junction shows stable operation over several weeks in vacuum, but current increases with time upon air exposure possibly due to the adsorbed water molecules near the molecule/gold nanoparticle contacts.
4.2 Introduction

As conventional silicon-based technology approaches its expected physical limits, researchers are exploring molecule-based electronics to continue to meet the Moore’s Law challenge of continuing device size miniaturization. Even though molecules will not likely supplant silicon logic technology, details of electronic conduction at metal/molecule interfaces is expected to be important for a range of advanced organic electronic devices and systems. Charge transport through a molecular junction is considered to be controlled by the mixing between discrete orbitals in a molecule and the continuum states in a metal, where the molecular orbital states are broadened and shifted by the large density of states in the metal. The effects of metal/molecule contact on molecular charge conduction is an active research area, and it is generally accepted that since electron state coupling at the metal/molecule interface must necessarily include a contribution from the orbital states in the bridge molecule itself, the molecule/metal interface must be evaluated in terms of the entire molecular junction.

Charge transport through organic molecules has been investigated using a variety of methods such as break junction, crossed wire tunnel junction, nanopores, and conducting probe atomic force microscopy. However, reliable fabrication of molecule-based devices and understanding conduction mechanisms through individual molecules are still critical issues. Particular difficulties are related to defect incorporation during processing, instability of metal-molecule contacts, and the possible interactions between multiple molecules in the junction.
Recently, Dadosh et al.\textsuperscript{22} worked to measure the conductance of single conjugated molecules using nanoparticle dimers trapped between the electrodes fabricated by electron beam lithography. Here we report the dielectrophoretic trapping and charge transport through similar nanoparticle/molecule/nanoparticle bridge structures consisting of \(~40\) nm gold nanoparticles linked by a single oligomeric phenylene ethynylene molecule (OPE) spanning a nanogap electrode structure. Lithographic definition of this nanogap is made relatively straightforward via angled metal evaporation of an easily fabricated, micro-scale electrode gap. This device structure can avoid the incorporation of defects during processing that can affect the measured conduction.\textsuperscript{30} We compare the performance of dielectrophoretically trapped structures with those formed by liquid evaporation, and analyze the conduction mechanisms through stable junctions with a single molecule (or a small number of molecules) as a function of temperature. We also examine the effect of ambient exposure on the device stability.

4.3 Experimental methods

The nanoparticle/molecule/nanoparticle structures (nanoparticle dimers) were synthesized according to previously published methods\textsuperscript{31} and are applied here as a means to form an electrical bridge across a planar nanoscale electrode gap. To form the nanoparticle/molecule/nanoparticle “dimers”, oligomeric phenylene ethynylene structures (OPEs) terminated with thioacetate functionalities were bridged between two \(~40\) nm gold nanoparticles. OPEs have been identified as promising candidates for molecular wires based
on their linear, rigid structures, and extended conjugation. Further, use of these molecules permits comparison to previously reported electronic measurements. The nanoparticles were citrate-capped gold particles, used as received from Ted Pella, Inc. A solution containing 2 mL of 0.15 nM particles was diluted with 2.5 mL 3 mM sodium citrate. A stoichiometric amount of the OPE “linker” was dissolved in 0.5 mL 2:3 THF:ethanol solution and was added slowly over a period of approximately 2 hours and then stirred for additional two hours. The basic citrate nanoparticle solution provided a pH sufficient to deprotect the aromatic thioacetate groups, generating thiolates in situ. The two reactive ends of the molecule could then bond with the nanoparticles and form dimer structures. Aggregate formation was avoided by using low nanoparticle concentrations, slow addition, and constant stirring. Transmission electron microscopy (TEM) was utilized to evaluate the statistical distribution of synthesized particles. Approximately 20 % of the particles were formed as dimers, and approximately 10 % formed trimers. The remaining particles remained unbound. The solution was then used as prepared to introduce the nanoparticle dimers to the electrode structure. Methods to separate and isolate dimers from individual particles including centrifugation filtration and size exclusion chromatography are currently being investigated.

4.4 Results and discussion

Figure 4.1 shows the molecular structure of the OPE “linker” molecule, as well as a TEM image of a typical nanoparticle/molecule/nanoparticle dimer. The diameter of the nanoparticles is ~40 nm and the gap between nanoparticles corresponds to ~2 nm. This
approach allows only a small number of molecules (possibly only one) to be bound between each pair of nanoparticles that form the dimer structure. The subsequent assembly of the dimer into the nanoscale gap then allows the charge transport characteristics of the OPE linker “test molecule” (or molecules) to be measured and evaluated.

Figure 4.1  (a) The molecular structure of the oligomeric phenylene ethynylene molecule (OPE) bridged by gold nanoparticles. (b) TEM image of a OPE-linked nanoparticle dimer consisting of gold nanoparticles with a diameter of ~40 nm.

Figure 4.2 shows the nanogap structure fabricated by angled metal evaporation. First, Au(90 nm)/Ti(10 nm) metal layers were e-beam evaporated on 150 nm thermally grown SiO₂ on p-type Si, then etched to form electrodes with large (10 micron) gaps. Then, Pd
evaporation was carried out with a tilt angle of ~40° to form a nano-scale trench. A resist lift-off step was used to define the metal contact pads and isolate individual electrodes. Palladium was used as a second metal because it was found to minimize damage to the resist layer, enabling lift off in acetone with sonification and isopropanol. Samples were then rinsed with deionized water and dried in a stream of nitrogen gas and transferred directly to the vacuum-compatible probe station for the dimer trapping procedure and subsequent electrical characterization. This procedure enabled many pairs of nanoscale electrodes to be fabricated in parallel, so that several test structures could be fabricated together.

Figure 4.2  Schematic structure of a nanogap electrode fabricated by angled metal evaporation onto a micro-gap electrode. Pd (30 nm) was evaporated onto the Au(90 nm)Ti(10 nm)/SiO₂(150 nm)/p-type silicon substrate with a tilt angle of ~40°. Metals were evaporated at a rate of ~0.5 Å/s in a chamber pressure of ~1.0E-7 Torr. The nanogap structure of ~70 nm was formed between the electrodes.
Trapping of an OPE-linked gold nanoparticle dimers was performed in the probe station by placing a ~3 µL droplet of the suspension onto the electrode surface. The drop typically covered many electrode pairs, enabling several samples to be prepared in one set of experiments. To promote trapping of the nanoparticle dimers, alternating current electric field was applied to the electrodes.\textsuperscript{22,29,34} The voltage was typically 1 \sim 3 VAC at a frequency of 1 kHz \sim 1 MHz for approximately 30 \sim 120 seconds. After trapping, samples were dipped in high purity deionized water for 30 sec and dried in a stream of nitrogen gas. An AC voltage was generated using a precision LCR meter (Agilent 4284A) and computer-controlled using LabView from National Instruments.

The receding meniscus method was also performed to compare the contact formation and stability. In this approach, a droplet of nanoparticle solution (~3 µL) was applied to the nanogap electrodes using a conventional pipette. The capillary force exerted on the surface drags the particles across the surface until they are physically trapped into the electrode gap.\textsuperscript{35} In our experiments, the solution was introduced near the electrode gap, causing particles to flow into the gap during water evaporation.

Atomic force microscopy (AFM) measurements were performed in tapping mode under ambient conditions using a Digital Instrument AFM with a Nanoscope IIIa controller (Santa Barbara, CA). The charge transport measurements were carried out in the probe station under vacuum of \textasciitilde 5\times10^{-4} Torr using a Keithley 2602 system. The sample was cooled down from 290 to 80 K by flowing liquid nitrogen (LN\textsubscript{2}) into the cryostat in the probe station and controlled by using a temperature controller (Model: ST-100-2PROB, Janis Research Company).
The alternating electric field produces a dielectrophoretic force, \( F \), that attracts and aligns the OPE-linked gold nanoparticle dimers into the nanogap electrodes. The magnitude of this force is given by\(^{36}\)

\[
F(\omega) = 2\pi\varepsilon_m r^3 \text{Re}(f_{CM}) \nabla |E_{rms}|^2
\]  

(1)

where \( \omega \) is the angular field frequency, \( r \) is the particle radius, \( \varepsilon_m \) is the dielectric constant of the medium, \( \nabla |E_{rms}|^2 \) is the gradient of the square of the RMS electrical field, and \( f_{CM} \) is the Clausius-Mossotti factor. The DEP force depends on \( \nabla |E_{rms}|^2 \), (a factor related to the geometry of electric field) and on the real part of \( f_{CM} \), the in-phase component of the particle’s effective polarizability. The nanoparticle/molecule/nanoparticle assemblies used here consist of two conducting spheres linked by a test OPE molecule. To understand how the dielectrophoresis is involved in trapping the nanoparticle dimer between the nanogap electrodes, the electric field distribution in the electrode geometry was simulated using the FEMLAB multiphysics modeling program (COMSOL, Burlington, MA). The electric field in FEMLAB was calculated by several steps. The scaled side views of the system near the nanogap electrodes, where the trapping experiments were carried out, are shown in Figure 4.3. The subdomains were the two asymmetrical metal electrodes (\( \varepsilon \sim \infty \)) and the aqueous dielectric medium (\( \varepsilon \sim 80 \)). The boundaries were: 1) the left metal electrode with Pd(30 nm)/Au(90 nm)/Ti(10 nm) (applied voltage = 2 V, positive half-cycle of the AC field); 2) the right palladium (Pd) electrode with a thickness of 30 nm (grounded); 3) the gold nanoparticles with a diameter of \( \sim 40 \) nm (continuous); and 4) the other boundaries with electrical shielding. Next the solution space was triangulated into a conformal mesh. Since
the physical properties inside the elements remain constant, no mesh elements exist across subdomains or boundaries. Then the Poisson equation was solved for all elements to obtain the electric field distribution. Simulation results of the electric field distribution in the nanogap electrodes with 2D electrostatic calculations are shown in Figure 4.3.

Figure 4.3 Simulation results of electrical field distribution using FEMLAB. (a) Electric field contour in the electrodes with a nanogap of ~70 nm. The white solid arrow directs the increasing electrical field gradient. (b) Electrical field distribution containing a single OPE-linked gold nanoparticle dimer between the nanogap electrodes. The electric potential was assumed 2 V.
Since the permittivity of the dimer ($\varepsilon_p$) is $\sim$infinity and that of medium ($\varepsilon_m$) is approximately 80, $\text{Re}(\omega)_{CM}$ is calculated to be approximately 1. So $\text{Re}(\omega)_{CM} > 0$ and a positive DEP force exists in our system, which means that the dimer is expected to move towards increasing field strength, as indicated by the arrow shown in Figure 4.3a. The highest field strength is observed at the electrode edges, so the dimer is expected to be driven there. Figure 4.3a shows that the highest field strength occurs on the right hand side electrode edge, so that a dimer is expected to be make contact initially to the right side. Figure 4.3b shows the electric field distribution of the system containing a OPE-linked gold nanoparticle dimer between the nanogap electrodes. The simulation suggests that one nanoparticle of the dimer first contacts the right electrode edge (with the highest electric field gradient) and then the other nanoparticle of the dimer contacts the left electrode. The AFM line profile of a dimer experimentally trapped between the nanogap electrodes is in good agreement with these simulation results, as shown below.

The trapping experiments were performed in the probe station using dielectrophoresis. The trapping conditions of a OPE-linked gold nanoparticle dimer and their results are summarized in Table 1. When 1 VAC was applied to the electrodes, no trapping was observed, indicating the applied bias was lower than the threshold voltage needed to drive a dimer to the nanogap electrodes. However, dimer trapping was observed when 2 VAC or greater was applied. As the frequency is increased, dimers are more strongly attracted to the central region between the electrodes. The best results were observed at 2 VAC, 1 MHz, and 60 sec in our system, where seven dimers were successfully trapped out of a set of experiments involving 9 trials. Note that this method can also, in principle, attract individual
particles. However, these are too small to bridge the gap and thus would not complete the electrical circuit.

**Table 4.1** Experimental trapping results of a OPE-linked gold nanoparticles dimer.

<table>
<thead>
<tr>
<th>Freq.</th>
<th>AC bias</th>
<th>1 V</th>
<th>2 V</th>
<th>3 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 MHz</td>
<td>Open</td>
<td>Trapped (~78%)</td>
<td>Trapped (~65%)</td>
<td></td>
</tr>
<tr>
<td>100 KHz</td>
<td>Open</td>
<td>Trapped (~40%)</td>
<td>Ohmic (~50%)(^a)</td>
<td></td>
</tr>
<tr>
<td>1 KHz</td>
<td>Open</td>
<td>Open</td>
<td>Ohmic (~50%)(^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Ohmic refers to the linear current-voltage curve with above 10 mA in the bias range of -1 to +1 V.

Figure 4.4a shows the tapping mode atomic force microscopy (AFM) image of a OPE-linked gold nanoparticle dimer trapped between two electrodes. SuperSharpSilicon probe tips (SSS-NCH, Nanosensors\(^{TM}\)) were used with a typical tip radius of curvature of 2 nm, providing high resolution AFM images in the nanogap region. The nanogap width is ~70 nm. One AFM line profile measured across the electrode-dimer-electrode structure and its corresponding schematic structure are shown in Figure 4.4b. The AFM results that show the position and orientation of a dimer trapped between the nanoscale electrodes are consistent with the dielectrophoresis simulation results discussed above and shown in Figure 4.3.

Results of room temperature current vs voltage measurements through a OPE linked gold nanoparticle dimer are shown in Figure 4.5. The data show the results from seven successful molecule/nanoparticle/electrode assembly experiments carried out at 2 VAC, 1
MHz, 60 s. Each data point represents the average value of five measurements made on the same molecule structure.

**Figure 4.4** (a) Atomic force microscopy (AFM) image of the OPE-linked gold nanoparticle dimer trapped between the electrodes with ~70 nm nanogap. (b) Schematic drawing corresponding to the line profile of (a), where the red solid line is the real line profile across a trapped dimer.
Figure 4.5  Current versus voltage characteristics for seven different devices with a single OPE-linked gold nanoparticle dimer trapped between the nanogap electrodes at 2 VAC, 1 MHz, and 60 sec. All the data points are the average values of five measurements on each individual structure.

Because of the strong covalent bonding between the gold nanoparticles and the thiol groups on the molecule, the molecule is expected to displace the citrate capping layer on the nanoparticle, so that the primary source of resistance in the system is the linking molecule itself. The current-voltage curves are symmetric in positive and negative bias directions, and the resistance is measured from the slope of the line in the low voltage region (–0.2 to +0.2 V). The resistance values range from 0.2 ± 0.02 to 2.8 ± 0.1 GΩ for seven different samples. These resistance values through a trapped OPE-linked gold nanoparticle dimer are consistent with values (1.7 ± 0.4 GΩ) expected for a single molecule of oligophenylene-
ethynylendithiol (OPE) without a substitutional group (-OC₆H₁₃). The data in Figure 4.5 therefore is consistent with a single OPE molecule (or a small number of molecules) bridging the gold nanoparticles.

To confirm the dielectrophoretic trapping results, two test samples were prepared as control experiments. First, a droplet of solution without nanoparticle dimers was placed on the electrode samples and an alternating electric field was applied. Second, a droplet of solution containing dimers was applied to the chips without an alternating electric field. Test samples were then processed similarly to the dimer samples, and measured under vacuum. Both test samples showed no current through the electrodes, verifying charge transport characteristics in Figure 4.5 are only through a OPE-linked gold nanoparticle dimer assembled by the DEP force between the electrodes.

Current-voltage characteristics shown in Figure 4.5 measured in vacuum just after dimer trapping exhibit a range of current values over approximately an order of magnitude. Two possible reasons for the large variation can be suggested. One factor is the number of the linker molecules (OPE) between the two gold nanoparticles. If two OPE molecules are bound in the nanoparticle dimer, a larger current would be expected. A factor of 2, consistent with two parallel conductance pathways, however, is not enough to explain the observed factor of 10 range in current values. The other more likely factor is different contact properties between the gold nanoparticle and the electrode. Dadosh et al.²² reported ~77 % of trapped dimers showed too low conductivity due to poor contact properties between one of the particles and the electrode, and ~23 % showed high conductivity with conductance differences as large as an order of magnitude. Therefore, it is thought that the contact
properties between one of the nanoparticles and the electrode, formed during trapping using
dielectrophoresis, affects the initial current level of the trapped dimer. However, as shown
below, storing the junctions in vacuum results in very stable I-V properties, whereas
exposing them to air generally results in a gradual increase in current flow. These results
suggest some variability or change in the details of the molecule/metal linkage could account
for the variation in current levels observed in Figure 4.5, as discussed below.

Samples formed by the receding meniscus method were compared to samples
assembled by DEP. Data showing a typical I/V trace of a DEP assembled structure is shown
in Figure 4.6a, and one formed by the meniscus method are shown in Figure 4.6b. Samples
formed by dielectrophoresis are observed to withstand 2 V applied and no open circuit
occurred after tens of bias sweeps, whereas the samples formed using the meniscus force
typically resulted in open circuits after applying 2 V. We note that the current through a DEP
assembled structure is higher (~3 nA at 1 V) than for a typical sample formed by the
meniscus method (<1 nA at 1 V), also consistent with better quality contacts for the DEP
assembly. These results suggest that the dielectrophoretic force may help the gold
nanoparticle to form a good physical contact to the Pd planar electrode, whereas the
nanoparticle/electrode bond is not as strong in the meniscus approach. The results show that
the dielectrophoresis approach is strongly preferred for the formation of stable contacts.

The stability and repeatability of a representative molecular junction stored in
vacuum is illustrated in Figure 4.7. The figure shows data from 100 cycles of I/V
measurements made under vacuum from one same sample over a period of approximately 7
hours.
Figure 4.6  Current versus voltage characteristics when applied up to 2 V for the OPE-linked gold nanoparticle dimer bridging the nanogap electrodes using the trapping methods of (a) dielectrophoresis and (b) receding meniscus.
Figure 4.7  Temporal current versus voltage fluctuations with 100 cycles of measurements under vacuum of $\sim 5 \times 10^{-4}$ Torr for about 7 hours. Only 40 out of 100 current versus voltage traces are shown here.

No significant temporal current fluctuation was observed, indicating that stable contacts were formed between the electrode and the nanoparticle and also between the nanoparticle and the thiol contacting group.

Temperature dependent current versus voltage characteristics ($I(V, T)$) were measured to investigate the conduction mechanisms of the OPE molecule in the nanoparticle/molecule/nanoparticle bridge assemblies. The conduction is expected to consist of two distinct mechanisms with different temperature dependences.$^{39}$ Thermionic emission
or hopping conduction shows temperature-dependent current-voltage characteristics, whereas
direct or Fowler-Nordheim tunneling shows temperature-independent characteristics. Figure
4.8a shows a representative set of $I (V, T)$ traces measured between 290 and 80K through a
single OPE-linked gold nanoparticle dimer.

**Figure 4.8** Temperature dependent charge transport characteristics through a single OPE-
linked gold nanoparticle dimer bridging the nanogap electrodes. (a) Current-voltage
characteristics, $I (V, T)$ at selected temperatures (80, 110, 150, 200, and 290 K). (b) Arrhenius
plot generated from (a) $I (V, T)$ data from 0.1 to 1.0 V. (c) Plot of $\ln (I/V^2)$ versus 1/V at
selected temperatures from 0.01 to 1.0 V, where only logarithmic growth is observed. (d)
Plot of $\ln (I/V^2)$ versus 1/V at 290 K from 0.05 to 2.0 V. Transition from logarithmic growth
to linear decrease is observed at ~1.5 V, indicating transition from direct tunneling to Fowler-
Nordheim tunneling.
No significant temperature dependence of I (V, T) was observed. An Arrhenius plot of ln (I) versus 1/T generated from the data in Figure 4.8b shows a very small temperature dependence in the current for a bias between 0 to 1.0 V, suggesting some small influence of a thermally activated process (E_a ~ 4 meV) in addition to the primary tunneling transport. Plots of ln (I/V^2) versus 1/V can be used to distinguish direct tunneling through a rectangular barrier (V < Φ_B/e) from Fowler-Nordheim tunneling through a triangular barrier (V > Φ_B/e), where Φ_B is the barrier height. Figure 4.8c shows plots of ln (I/V^2) versus 1/V and only logarithmic growth is observed, indicating direct tunneling behavior is dominant in the bias range (0 to 1 V). For the sample in Figure 4.8d at room temperature, a bias is applied up to 2 V and a marked change in slope is observed at ~1.5 V, indicating transition from direct tunneling to Fowler-Nordheim tunneling. The transition from direct tunneling to Fowler-Nordheim tunneling is consistent with the recent report by Beebe et al.\textsuperscript{40} showing a similar transition for mono-thiol terminated phenyl molecules measured in a crossed-wire and conducting probe junctions. We note that the transition voltages observed here for the oligophenylene-ethynylenedithiol molecule (~1.5 V) is larger than that observed (0.67 - 0.82 V) for a similar mono-thiol junction.

The ambient stability of a single OPE-linked gold nanoparticle dimer trapped in the nanogap electrodes was investigated. Figure 4.9 shows the log scale data corresponding to different measurements of the same device at different time intervals after the structure was made. Figure 4.9a shows a device kept under vacuum, and no significant change in the measured current is observed over 13 days. However, devices exposed to ambient laboratory
air, shown in Figure 4.9b, show different current behavior, where the currents (shown at 1 V) first exponentially increase by a factor of 4-10 with days and then begin to saturate.

**Figure 4.9** The ambient stability of the OPE-linked gold nanoparticle dimer trapped between the nanogap electrodes. (a) Data correspond to different measurements of the same device kept in vacuum at different time intervals after the devices were made. (b) For devices stored in lab air, the current (measured at 1 V for five different dimer structures) is observed to increase over several weeks and then begin to saturate. All the data points represent the average values of five measurements. The dotted line highlights the point corresponding to an apparent change in slope in log(current) vs time. All lines are drawn as a guide to the eye.
We found that generally, the time that devices took to stabilize depended on the initial measured current. Devices starting with smaller initial current took a longer time to stabilize than those starting with a larger current. The initial rate of current increase with time, determined from the slopes in the linear region in Figure 4.9b, is observed to be similar for all the devices measured.

The reversibility of the current change was tested by putting the samples exposed to ambient air into a desiccated vacuum ($10^{-3}$ Torr) for one week. For samples initially exposed for only a few days (i.e. current change was still in the rapidly increasing region of Figure 4.9b), a partial recovery (i.e. decrease) of current was observed toward the initial pre-exposure value. However, samples exposed for many days (in the saturation region in Figure 4.9b) exhibited little change in current after vacuum exposure. This behavior indicates the current changes are initially somewhat reversible, but eventually become more irreversible upon continued exposure.

The stability of the current measured in vacuum and the current change with time observed upon air exposure suggests the magnitude of the current flow is affected by impurities from the ambient impinging on the molecular junction. Of the several possible reasons for current changes with time in ambient conditions, the most plausible is a change due to adsorption of ambient impurities in the atmosphere, the most relevant of which is likely to be water vapor. The role of water on the operation of inorganic electronic devices has been considered previously. For example, hysteresis is observed to persist in transistor devices stored in vacuum because the SiO$_2$-bound water does not completely desorb in vacuum at room temperature.$^{41}$ Hysteresis is not observed in our bridge structures and water
on the SiO₂ layer beneath the gold electrodes in our structure is not likely to affect our measurements. Electrochemical reactions at molecule/metal interfaces have been proposed to explain time-dependent current flow in molecular monolayers. In the system studied here, direct covalent contacts are expected between the OPE linker molecule and gold nanoparticles. These contacts did show ambient instability, but were sufficiently stable that even after the devices were exposed to air, a number of sweeps to 2 V bias did not cause the junctions to short or otherwise break down. It is possible that water molecules adsorbed near the gold-thiol or gold/palladium contacts may affect the current flow, possibly through partial electrochemical oxidation of the metal or partial reconstruction of the gold nanoparticle surface. Even with this instability, results show that molecular conduction in single-molecule junction measurements can be kept stable over several weeks when the junctions are stored in moderate vacuum, and strategies can be envisioned to control the stability of conductivity in molecular junctions.

4.5 Conclusions

Nanoparticle/molecule/nanoparticle dimer assemblies have been successfully trapped by dielectrophoresis to bridge nanogap electrodes. Scanning probe microscopy images of the trapped particle dimers are in good agreement with results expected from simulations of the electric field generated during dimer trapping. Temperature dependent charge transport measurements through an OPE molecule linked between nanoparticles indicates highly stable contacts are formed, and a transition from direct tunneling to Fowler-Nordheim tunneling occurs at ~1.5 V. The ambient stability of the dimer assemblies shows that current increases
exponentially with time and then begins to saturate possibly due to adsorption of water near the contact between the molecule and the gold nanoparticle.

Acknowledgements

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4.6 References


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Chapter 5

Real-time conductivity analysis through single-molecule electrical junctions*

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*My contributions to this work include developing the nanoscale electrodes, process and conditions of the dimer assembly onto the electrodes. I also performed all the electrical characterization in real time during trapping and post-assembly exposure, and analysis of electrical results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. The design of experiments was carried out primarily by Dr. Gregory Parsons and me. The synthesis and assembly of the molecule into the dimers were performed by the Gorman research group including co-authors, Dr. Christopher Gorman, Jennifer Ayres and Kusum Chandra.
Conductance through single molecule junctions, consisting of nanoparticle/molecule/nanoparticle units between nanoscale planar electrodes, was monitored in real-time during several process sequences, including dielectrophoretic directed self assembly and post-assembly modification. Assembly faults are directly detected in real-time when non-ideal assembly conditions result in molecular junction failure and nanoparticle fusion in the junction. Real-time conductivity measured through the junction was sensitive to ambient conditions, and changes persisted over several days of exposure. Atomic layer deposition of Al₂O₃ was used to encapsulate and isolate the molecular junctions, and the effect of the deposition process sequence on current through the junction was evaluated in real-time. Results indicate that the current measured during atomic layer deposition is sensitive to the chemical oxidation and reduction reactions proceeding in the 1-2 nanometer confined region between assembled nanoparticles.
5.2 Introduction

There is considerable interest in methodologies to measure and evaluate current flow through molecular electronic junctions.¹ In particular, the measurement of charge transport of a single or a small number of molecules has been extensively performed using break junction and various scanning probe techniques.²⁻⁸ Single molecule electron transfer dynamics have been studied theoretically.⁹⁻¹¹ Most of these analyses are performed in well defined and controlled ambient, and the influence of environmental impurities (i.e., H₂O) on the charge transport is just beginning to be analyzed and understood.¹² We have recently developed a molecular electronic characterization test-bed that utilizes a symmetric pair of gold nanoparticles, ~ 40 nm in diameter, joined together by a single or small group of conjugated oligomeric phenylene ethynylene (OPE) molecules. These nanoparticle/molecule/nanoparticle structures¹³,¹⁴ are subsequently assembled between nanoscale test electrodes to enable current through the molecule to be characterized. This molecular analysis approach is unique because it allows the molecular junction samples to remain physically stable over extended periods (several months to date), allowing molecular conductance to be observed and characterized under a range of conditions after fabrication.¹⁴

In this article, we report real-time monitoring of conductance through nanoparticle/molecule/nanoparticle junctions during dielectrophoretic trapping,¹⁵ enabling immediate detection of a specific fault ascribed to loss of the active molecule and fusing of the nanoparticles in the junction. After successful junction formation, monitoring of the conductance in real-time during other modification and exposure sequences was also performed over short and long-term time scales, giving insight into chemical processes
occurring in the 1-2 nm gap defined by the molecule covalently bound between the pair of nanoparticles.

5.3 Experimental Methods

_Dimer Synthesis._ The nanoparticle/molecule/nanoparticle “dimer” structures were synthesized as previously described\(^14,16\) using oligomeric phenylene ethynylene molecules (OPEs) terminated with thioacetate functionalities bridged by two gold nanoparticles with a diameter of \(~40\) nm. The nanoparticles are used here to connect the molecule electrically between nanoscale metallic planar electrodes. Figure 5.1a-b show the molecular structure of the OPE molecule linked by two gold nanoparticles and the transmission electron microscopic (TEM) image of the synthesized dimer with a Philips CM12 TEM operated at 100 keV, respectively. This result shows that the TEM image is consistent with the expected dimer structure that the diameter of the gold nanoparticles is \(~40\) nm and the length of the OPE molecule is \(~2\) nm. It is expected that this approach allow only a small number of molecules (possibly a single molecule) to be bound between the two gold nanoparticles.\(^14\) TEM was also used to evaluate the statistical distribution of synthesized nanoparticles as shown in Figure 5.1c, where 173 particles were counted. The typical distribution of single nanoparticles, dimers, and trimers (with three nanoparticles in a group) in the synthesized solution was found to be 62, 31, and 7 %, respectively.

_Fabrication of Electrical Test beds._ The fabrication process of the nanoscale electrode gaps was described in detail elsewhere.\(^17\) Figure 5.2a exhibits the cross-sectional
view of patterns used, consisting of the SiO$_2$ layer (~160 nm) thermally grown on a Si (100) substrate, the first patterned metal of Au (90 nm)/Ti (10 nm) with a gap width of ~10 µm, and the second metal of Pd (20 nm) evaporated onto the patterned first metal layer using an oblique angled metal evaporation with a tilt angle of ~50 $^\circ$ from the normal to the surface. Figure 5.2b shows the plan-view scanning electron microscopic (SEM) image of the nanoscale electrode gap (~70 nm) formed in Figure 5.2a, using Hitachi S-3200 with an accelerating voltage of 30 kV. This approach allows the large-area parallel fabrication of nanoscale electrode gaps, whose typical optical image is displayed in Figure 5.2c.

Dielectrophoretic Trapping. Dielectrophoretic trapping of a nanoparticle dimer was carried out in the probe station at room temperature after putting a ~3 µl droplet of the suspension onto the electrode surface,$^{13,14}$ where the nanoparticle solution consists of ~90% deionized water and ~10% THF/ethanol. The trapping conditions used were an alternating current (AC) electric field of 1-3 VAC, a frequency of 1 kHz - 1 MHz, and a trapping time of 20-120 s. After trapping, samples were rinsed with deionized water and dried in a gentle stream of nitrogen gas. Best trapping conditions were found at 2 V, 1 MHz and 60 s, where 51 samples out of 58 experimental trials were trapped with reasonable current level (neither shorting nor ~pA current). AC voltage was generated using a precision LCR meter (Agilent 4284A) and computer-controlled using LabView from National Instruments, enabling real-time conductance change to be monitored during dielectrophoretic trapping.

Atomic Layer Deposition. Atomic layer deposition (ALD) of Al$_2$O$_3$ was carried out to coat fabricated molecular junctions, where trimethylaluminum (TMA) and deionized water
were used as precursor and oxidant gas, respectively. Argon was used as a carrier and purge gas. One reaction cycle of ALD consists of TMA dose (1 s)/ Ar purge (20 s)/ H₂O dose (0.3 s)/ Ar purge (60-120 s) at the growth temperature of 50 °C. The operating pressure was held at 0.5 Torr.

_Electrical Characterization._ During dielectrophoretic trapping, the in-situ conductance monitoring was performed in a vacuum-compatible probe station (Janis Research Co., Inc.) using an Agilent 4284A LCR meter. The LCR meter enabled recording of the ac current through the electrode gap in real-time. After trapping, current-voltage (I-V) measurements were initially carried out in vacuum of ~5×10⁻⁴ Torr using a Keithley 2602 Sourcemeter. To investigate the effect of different gaseous environments (inert argon gas and ambient air) on the current change of a sample, the current through a junction was monitored in real-time as the pressure and gas composition was varied in the probe station chamber. For these measurements, a continuous dc bias of 0.5 V applied using a Keithley 230 voltage source and a Keithley 6512 electrometer, which are computer-controlled using LabView from National Instruments. The effect of sample heating was also characterized in the probe station, where the temperature was controlled from 30 to 90 °C using a 331 temperature controller (LakeShore).
Figure 5.1  (a) The molecular structure of an oligomeric phenylene ethynylene molecule (OPE) used in this study. (b) TEM image of an OPE-linked nanoparticle dimer consisting of two ~40 nm diameter gold nanoparticles. (c) The typical statistical distribution of particles found in the sample solution used for directed assembly, including units containing a single nanoparticle, two nanoparticles (dimers), and three nanoparticle clusters (trimers). For this sample set, 173 particles were counted using TEM.
Figure 5.2  (a) Schematic of the nanoscale electrode gap fabrication procedure, consisting of SiO$_2$ layer (~150 nm) thermally grown on a Si (100) substrate, a patterned bi-layer of Ti/Au (10 nm/90 nm thick) followed by a layer of palladium (20 nm) deposited at an oblique angle to form the nanoscale electrode gap. The thickness and width of each layer are exaggerated for clarity. (b) A plan-view scanning electron microscope (SEM) image of an example nanoscale electrode fabricated with a gap width of ~70 nm. (c) An optical image of a typical fabricated set of nanogap electrodes showing capability for parallel fabrication.
5.4 Results and discussion

Applying an ac voltage between the nanoscale electrodes in the presence of the molecule/nanoparticle aqueous suspension develops a dielectrophoretic force that directs the assembly of the molecule/nanoparticle units onto the contact electrodes.\textsuperscript{14} It has been previously shown\textsuperscript{18} that dielectrophoretic trapping of a conducting nanoparticle can be controlled using a shunt resistor to modify the voltage across the gap after assembly. For the experiments reported here, applying 1 V AC at 1 MHz to the electrodes typically resulted in only \textasciitilde pA levels of current flow between the electrodes, and successful trapping was not observed, likely due to the relatively small applied dielectrophoretic force. At 2 V AC, successful trapping is often achieved, but no significant change in conductance is generally detected upon successful trapping of the nanoparticle/molecule/nanoparticle dimer. The lack of signal change upon trapping results because the resistance through the OPE junction exceeds that of the aqueous solution used to suspend and deliver the nanoparticle dimer units. Figure 5.3a shows the conductance measured as a function of time during the successful trapping of a molecule/nanoparticle dimer unit performed at 2 V AC and 1 MHz. A schematic drawing of the trapped sample geometry is shown in Figure 5.3b, and Figure 5.3c shows I-V traces, measured after drying under vacuum for several hours, for several different samples after successful dielectrophoretic directed assembly. Symmetric I-V curves were observed consistent with common non-resonant tunneling. The observed range of current levels is attributed to differences in the contact properties between the gold nanoparticle and the metal electrode during trapping of the dimer.\textsuperscript{13}
Figure 5.3  (a) *In-situ* AC conductance monitoring during dielectrophoretic trapping at 2 VAC and 1 MHz for 60 s. The measured conductance does not substantially change upon successful trapping of a nanoparticle/molecule/nanoparticle dimer unit. (b) Schematic drawing showing the trapping state and current flow for (a). (c) I-V curves obtained from 10 different samples measured in a vacuum probe station after trapping.
Figure 5.4  (a) In-situ conductance monitoring during dielectrophoretic trapping at 3 VAC and 0.1 MHz for 60 s. The sharp increase in conductance observed during trapping indicates fusing of the nanoparticles, resulting in a faulty junction. (b) Schematic drawing describing the trapping state and current flow for (a). (c) Representative I-V curve measured in a vacuum probe station after trapping.
In contrast, when a dimer is trapped at higher applied voltage a sharp conductance increase was often observed during trapping. An example is shown in Figure 5.4a where the conductance increases by more than a factor of 100 upon trapping using 3 VAC at 100 kHz. The conductance increase is ascribed to nanoparticle coalescence or fusion, shown schematically in Figure 5.4b, leading to an ohmic I-V trace after drying, as shown in Figure 5.4c.

After successful assembly of the junction, current was measured in real-time under various ambient conditions. Figure 5.5 shows the normalized current through an example junction as a function of time during sequential exposure to vacuum, inert gas pressure, and atmospheric air pressure. For this particular sample, the current is normalized to a value of $1.24 \times 10^{-8}$ A at 0.5V. The lower panel in Figure 5.5 shows the corresponding recorded pressure vs time. When inert argon gas was supplied to the vacuum probe station at 760 Torr, no significant current change was observed. However, upon exposure to ambient air, the current rapidly decreased (within a few minutes) and stabilized. After approximately 10 minutes, evacuating the system resulted in reversible recovery of the current to its original starting value in vacuum. Similar results were reported by Long et al. and are consistent with the gold-thiol contacts undergoing reversible oxidation upon exposure to ambient water vapor. In the nanoparticle/molecule/nanoparticle junction, the contacts between the nanoparticle and the OPE linker molecule are expected to be more sensitive to ambient and other variations than the contacts between the nanoparticles and the metal electrodes.

Figure 5.6 shows the longer-term (>10 days) stability of nanoparticle/molecule junctions stored under vacuum and ambient air.
Figure 5.5  Real-time current flow through a dimer junction measured using a continuous bias of 0.5 V upon alternating exposure to inert argon gas, vacuum, and ambient air as a function of time for one sample. The typical curve of pressure change as a function of time is also shown. When exposed to air, the current decreased then recovered after air evacuation. The measured current was normalized to the starting initial value (1.24×10^8 A) in vacuum.

For these measurements, the samples were stored in air with no bias applied. Data in Figure 5.6a indicates that when a sample was kept in vacuum over many days, there was no significant change in junction current. Figure 5.6b shows that in air, a small rapid decrease in current (consistent with data in Figure 5.5) is followed by a slower exponential increase and eventual saturation in current flow. The current increase could correspond to partial
electrochemical reaction or reorganization of the nanoparticle surface.\textsuperscript{20,21} It is also possible that for longer times water vapor accumulating in the junction region may lead to additional current pathways and a net increase in current flow.

**Figure 5.6** The effect of long-term storage environments on the current change of the OPE-linked gold nanoparticle dimers assembled between nanoscale electrodes. (a) A sample maintained in vacuum shows no significant current change over more than 10 days. (b) Upon air exposure, a sample shows a rapid decrease in conductivity followed by a slow increase and saturation. The line is drawn as a guide to the eye.
The possible affect of applied bias over several hours was also evaluated, and results are shown in Figure 5.7, where a continuous dc bias of 0.5 V was applied in vacuum and in air. For a sample kept in vacuum, oscillations in current flow were observed that correspond to approximately ±3-5 % of the magnitude of the average current value. In air, a larger variation in current was observed, corresponding to more than ±10 % of the average current value. An increase in the average current value is also observed, consistent with the results in Figure 5.6, where bias was applied only at each measurement point. The results suggest that the applied bias did not have a significant effect on the current measured through the junction. Under higher applied bias (1.5-2 V) over several hours, a larger fluctuation in current was observed, possibly due to bias-induced structural instabilities or a local heating in the molecule junction. Effects of heating were observed directly by applying thermal treatments between 30 and 90 °C in vacuum to example molecular junctions. The current during and after heat treatment were collected, and the results are shown in Figure 5.8. The results show that a moderate thermal treatment of 50 °C resulted in a modest increase in current flow after cooling for 24 hours back to room temperature, whereas treatments at higher temperatures lead to larger irreversible changes, up to a factor of 3 upon heating to 90 °C.

In order to evaluate possible encapsulation and long-term stabilization of molecular junctions, atomic layer deposition of Al₂O₃ was performed on the nanoparticle dimer trapped between the nanoscale electrode gaps, where the sample was heated to 50 °C during film deposition. The atomic layer deposition process is particularly attractive for this
application because the high conformality of the resulting coating is expected to result in coatings that fully enclose and isolate the junction.

Figure 5.7 The stability of the current flow through a molecule junction with continuous applied bias of 0.5 V is observed to depend on the ambient condition. For a sample in vacuum, trace (a) shows relatively small oscillations over several hours, whereas in air, a sample shows much larger oscillations and an overall increase in current flow, consistent with the longer-term result shown in Figure 5.6. For measurement in ambient, the sample measurement stage was isolated from air flow during analysis.
Figure 5.8  Sample heating at moderate temperatures are observed to affect junction conductance measured in vacuum. When a device was heated to 50 °C or less, a relatively small and reversible current change was observed. However, irreversible current increase was observed when heating to 70 °C or above. Here the measured current was normalized to the original value before heating in vacuum. All lines are drawn as a guide to the eye.

After encapsulation, the stability of the molecular junction was compared to an uncoated sample as shown in Figure 5.9a. The conductivity of the uncoated sample is observed to change upon air exposure, whereas the coated sample is observed to be stable upon air exposure, similar to the sample exposed to only argon. In order to observe the effects of the atomic layer deposition process on the molecular junction, the current through the junction was evaluated in real-time during film processing at 50 °C, and results are shown in Figure 5.9b. The inset shows an optical image of the nanogap with electrodes wired for external electrical feed-through contact.
Figure 5.9  (a) Current flow monitored as a function of time in air and argon for an assembled molecular junction, and a similar junction exposed to air after encapsulation using atomic layer deposition of Al₂O₃ at 50 °C.  (b) In-situ current monitoring during the atomic layer deposition procedure at 50 °C. The repeating current variation corresponds to the deposition reaction consisting repeating cycles of TMA exposure (1 s), argon purge (20 s), water exposure (0.3 s), and argon purge (60 s). The inset shows an optical image of nanogap electrode sample measured. The measured current was normalized to the starting initial value in vacuum.
The atomic layer deposition process involves sequential exposure of the sample to trimethylaluminum, TMA (for 1 second), followed by argon purge (20 s), water exposure (0.3 s) and another argon purge (60 s). The current response during two sequential deposition cycles is observed in Figure 5.9b, and the current change is found to correspond directly to the reactant exposure and purge cycle steps. It is interesting to note that the current is observed to decrease during the TMA exposure, and increase rapidly during the water exposure step. The rapid increase during water exposure is opposite to the decrease observed under air exposure which was ascribed to reaction with ambient water in the atmosphere. One likely explanation for this difference is that the water exposure during ALD is substantially higher than during ambient exposure, giving rise to water film coverage across the nanoparticle junction, resulting in an additional lower resistance pathway for current to flow during the ALD water exposure step.

We note that in this process, the magnitude of the current change during TMA and water exposure may be correlated to the extent of reactions occurring within the 1-2 nm confined region between the nanoparticles and defined by the molecule length. Further analysis of real-time current flow through physically stable molecular junctions could be used to probe a variety of physical and chemical mechanistic processes at the single-molecule level.

5.5 Conclusions

Real-time conductance variations in molecular junctions can be analyzed for a variety of process sequences, including fault detection during dielectrophoretic directed self
assembly, and during post fabrication junction modification or vapor exposure. The physical stability of the nanoparticle/molecule/nanoparticle junctions is particularly attractive for long-term evaluation (over several weeks) of junction stability and performance. Real-time current changes observed during coating of the nanoparticle junctions by atomic layer deposition corresponded directly to the reactant cycle times employed in the procedure, and the current can give insight into the chemical reaction sequence occurring in the nanometer-scale confined region between the nanoparticles used to form the junction.

Acknowledgements

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5.6 References


Chapter 6

Electron transport dependence on molecular length and structure using single molecule nanoparticle/molecule(s)/nanoparticle junctions*

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*My contributions to this work include developing the nanoscale electrodes, process and conditions of the dimer and trimer assembly onto the electrodes. I also performed all the electrical characterization and analysis of electrical results. I worked independently on the text. The design of experiments was carried out primarily by Dr. Gregory Parsons and Dr. Christopher Gorman, Jennifer Ayres and me. The synthesis and assembly of the molecule into the dimers and trimers were performed by the Gorman research group including co-authors, Dr. Christopher Gorman, Jennifer Ayres and Kusum Chandra.
6.1 Abstract

The nanoparticle/molecule/nanoparticle ‘dimer’ and ‘trimer’ structures with longer molecular length (up to 4.7 nm) were synthesized and trapped successfully in the nano-scale electrode gaps, which was fabricated up to less than 30 nm using oblique angled metal evaporation technique. The current-voltage measurements through a series of dimers showed that the OPE molecules could serve as an effective molecular wire over long distances due to the very weak length dependence ($\beta \approx 0.12 \text{ Å}^{-1}$) on the electron transport. The effect of molecular structure on the electron transport was compared between linear-type (in dimers) and Y-type OPE molecules (in trimers), demonstrating that the linear resistance and conductivity was not significantly affected even though a little larger current flow was observed at 1 V for the trimers.
6.2 Introduction

The effort to understand the electron transport through single (or a small number) molecules connected to two metal electrodes has expedited the development of molecular-scale electronics experimentally as well as theoretically in recent years. The electron transport properties of organic molecules depend not only on device geometry and metal-molecule contact properties, but also on the chemical/electronic structure of molecules in junctions including molecular length, substitution (i.e., redox molecules) and extent of conjugation. In particular, the length dependence of electron transport across π-conjugated single molecules or self-assembled monolayers (SAMs) has previously been investigated with a variety of experimental measurements including electrochemical, mercury drop electrode, conducting probe atomic force microscope (CP-AFM), scanning tunneling microscope (STM) as summarized in Table 6.1. These studies have mainly focused on molecules with relative short molecular length (typically less than 2 nm lengths) as well as only one thiol bound to the electrode. Currently, the strategies of chemical synthesis for molecular wires continuously place an emphasis on the molecular length for practical applications. Only few studies have recently addressed the weak length dependence of resistance in conjugated molecules (i.e., oligoanilines, carotenoid polyenes, and Ruthenium (II) Bis(σ-arylacetylide) complexes) with longer molecular length (up to 4.7 nm) between two electrodes. Electrical characterization for conjugated molecular wires even with 7 nm long has been performed as well.
Table 6.1 The measured values of $\beta$ for conjugated molecules connected to metal electrodes with different experimental systems.

<table>
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<tr>
<th>System</th>
<th>Measured molecules</th>
<th>$\beta$ (Å⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical</td>
<td>OPE thiol SAMs on Au</td>
<td>0.36-0.43</td>
<td>12-13</td>
</tr>
<tr>
<td></td>
<td>OPV thiol SAMs on Au</td>
<td>0.06</td>
<td>14</td>
</tr>
<tr>
<td>Mercury drop</td>
<td>Ag-OP thiol SAMs/C16 SAM-Hg</td>
<td>0.61±0.1</td>
<td>15</td>
</tr>
<tr>
<td>CP-AFM</td>
<td>OP thiol SAMs on Au</td>
<td>0.35-0.61</td>
<td>16-17</td>
</tr>
<tr>
<td></td>
<td>oligoacene thiol SAMs on Au</td>
<td>0.5±0.09</td>
<td>18</td>
</tr>
<tr>
<td>STM</td>
<td>nitro-based OPE thiol SAMs</td>
<td>0.15-0.45</td>
<td>19</td>
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<tr>
<td></td>
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<td>20-21</td>
</tr>
<tr>
<td></td>
<td>single OP thiol on Au</td>
<td>0.55±0.0.02</td>
<td>22</td>
</tr>
</tbody>
</table>

*a* OPE: Oligo(phenyleneethynylene).
*b* OPV: Oligo(phenylenevinylene).
*c* OP: Oligophenylene.

In our previous studies, the I-V characteristics were measured and evaluated with a dimer, consisting of single (or a small number) oligo phenylene ethynylene molecules (OPEs) bridged by two ~40 nm gold nanoparticles, trapped between the nanoscale electrode gaps.²⁹, ³⁰ Here we extended this work to investigate the dependence of molecular resistance (or conductance) on molecular length of a series of single OPE dithiol molecules (up to 4.7 nm between two sulfur atoms) with covalently bound to gold nanoparticles to extract the electronic decay constant ($\beta$) and effective contact resistance using the dimer structures. The chemical bonding of gold-thiol in metal-molecule junctions is considered to enhance strong electronic coupling³¹ between the chain ends, facilitating electron transport over long distance. The dependence of different molecular structures such as linear-type (in dimer) and Y-type (in trimer) with similar molecular length on the electron transport will be discussed as well.
There are several advantages of using the OPE molecules as a basic building block of molecular wires: First, the energy gap (~3.5 eV) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the OPE molecule is lower than that of saturated molecules (~7 eV). Second, cylindrical symmetry of the acetylene unit make it possible to maintain the extended $\pi$-electron conjugation at any degree of rotation. Third, the synthetic flexibility is available by combining the phenyl ring with various functional substituents (i.e., NO$_2$, NH$_2$ etc) providing the unique electrical properties such as negative differential resistance (NDR). Fourth, the rigid rod-like $\pi$-conjugated bridge structure of the OPE is well suited to maintain the nanoparticle/molecule/nanoparticle structure, preventing any aggregation (i.e., direct contacts) between nanoparticles.

This article demonstrates that the OPE dithiolates bridged by nanoparticles can be used as a molecular wire for the effective electron transport over long distance because of very weak length dependence ($\beta \sim 0.12$), and also open up the pathway to explore potential three-terminal devices with asymmetrical Y-type molecules linked by three metal electrodes. Recently, a theoretical study has been reported on quantum interference effect transistor utilizing molecular structures with three substituents connected to the center of benzene molecule, which are structurally somewhat similar to the trimer used here.

6.3 Experimental Methods

The nanoparticle/molecule/nanoparticle ‘dimer’ and ‘trimer’ structures with different molecular lengths were synthesized as previously described, using linear-type OPE molecules bridged by two ~40 nm gold nanoparticles and Y-type OPE molecules bridged by
three ~15 nm gold nanoparticles, respectively. The acetyl groups within the thioacetate-terminated OPE molecules are removed during synthesis (i.e., in-situ deprotection) so that the thiols bind covalently to gold nanoparticles. The only real difference in the synthesis of dimers and trimers compared to the previous method\textsuperscript{35} is the rate of addition of the OPE linker molecules, which was added slowly without waiting 10 min between additions. It did not appear to make any difference in the statistical distribution using the transmission electron microscopic image (TEM), which was collected with a Philips M12 transmission electron microscopy operated at 100 keV.

The nano-scale electrode gaps were fabricated as described in detail elsewhere.\textsuperscript{10} The first metal layer of Au (60-90 nm)/Ti (5-10 nm) was deposited and patterned on the thermally grown SiO\textsubscript{2} layer on a Si (100) substrate. Then the second metal layer of Pd (10-20 nm) was evaporated onto the patterned first metal layer with a gap width of ~10 \textmu m using oblique angled metal evaporation with a tilt angle of 40-50\degree from the normal to the surface. The nanogap width is proportional to the thickness of the patterned first metal layer and the evaporation angle of the second metal layer. The process parameters were tuned to make the electrode gaps less than 30 nm, enabling the assembly of the trimers with a nanoparticle diameter of ~15 nm in the nanoscale trench. The atomic force microscopy (AFM) measurements of the fabricated nano-scale electrode gaps were carried out in tapping mode under ambient conditions using a Digital Instrument AFM with a Nanoscope IIIa controller (Santa Barbara, CA). AFM probe tips (SSS-NCH, Nanosensors\textsuperscript{TM}) with a typical tip radius of curvature of 2 nm were used to enable high resolution AFM images in the nanogap region.
Dielectrophoretic-directed self-assembly of OPE-linked nanoparticle dimers and trimers were performed in the probe station at room temperature by placing a ~3 µl droplet of the suspension onto the electrode surface as described previously.\textsuperscript{29} The typical trapping conditions used were an alternating current (AC) bias voltage of 2-3 V at a frequency of 1 MHz for approximately 60-120 sec. An AC voltage was generated using a precision LCR meter (Agilent 4284A) and computer-controlled using Labview from National Instruments, enabling the \textit{in-situ} monitoring of conductance during dielectrophoretic trapping.\textsuperscript{30} Immediately after trapping, the probe station (ST-100-2PROB, Janis Research Co.) containing samples was evacuated to \(\sim 5 \times 10^{-4}\) Torr at least 8 hrs and then current-voltage (I-V) measurements were performed using a Keithley 2602 sourcemeter. Each sample was measured at least 3-5 times and then averaged to show the representative value.

\textbf{6.4 Results and discussion}

\textbf{Molecular Design and Synthesis.} As shown in Figure 6.1, two different linear-type and Y-type molecular structures with thioacetate-terminated oligo(phenyleneethynylene)s (OPEs) are designed in order to study the dependence of charge transport on molecular length and structure. The first molecular structure is used to form a dimer with a series of linear OPEs bridged by two \(~40\) nm gold nanoparticles, where the respective molecular lengths (the distance between the two sulfur atoms) are estimated to be 2.0 nm (\(n=1\)), 3.4 nm (\(n=2\)), and 4.7 nm (\(n=3\)) by using MM2 (Chem 3D) software to determine the distance between two sulfur atoms.
It is known that OPE molecules possess poor solubility, which is one of the major limiting factors in the design of increasing molecular length. To overcome the solubility problems, 2, 5-dialkoxo-substituted derivatives of the OPE molecule were synthesized. The second molecular structure is used to form a trimer with a series of Y-type OPEs bridged by three ~15 nm gold nanoparticles, which are symmetrical with respect to the central benzene ring. Thus the current flow through each leg of the trimer is the same in all directions. Especially for trimers, careful molecular design between three nanoparticles and a Y-type OPE molecule are necessary prior to their usage to circumvent a direct contact (i.e., aggregate).
between them, leading to high conductivity through the citrate capping molecules covering nanoparticles, not the OPE molecules of interest. Figure 6.2 shows the trimer structure with Y-type OPE linker molecule bridged by three gold nanoparticles. From the right-angled triangle geometry, the gap distance \( G \) between two gold nanoparticles can be estimated as a function of the radius of a gold nanoparticle \( R \) and the molecular length \( L \) of one leg of the Y-type molecule (i.e., the distance from the sulfur atom to the center of the benzene ring plus 0.23 nm of gold-thiol bond length), leading to the relationship of \( G = 1.73L - 0.266R \). Here the citrate-capping layer was assumed to be \(~0.4\) nm, so the real gap between the nanoparticles is estimated to be \( G - 0.8 \) nm considering the thickness of two capping layers.

![Figure 6.2](image)

**Figure 6.2** Design of the Y-type OPE linker molecule bridged by three \(~15\) nm gold nanoparticles. \( G, R, \) and \( L \) denote the gap distance between two gold nanoparticles, the radius of a gold nanoparticle, and the estimated molecular length from the center of benzene ring to the gold atom (the gold-thiol distance is assumed \(0.23\) nm), respectively. Sin \(60 = (R+G/2)/(R+L)\), that is, \( G = 1.73L - 0.266R \) can be deduced from the right-angled triangle geometry. \( G \) is used to predict the gap distance between the nanoparticles, circumventing direct contact (i.e., aggregate) between particles.
The calculated gap distance corresponding to the trimer with n=2, 3, 4 is shown in Table 6.2. For trimers composed of 12-15 nm gold nanoparticles used in this study, the finite gap distance suggests that the measured electron transport originate from the active OPE molecules connected to nanoparticles. However, in the case of trimers with larger than 20 nm particles, we can predict that it is not possible to synthesize with (IV) molecule (n=2) in terms of molecular design.

Table 6.2  
Gap distance (G) between two nanoparticles as a function of the radius of a nanoparticle (R) and the estimated molecular length (L)a.

<table>
<thead>
<tr>
<th>diameter</th>
<th>radius</th>
<th>G (L=1.93) no cit</th>
<th>G (L=1.93) cit</th>
<th>G (L=2.62) no cit</th>
<th>G (L=2.62) cit</th>
<th>G (L=3.3) no cit</th>
<th>G (L=3.3) cit</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.5</td>
<td>2.67</td>
<td>1.87</td>
<td>3.96</td>
<td>3.16</td>
<td>5.04</td>
<td>4.24</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>2.01</td>
<td>1.21</td>
<td>3.30</td>
<td>2.50</td>
<td>4.38</td>
<td>3.58</td>
</tr>
<tr>
<td>15</td>
<td>7.5</td>
<td>1.34</td>
<td>0.54</td>
<td>2.63</td>
<td>1.83</td>
<td>3.71</td>
<td>2.91</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0.68</td>
<td>-</td>
<td>1.97</td>
<td>1.17</td>
<td>3.05</td>
<td>2.25</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>0.64</td>
<td>-</td>
<td>1.72</td>
<td>0.92</td>
</tr>
</tbody>
</table>

a Estimated molecular length (L) consists of the calculated length from the center of the benzene ring to the sulfur atom plus the gold-thiol bond length, which was assumed to be 0.23 nm. Here L=1.93, 2.62 and 3.3 nm correspond to the estimated molecular length for the trimers with n=2 (7 rings), n=3 (10 rings) and n=4 (13 rings), respectively.

The statistical distribution of synthesized nanoparticle structures with different molecular length was obtained based on the number of particles counted from the transmission electron microscope (TEM) image as shown in Table 6.3. The statistical distribution is not significantly affected by the variation of molecular length in both dimers.
and trimers. For dimers, approximately 30% was found for the particles bound in dimers. For trimers, approximately 20% was observed for the particles bound as trimers.

Table 6.3 The statistical distribution\textsuperscript{a} of synthesized dimers and trimers with different molecular length.

<table>
<thead>
<tr>
<th>type</th>
<th>compound</th>
<th>total particles counted</th>
<th>statistical distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>single particles</td>
</tr>
<tr>
<td>dimer</td>
<td>I (n=1)</td>
<td>173</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>II (n=2)</td>
<td>274</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>III (n=3)</td>
<td>140</td>
<td>64</td>
</tr>
<tr>
<td>trimer</td>
<td>IV (n=2)</td>
<td>274</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>V (n=3)</td>
<td>274</td>
<td>49</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The statistical distribution data were obtained based on the number of particles counted from the TEM images. There can be observed variations between samples since the TEM is not a very accurate method for determining the statistical information about the samples. However, it still provides some useful data to compare.

Fabrication of Nanoscale Electrode Gaps and Assembly of Particles. The nanoscale electrode gaps were fabricated using angled metal evaporation technique as mentioned before. For the dielectrophoretic trapping of particles between them, the nanogaps should be less than the particle size, suggesting the nanogaps of less than 80 nm and 30 nm are necessary for the dimers and trimers, respectively. Figure 6.3 shows the AFM image of the fabricated nano-scale electrode gaps. The inset displays the real line profile across the nanogap region, showing that the formation of nanogaps less than 30 nm can be achieved by tuning the process parameters (i.e., the thickness and etching profile of the first metal and
evaporation angle etc.) during angled metal evaporation. Further, I-V measurements of all the fabricated nanogap electrodes were performed before trapping, which showed only \(\sim\)pA current level ensuring the formation of the nano-scale electrode gaps.

Figure 6.3 The atomic force microscopic (AFM) image of the typical nano-scale electrode gaps (less than 30 nm) especially for the trapping of trimers, which are fabricated by angled metal evaporation technique. The inset shows the real line profile across the nanogap region, consistent with the expected device structure.

As predicted from the electrical field distribution using FEMLAB simulation and the AFM image of trapped dimer samples in the previous study,\textsuperscript{29} Figure 6.4 shows the expected structures of samples trapped between the nano-scale electrode gaps. The upper inset shows a typical TEM image of a dimer (III) with \(n=3\) and the lower inset exhibits that of a trimer (V) with \(n=3\), respectively. The particle size, molecular length and the gap distance are in good agreement with the expected values as shown in Table 6.2.
Figure 6.4  Schematic diagrams for the expected structures of samples trapped between the nanoscale electrode gaps using dielectrophoretic trapping method. (a) The dimer sample with linear OPE molecule(s) bridged by two ~40 nm gold nanoparticles. The inset shows the representative TEM image of a dimer (III) with n=3. (b) The trimer sample with Y-type OPE molecule(s) bridged by three ~15 nm gold nanoparticles. The inset shows the representative TEM image of a trimer (V) with n=3. Here the scale bar denotes 20 nm length.
Current-voltage (I-V) characteristics of the nanoparticle/linear-type OPE(s)/nanoparticle dimer. In the previous study, we have shown that the nanoparticle/molecule/nanoparticle structures enable to measure I-V characteristics through single (or a few) molecules over long period (several weeks) and real-time conductance change with alternating exposure of different gas environments after trapping between the nano-scale electrode gaps. Here we have extended the method to OPE molecules with longer molecular lengths (2.0 nm (I) to 4.7 nm (III)) to investigate the length dependence of resistance. Figure 6.5 shows the average current-voltage curves obtained from 8-12 different samples for each dimer structure (I-III) with error bars (i.e., standard deviation). The nonlinear I-V curves were observed between ±1 V and the symmetrical I-V curves were also found consistent with symmetrical gold-thiol (Au-S) bonding at both ends of nanoparticle-molecule junctions. Figure 6.6a shows the dependence of resistances on the molecular length of the conjugated OPE molecules. The average resistances were estimated from the reciprocal of the slope of the I-V curves in the low bias region of ±0.2 V. The semilog plot of tunneling resistance vs the molecular length was linear, suggesting the mechanism of coherent non-resonant tunneling. Thus the resistance $R$ is described by

$$R = R_0 \exp(\beta s)$$  \hspace{1cm} (1)

Where $R_0$ is the effective contact resistance, $\beta$ is the electronic decay constant which is structure-dependent in the molecules, and $s$ is the separation distance between electrodes. Here the $s$ value consists of the molecular length between two sulfur atoms calculated by MM2 (Chem 3D) software and 2.3 Å for each Au-S bond. The $\beta$ value of 0.12 ± 0.3 Å⁻¹ was obtained from the slope of the resistance vs the molecular length, showing substantially
weak dependence of resistance on the molecular length. This low $\beta$ value is in agreement with the range of experimental values as well as theoretical values. The theoretical minimum $\beta$ value for tunneling through a molecular wire was reported $\sim 0.05 \ \text{Å}^{-1}$ and the $\beta$ value of the planar oligo($p$-phenylene) dithiolate wires was calculated $0.165 \ \text{Å}^{-1}$.$^{37, 38}$ Experimentally, Frisbie and co-workers$^{27}$ reported the $\beta$ value of $0.09 \ \text{Å}^{-1}$ for ruthenium (II) bis($\sigma$-arylacetylide) complexes (2.4 nm to 4.9 nm), and Lindsay and co-workers$^{25}$ also reported the $\beta$ value of $0.06$-$1.0 \ \text{Å}^{-1}$ for oligoanilines (2.4 nm to 4.7 nm), both of which are structurally similar to the OPE molecule.

**Figure 6.5** The average current vs voltage characteristics through the OPEs with different molecular length in dimer structures, in which each data point represents the average value obtained from 8-12 different samples and also I, II and III compound correspond to $n=1$, 2 and 3, respectively. Here the error bars mean the standard deviation.
Figure 6.6  (a) The average resistance vs molecular length in the dimer samples, in which the resistance was obtained at the low bias region (±0.2 V). The electron decay constant (β) was estimated to be $0.12 \pm 0.03 \text{ Å}^{-1}$ and the effect contact resistance ($R_c$) was $\sim 4 \times 10^6 \Omega$.  (b) The effect of the applied bias voltage on the value of beta between 0 and 1 V. The beta value was not significantly changed with the bias voltage up to 1 V.
There are several factors to be responsible for these low $\beta$ values across these molecules measured, which are not considered to be independent of each other. First, our method of making “chemical” contacts with both thiols covalently bound to the metal nanoparticles lead to strong electronic coupling between metal and molecular orbitals in comparison with “mechanical” contact with only one end covalently bound to the metal electrode. It was reported that the $\beta$ value for both ends bound to metal electrodes can be lowered almost twice than that for only one end bound to metal electrode. Second, the extended $\pi$-conjugation (co-planarity) along the OPE molecules with long molecular length can facilitate the electron transport effectively since the HOMOs get closer to the Fermi level of the metal electrode with increasing molecular length. Third, the HOMO-LUMO gap was reported to be decreased with increasing molecular length. The effective barrier height ($\phi$) to transport is smaller than what would be predicted from the simple offset of the Fermi level and the energy of a molecular state due to the density of states in molecular junctions from the mixing of molecular orbitals and metal electrodes. For the conjugated molecules, the effective barrier height can be calculated using the following equation:

$$\beta = \frac{4\pi}{\hbar} (2m\phi)^{1/2}$$

where $m$ and $\phi$ are the electron effective mass and effective barrier height, respectively. $m=0.16m^*$, which was calculated as effective mass of electron through a molecular wire such as phenylene oligomers, was used here. The effective barrier height was calculated to be $\sim 14$
meV. Lastly, the possible shift from direct tunneling to other electron transport mechanisms (i.e., hopping or resonant tunneling)\textsuperscript{19,25,27} could enhance the conductance across the long molecular wires.

The effective contact resistance ($R_c$) was estimated to $\sim 4 \text{ M}\Omega$ from the extrapolation of resistance to the zero length in Figure 6.6a. This value is larger than what would be expected from the direct contact between two gold nanoparticles at zero molecular length, which would be closer to the quantum of resistance, $\hbar/2e^2$ ($\sim 12.9 \text{ k}\Omega$) as reported by a gold-coated CP-AFM.\textsuperscript{18} The citrate-capped single gold nanoparticle was trapped in the same test beds as used in dimers and then the resistance was measured to be $\sim 2 \text{ M}\Omega$.\textsuperscript{5,43} So the high effective contact resistance possibly arises from the contact resistance in the junctions of a citrate-capped nanoparticle and electrode. Figure 6.6b shows the dependence of $\beta$ value as a function of the applied bias voltage between 0 and 1 V. The values of $\beta$ was obtained to be $\sim 0.12 \text{ Å}^{-1}$, which was not so dependent on the bias range up to 1 V suggesting that the direct tunneling is the dominant transport mechanism in the dimer structures used.

**I-V characteristics of the nanoparticle/Y-type OPE(s)/nanoparticle trimer.** To investigate the effect of molecular structure such as linear type in dimers and Y-type in trimers on the electron transport, I-V characteristics of (IV) and (V) compounds were measured in vacuum after trapping in the electrical test beds similar to the dimers as shown in Figure 6.7. Each data point was obtained from the average of 8-10 different samples for each compound. Symmetrical I-V characteristics were observed due to the symmetrical gold-thiol bonds within the trimer structure.
Figure 6.7  Average current vs voltage (I-V) characteristics for the 8-10 different trimer samples with (IV) 7 rings and (V) 10 rings linked by three ~15nm gold nanoparticles. Here the error bars denote standard deviation.

The I-V curves of (IV) and (V) compound were found to be similar to that of the (II) and (III) in Figure 6.5, respectively. So the linear resistance at low bias regime (±0.2 V) and conductance at 1V were compared between them in detail as displayed in Table 6.4. The results showed the similar linear resistance, but a little larger conductance for the trimer compared to the dimer samples. This might be attributed to the existence of the substituent groups attached to the center of the benzene in the dimers. There are some reports about the substituents effect of the central benzene ring on the electron transport. The molecular conductance was reported to be decreased with a higher electron-withdrawing substituent in the order of I(NH₂) > I(H) > I(NO₂). However, the alkoxy substituents added to provide
solubility to the molecule was reported not to affect the electron-transfer rates significantly in the conjugated molecules.\textsuperscript{15} So results suggest that the electron transport through conjugated molecules such as OPEs is not influenced dramatically even though the molecular structure was changed from the alkoxy-substituted linear-type dimers to Y-type trimers, enabling to predict the electron transport properties through trimers indirectly by measuring their corresponding dimers.

\textbf{Table 6.4}  Comparison of linear resistance and conductance (at 1V) between dimers and trimers with similar molecular length.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Estimated molecular length (nm)</th>
<th>Linear resistance (Ω)</th>
<th>Conductance (I/V) at 1 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>linear (5R)</td>
<td>3.9</td>
<td>(3.3±1.8)×10^8</td>
<td>(5.4±2.4)×10^9</td>
</tr>
<tr>
<td>IV</td>
<td>Y-type (7R)</td>
<td>3.9</td>
<td>(3.4±4.8)×10^8</td>
<td>(8.7±6.4)×10^9</td>
</tr>
<tr>
<td>III</td>
<td>linear (7R)</td>
<td>5.2</td>
<td>(1.8±1.2)×10^9</td>
<td>(1.0±0.4)×10^9</td>
</tr>
<tr>
<td>V</td>
<td>Y-type (10R)</td>
<td>5.2</td>
<td>(1.8±1.5)×10^9</td>
<td>(1.3±0.8)×10^9</td>
</tr>
</tbody>
</table>
6.5 Conclusions

The nanoparticle/molecule/nanoparticle ‘dimer’ and ‘trimer’ structures with a series of different molecular length (up to 4.7 nm) were synthesized and trapped successfully in the nano-scale electrode gaps, which was fabricated up to the gap width of less than 30 nm using oblique angled metal evaporation technique. The current-voltage measurements of three series of dimers showed that the OPE molecules can serve as an effective candidate for molecular wire over long distances due to the very weak length dependence ($\beta \sim 0.12 \text{ Å}^{-1}$) on the electron transport. The effect of molecular structure on the electron transport was compared between linear-type (in dimers) and Y-type OPE molecules (in trimers), showing that the linear resistance and conductivity was not significantly influenced despite a little larger current level observed for the trimers. Recently, a quantum interference effect transistor was demonstrated theoretically with three substituents attached to the benzene ring, in which the source and drain electrodes are connected via conducting polymers such as polythiophene to the center of the benzene ring, and the gate electrode is connected to an alkene group. So it would be possible to fabricate practical three-terminal devices by utilizing an asymmetrical trimer structure or modifying the device structure even with the symmetrical trimer used here.

Acknowledgements

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6.6 References


Chapter 7

Toward three-terminal molecular devices using nanoparticle/Y-type molecule/nanoparticle trimeric structures*

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*My contributions to this work include developing the nanoscale electrodes, process and conditions of the trimer assembly onto the electrodes. I also performed all the electrical characterization and analysis of electrical results. I worked independently on the text. The design of experiments was carried out primarily by Dr. Gregory Parsons and Dr. Christopher Gorman, Jennifer Ayres and me. The synthesis and assembly of the molecule into the trimers were performed by the Gorman research group including co-authors, Dr. Christopher Gorman, Jennifer Ayres and Kusum Chandra.
7.1 Abstract

A three-terminal molecular transistor was demonstrated using three ~15 nm gold nanoparticles bridged by a Y-type OPE molecular ‘trimers’, which was trapped in a nanogap electrode (<30 nm) by dielectrophoretic force. The SiO₂ gate oxide was reactive ion etched so that one of the three nanoparticles was in close contact with the heavily doped Si back gate. The current vs voltage characteristics showed a weak gate control with the modulation of source-drain current by a factor of ~2 over a gate bias of -2 to +2 V. The shift of the I-V curves observed with gate biases appears associated with a “double tunneling” transport mechanism in the device. The subthreshold slope (S) was estimated ~110 mV/decade from the plot of log-scale current vs voltage as a function of gate biases (0 to -2.5 V). This value of S represents switching phenomenon approximately three times faster than that of the molecular transistor simulated by Datta group.
7.2 Introduction

Considerable advances have been made in measuring and understanding the electron transport through single (or a small number of) molecules over the past years. However, most studies in molecular-scale electronics have been focused mainly on two-terminal devices, which do not always provide reliable evidence for the presence of molecules in the gap through current-voltage measurements. Therefore, the control of electron transport via a third electrode is highly desired and can be used as a field effect transistor (FET)-like device in addition to providing the clear signs for the presence of molecules inside the gap. A variety of gate configurations for realizing three-terminal devices have been developed theoretically and experimentally including back gate, electrochemical gate, and chemical gate. These methods can permit control of electron transport through a molecule by shifting its molecular energy levels between the Fermi energies of two metal electrodes through the gate bias. However, the experimental demonstration of FET behavior through single molecules has been difficult as a gate electrode needs to be placed close to the molecules for effective gate coupling. In our previous studies, the I–V characteristics were investigated through a dimer structure consisting of two ~40 nm gold nanoparticles bridged by a single (or a small number of) linear oligo phenylene ethynylene molecule (OPE), which was trapped between the nanoscale electrode gaps. In this study, we extend this work on two-terminal devices to three-terminal devices with three gold nanoparticles bridged by a Y-type OPE molecule ‘trimers’, in which two gold nanoparticles were contacted to two metal electrodes and the third gold nanoparticle closely contacted to the heavily doped Si back gate with a dry etched SiO$_2$ layer. The gold nanoparticle trimers were trapped in the nanogap
electrode gaps using the dielectrophoretic force generated by an alternating current (AC) electric field. The source-drain current was changed within a factor of 2 with a gate bias of -2 to +2V, showing a weak gate effect in our device. Also I–V curves were matched well when the source-drain voltage was shifted by an amount of ~0.15 (gate bias). The subthreshold slope was obtained ~110 mV/decade from the log-scale source-drain current vs a gate bias of 0 to -2.5V. This is the first demonstration of a three-terminal molecular device, which consists of three molecular arms bridged by gold nanoparticles. These results are promising due to the low subthreshold slope, despite a weak gate effect. Further works are still necessary to understand the device physics in the structure.

7.3 Experimental Methods

The nanoparticle/molecule/nanoparticle structures ‘trimers’ were synthesized using Y-type molecules bridged by three ~15nm gold nanoparticles as described in the previous study.\textsuperscript{19} The acetyl groups within the thioacetate-terminated OPE molecules are removed during synthesis (i.e., in situ deprotection) so that the thiols bind covalently to gold nanoparticles. The transmission electron microscopic (TEM) image of the synthesized trimer was obtained with a Philips M12 transmission electron microscopy operated at 100 keV. The nano-scale electrode gaps were fabricated as previously described.\textsuperscript{20} The first metal layer of Au (90 nm)/Ti (10 nm) was deposited and patterned on the thermally grown SiO\textsubscript{2} layer (11 nm) on a Si (100) substrate. Then the second metal layer of Pd (11 nm) was evaporated onto the patterned first metal layer with a gap width of 10 µm using oblique angled metal evaporation process with a tilt angle of 40–50° from the normal to the surface. The thickness
of the patterned first metal layer and the evaporation angle of the second metal layer were
tuned to fabricate the electrode gaps less than 30 nm. Larger gap sizes would not hold
nanoparticle trimers of this size without an applied bias. Atomic Force Microscopy (AFM)
of the fabricated nanoscale gaps was carried out in tapping mode under ambient conditions
using a Digital Instrument AFM with a Nanoscope IIIa controller (Santa Barbara, CA). AFM
probe tips (SSS-NCH, NanosensorsTM) with a typical tip radius of curvature of 2 nm were
used to collect high resolution AFM images in the nanogap region. The reactive ion etching
(RIE) of the SiO2 within the nanoscale trench was performed using Semigroup 1000TP with
a gas supply of CHF3 (20 sccm) and O2 (5 sccm) at 100 W and 40 mTorr. The thicknesses of
the etched SiO2 film in the nanotrench and flat substrate were measured using AFM and an
Auto EL ellipsometer (Rudolph Technologies, Flanders, NJ) at an angle of incidence \( \Phi=70^\circ \)
and a wavelength \( \lambda=632.8 \) nm.

The trapping of OPE-linked nanoparticle trimers was performed using
dielectrophoresis in the probe station at room temperature by placing a \( \sim 3 \) µl droplet of the
suspension onto the electrode surface as described previously.\(^{18}\) The typical trapping
conditions used were an alternating current (AC) bias voltage of 2-2.4V at a frequency of
1MZ for 30–60 sec. An AC voltage was generated using a precision LCR meter (Agilent
4284A) and computer controlled using Labview from National Instruments. Immediately
after trapping, the probe station (ST-100-2PROB, Janis Research Co.) containing samples
was evacuated to \( \sim 5\times 10^{-4} \) Torr for \( \sim 8 \) h and then current-voltage characteristics were
measured using a Keithley 2602 sourcemeter.
7.4 Results and discussion

In previous works, the dielectrophoresis-directed self-assembly and electrical characterization was reported for nanoparticle/molecule(s)/nanoparticle ‘dimers’ consisting of two ~40 nm gold nanoparticles bridged by a linear OPE molecule.\textsuperscript{17, 18} In this study, a similar approach consisting of three ~15 nm gold nanoparticles bridged by a Y-type OPE molecule was utilized to investigate the trimers. Figure 7.1 shows the molecular structure of a Y-type molecule used to form a trimer structure. The distance from the center of the benzene ring to the sulfur atom was measured using Chem 3D software after MM2 energy minimization and determined to be 2.39 nm. Based on reported literature values, the gold-thiol bond length was assumed to be 0.23 nm,\textsuperscript{21} yielding a total arm length of 2.62 nm. The inset shows the TEM image of the synthesized trimer. The nanoparticle size and molecular length are in good agreement with those of the theoretical trimer structure. We note that careful molecular design is required to prevent direct contact between nanoparticles, resulting in the current flow through citrate-capping layer and not the OPE molecules of interest. The detailed molecular design of a trimer will be reported in other literature.\textsuperscript{22}

To make one out of three nanoparticles of a trimer contact to the heavily-doped Si back gate, the SiO\textsubscript{2} layer within nanoscale electrode gaps was dry etched by using reactive ion etching (RIE). The process parameters such as process pressure and etching time were tuned to avoid any possible leakage current through SiO\textsubscript{2} layer between the metal electrode and Si back gate. The thickness of etched SiO\textsubscript{2} were compared between the nanogap and flat surfaces, and as shown in Figure 7.2, they exhibited similar etching rate of ~20 nm/min. No significant etching selectivity was observed between the SiO\textsubscript{2} layer and the Si substrate at the
oxygen percentage of 20 % (CHF\textsubscript{3}= 20sccm, O\textsubscript{2}= 5sccm). All samples were electrically checked before trapping to ensure no leakage current in the device. Otherwise it is difficult to distinguish between the leakage current through a SiO\textsubscript{2} layer and the real current through OPE molecules after trapping.

**Figure 7.1** Molecular structure of a Y-type OPE molecule used to form a trimer structure. The inset shows the TEM image of a trimer synthesized with the Y-type OPE molecule bridged by three ~15 nm gold nanoparticles.
Figure 7.2  Etched SiO$_2$ thickness was obtained according to the RIE etching time. The etched SiO$_2$ thickness between the nanogap electrodes measured by AFM is almost similar to that of flat SiO$_2$ (160 nm)/Si measured by ellipsometer.

The AFM image of RIE-etched nanogap electrodes was obtained over a scan area 1 $\mu$m$^2$ in Figure 7.3a. The nanogap region can be easily observed between two metal electrodes. The AFM line profile across the nanogap electrodes was compared before and
after RIE of SiO$_2$ layer for 0.6 min as shown in Figure 7.3b. The height decrease was found to be 11–12 nm due to the etching of SiO$_2$ layer in the nanogap region.

![Figure 7.3](image)

(a) AFM image (1µm×1µm) of RIE-etched nanogap electrodes. (b) AFM line profile across the nanoscale electrode gaps before and after reactive ion etching of SiO$_2$ for 0.6 min.

The nanoparticle trimers were assembled into the RIE-etched nanoscale electrode gaps using dielectrophoresis. Nanoparticle trimers in solution were driven to the metal electrode gaps by the electric field gradients generated between two metal electrodes. Figure 7.4 shows the expected device structure with a nanoparticle trimer trapped between the nanogap electrodes. It is worth noting that precise combination of etched SiO$_2$ thickness, right-hand side 2$^{nd}$ metal thickness, and electrode gaps with the nanoparticle trimers can make it possible for one of the nanoparticles to closely contact the RIE-etched SiO$_2$/Si back gate, resulting in an effective gate control on the current ($I_{DS}$) through source and drain. More
than 2 out of 34 trials (i.e., success rate > 5%) showed the current modulation by the gate bias to the trimer in our experiments. The low success rate might be due to the device geometry with small variations in the nanoparticle sizes and trimer orientation reducing efficient gate coupling and resulting in a low success rate.

There are several mechanisms proposed in the literature to explain the gate effect in the molecular transistor device. One is the modulation of the electronic barrier of the molecules spanned between two metal electrodes by applying a gate bias. The other one is the quantum interference effect transistor, which utilizes destructive interference from molecular symmetry and controls quantum transport via decoherence or elastic scattering from a third lead. It is also noted that a gate oxide with a high dielectric constant and thickness less than 10% of the channel (molecule) length is highly desired for an effective gate control.

![Figure 7.4](image)

**Figure 7.4** Schematic diagram for the expected device structure with a trimer trapped between nanoscale electrode gaps. Here the S, D, and G symbol represent the source, drain, and gate, respectively.
Figure 7.5 shows the I–V characteristics of a trimer trapped between the nanogap electrodes with a SiO$_2$ thickness of ~2.8 nm after RIE etching. First, the current of a trimer was measured by applying two-terminal biases of $V_{DS}$, $V_{GD}$, and $V_{GS}$ as shown in Figure 7.5a. The current measured through source-drain contact was consistent with that measured without RIE etching of the SiO$_2$ layer. However there is no current flow detected through gate-drain and gate-source contacts due to the SiO$_2$ insulating layers. Figure 7.5b shows the current through source-drain terminal measured while applying gate bias ($V_{GS}$) to the Si back gate. A weak gate effect is observed and manifested in the current modulation by a factor of ~2 with a gate bias ($V_{GS}$) applied between -2 V and +2 V. This is probably due to the weak gate coupling of the OPE molecule to the gate bias voltage, which was also observed in the phenylene-based conjugated molecule such as 1,3-benzenedithiol$^{11}$ connected to two gold electrodes. However, the I–V curves were shifted to the right when a positive bias was applied to the Si back gate. When the origin of each I–V curve is aligned to the zero bias, they are matched well with one another as shown in Figure 7.5c. Thus total bias voltage ($V_t$) between source and drain can be described as the combination of the original source-drain voltage ($V_{DS}$) and some portion of gate bias voltage ($V_{GS}$) like this: $V_t = V_{DS} - \alpha V_{GS}$, where the $\alpha$ value was estimated to be ~0.15. A similar phenomenon was observed in the metal-oxide tunneling transistor device.$^{24}$ In our study, it is thought that the I–V characteristic in Figure 7.5b might be associated with “double tunneling” effect through the RIE-etched thin SiO$_2$ layer in the nanotrench and one leg of the Y-type OPE molecule of the trimer.

The subthreshold slope, S, represents the input voltage required to change the output current by an order of magnitude.
Figure 7.5  (a) Current vs voltage curves of a trimer after applying two-terminal bias ($V_{DS}$, $V_{GD}$, and $V_{GS}$).  (b) $I_D$ vs $V_{DS}$ curves with different $V_{GS}$ gate biases using a heavily-doped Si as a back gate.  (c) $I_D$ vs $V_{DS}$ curves shifted by an amount of $\alpha V_{GS}$, where $\alpha$ was obtained $\sim 0.15$. 

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Thus a small value of $S$ means that a small change in the input bias can modulate the output current considerably. The expression for $S$ is described by

$$\frac{1}{S} = \frac{d(\log I_{DS})}{dV_{GS}}$$

Figure 7.6 shows the log-scale source-drain current measured at -0.02V ($V_{DS}$) as a function of the gate bias voltage ($V_{GS}$) of 0 to -2.5V. The value of $S$ was estimated to be ~110 mV/decade. The typical value of $S$ for state-of-the-art MOSFETs is known $k_BT/q$ (~60 mV/decade at room temperature). Also the Datta group\(^7\) simulated a molecular FET assuming capacitive coupling between a molecule and the gate, where the dielectric constant and the thickness of the gate oxide layer are key factors to determine the effective gate coupling. The best reported $S$ value was 300 mV/decade even when ideal gate coupling (i.e., direct contact of a molecule to the Si back gate) was assumed. Our $S$ value is lower than the one reported by the Datta group possibly due to differences in the gate effect mechanisms.

We demonstrated that a three-terminal molecular device can be made by contacting one of the three nanoparticles closely to the RIE etched SiO\(_2\) layer/Si back gate. Results showed a weak control of the gate bias on the trimers, which might be related to a double tunneling phenomenon. Further experimental and theoretical study is however needed to understand electron transport mechanism as well as enhance the gate coupling in the device. For example, heterotrimers with different metal nanoparticles or asymmetric molecular structure consisting of phenyl and alkene molecules could be possible candidates for future study.
Figure 7.6  Current ($I_{DS}$) at $V_{DS}$= -0.02 V was measured with gate bias voltage ($V_{GS}$) applied from 0 to -2.5 V. The subthreshold slope (S) was estimated to be ~110 mV.

7.5 Conclusions

Three-terminal molecular devices were demonstrated using three ~15nm gold nanoparticles bridged by a Y-type symmetrical OPE molecules ‘trimers’, which were dielectrophoretically trapped in the nanogap electrodes less than 30 nm. The SiO$_2$ gate oxide was dry etched by RIE so that one of three nanoparticles was in close contact to the heavily doped Si substrate. The source-drain current was modulated by a factor of ~2 with a gate bias of -2 to +2 V, showing a weak gate effect in our device. The shift of I–V curves with gate bias voltages seems associated with a “double tunneling” transport mechanism. The subthreshold slope was estimated ~110 mV/decade from the plot of log-scale current vs voltage as a function of gate bias (0 to -2.5 V). This value presents three times faster
switching than the molecular transistor with an ideal gate coupling simulated by the Datta group. It is expected that our study could pave the way for a new three-terminal molecular device by using a Y-type molecule bridged nanoparticle trimers.

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7.6 References


Chapter 8

Nano-encapsulation and stabilization of single-molecule/particle electronics nano-assemblies using low-temperature atomic layer deposition*

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*My contributions to this work include developing the nanoscale electrodes, process and conditions of the dimer assembly onto the electrodes. I also performed atomic layer deposition of Al₂O₃ onto the dimer assembly and all the electrical characterization and analysis of electrical results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. The design of experiments was carried out primarily by Dr. Gregory Parsons and me. The synthesis and assembly of the molecule into the dimers were performed by the Gorman research group including co-authors, Dr. Christopher Gorman, Jennifer Ayres and Kusum Chandra.
8.1 Abstract

This work addresses a significant challenge in engineered molecular systems regarding both understanding and controlling the stability of molecule/nanoparticle nanostructures under ambient exposure. Results deal specifically with molecular electronic junctions, where electronic contacts and transport are known to be sensitive to sample history and ambient exposure. We demonstrate that low-temperature atomic layer deposition can gently encapsulate and stabilize molecular electronic junctions, making it feasible to handle and transport junctions in air for many days with minimal change in electronic conduction. These findings indicate the potential for long-term stability of advanced synthetic nanoparticle/molecule nanoconstructs. For this study, conductivity through nanoparticle/molecule/nanoparticle junctions is analyzed and found to be consistent with nonresonant charge tunneling through a single or small number of oligomeric phenylene ethynylene molecules in the electrical junction. The conductivity was stable in vacuum and inert gas, but under ambient exposure, the current initially decreased, then increased rapidly, followed by a slower rise, reaching a value exceeding 10 times larger than initially measured. After encapsulating functional devices using atomic layer deposition of aluminum oxide thin films at 30–50 °C, the junction showed conductance similar to the precoated values, and the current remained unchanged after more than 15 days under ambient exposure. The presence of the molecule junction after encapsulation was confirmed by the observed transition to Fowler–Nordheim tunneling and analysis of junction breakdown at high fields. The high conformality, precise thickness control, and low-temperature compatibility of the atomic
layer deposition method make it uniquely qualified to stabilize and protect molecular junctions and systems.
8.2 Introduction

Synthetic and engineered nanomaterial architectures are of significant interest for advanced optical, electronic, and nanostructural systems. One outstanding challenge in engineered molecular systems is to understand and control the stability of the molecular structures under ambient exposure. This problem is particularly acute in the field of molecular electronic junctions, where electronic contacts and transport mechanisms can be highly sensitive to sample history and ambient exposure. Although the physical and chemical stability of molecular monolayers over extended periods (weeks to months) in ambient atmosphere have been investigated by many groups,\textsuperscript{1, 2} the stability of charge transport through isolated molecular junctions during extended ambient exposure is less widely characterized,\textsuperscript{3} and methods to protect the junctions from the environment have been only briefly discussed.\textsuperscript{4} Here we demonstrate a novel method based on low-temperature, atomic layer, thin-film deposition to effectively encapsulate and isolate functional molecular electronic junctions, enabling long-term stable characterization. The ability to stabilize molecular junctions may give rise to new methods; for example, to construct stable organic/inorganic nanoframeworks, or stabilize advanced molecular electronic circuitry.

The current versus voltage (I–V) characteristics of single or small groups of molecules have been extensively investigated\textsuperscript{5, 6} using break junctions,\textsuperscript{7–9} scanning probe techniques,\textsuperscript{10–12} and nanoparticle bridge structures.\textsuperscript{13, 14} An extension of the nanoparticle bridge involves formation of nanoparticle/molecule/nanoparticle structures, referred to here as “nanoparticle dimers”,\textsuperscript{15, 16} and contacted across nanoscale metal electrodes. This approach is particularly attractive because (i) the molecules are covalently bound to the
metal nanoparticles; (ii) the structure can, in principle, be amenable to parallel fabrication; (iii) the structures can be maintained electrically connected for long periods of time (days and weeks), enabling time- and temperature-dependent current to be characterized.

In this article, nanoparticle/molecule/nanoparticle structures, consisting of ~40 nm gold nanoparticles linked by a single (or small number of) oligomeric phenylene ethynylene molecules (OPEs), were synthesized and electrically bridged across planar nanoscale electrode gaps.\textsuperscript{16, 17} The stability of the current through the junction was investigated and characterized upon exposure to ambient lab air, and under alternate exposures to air and vacuum. To improve the ambient stability of the dimer, passivation of nanoparticle/molecule/nanoparticle structures was investigated using atomic layer deposition (ALD) of Al\textsubscript{2}O\textsubscript{3}. The ALD process involves sequential exposures of a sample to surface-saturating exposures of reactive precursors used in the deposition. For the case of Al\textsubscript{2}O\textsubscript{3} ALD, trimethylaluminum and water vapors are typically used, and exposures are separated in time using Ar gas flow. Repeating the reactant exposure cycles allows the resulting film thickness to be controlled with near monolayer precision. There are numerous reports describing the application of ALD Al\textsubscript{2}O\textsubscript{3} for coating zirconia nanoparticles\textsuperscript{18} and carbon nanotubes,\textsuperscript{19, 20} and for passivation layers for organic light emitting diodes (OLEDs).\textsuperscript{21, 22} It is well-known that ALD can form extremely continuous, uniform, and conformal films,\textsuperscript{23} and Al\textsubscript{2}O\textsubscript{3} films can be grown by ALD at temperatures below 100 °C.\textsuperscript{24} The gold–sulfur (Au–S) bond is sufficiently strong that it is expected to remain stable under processing at moderate elevated temperatures,\textsuperscript{25, 26} allowing the coating process to not significantly modify the chemical structure of the molecule or molecule/metal contact. We report here initial detailed
investigation results for low-temperature passivation of functional molecular electronic junctions using atomic layer deposition technology.

8.3 Experimental methods

Nanoparticle/Molecule/Nanoparticle Fabrication and Electrical Contact Formation.

To form the dimers, OPE structures terminated with thioacetate functionalities were bridged by two ~40 nm gold nanoparticles (citrate-capped, Ted Pella, Inc.) after in situ deprotection of the acetyl group. A stoichiometric amount of the OPE molecules was mixed with the solution containing gold nanoparticles, which maintains their respective ratio of 1:2, in order to avoid the aggregate formation. The TEM image of an uncoated dimer in Figure 8.1a was obtained with a Philips CM12 TEM operated at 100 kV, where images were captured using a Gatan 780 camera and Digital Micrograph software. TEM was also used to evaluate the statistical distribution of synthesized nanoparticles. For approximately 173 items counted, 62 % were isolated particles, 31 % were bound in dimers, and 7 % were formed as trimers (i.e., three nanoparticles bound together). The plan-view SEM image in Figure 8.1b was collected at a magnification of 120000 using Hitachi S-3200 with an accelerating voltage of 30 kV. Trapping of OPE-linked gold nanoparticle dimers was performed in the probe station by placing a ~3 μl droplet of the dimers suspended in aqueous solution onto the electrode surface. For dielectrophoretic trapping, an alternating current electric field was applied to the electrodes. The voltage was typically ~1–3 VAC at a frequency of 1KHz to 1MHz for 20–120 s. After trapping, samples were rinsed in deionized
water for 30 s and dried in a stream of nitrogen gas. The best conditions for dielectrophoretic trapping of dimers were observed to be 2 VAC, 1 MHz and 60 s, where successful trapping of 51 devices out of 58 experimental trials (i.e., success rate of ~88%) was achieved. In this case, success is achieved when a reasonably self-consistent current level (i.e., not shorted, and not open) is measured after trapping. Typically, AFM analysis shows one to three dimers trapped in the electrode nanogap. The AC voltage was generated using a precision LCR meter (Agilent 4284A) that is computer-controlled using LabView from National Instruments. Further details of the nanogap electrode fabrication procedure and the assembly of dimers within them are described elsewhere.\textsuperscript{16}

\textit{Atomic Layer Deposition and Film Characterization.}

Atomic layer deposition of Al\textsubscript{2}O\textsubscript{3} was performed using trimethylaluminum (TMA, Al(CH\textsubscript{3})\textsubscript{3}) and deionized water as precursor and oxidant gas, respectively. Argon was used as a carrier and purge gas. The deposition was carried out in a homebuilt hot-wall quartz tube reactor. TMA was obtained from STREM Chemicals and used as received. Argon gas was purified using a DRIERITE gas purifier to remove possible moisture and impurities from the gas line. One typical reaction cycle of ALD consists of TMA dose (1 s)/Ar purge (20 s)/H\textsubscript{2}O dose (0.3 s)/Ar purge (20–120 s). Samples were exposed to a vacuum of \textasciitilde10^{-6} Torr for 30 min in order to obtain a uniform temperature distribution in the reaction chamber before ALD coating. The growth temperature ranged from 30 to 100 °C and the operating pressure was maintained at 0.5 Torr with a total gas flow rate of 100 sccm. The control volume was used to supply constant amount of a precursor and oxidant gas during each cycle.
After deposition, the film thickness of Al₂O₃ on planar silicon substrates was measured using Auto EL ellipsometer (Rudolph Tech.) at an angle of incidence \( \Phi = 70^\circ \) and a wavelength \( \lambda = 632.8 \) nm. To characterize and examine conformality of the Al₂O₃ coatings on the dimer structures, several OPE-linked gold nanoparticle dimers were placed on a carbon support film on a copper grid (carbon type A obtained from Ted Pella, Inc.) The TEM copper grid was initially baked at \(~120^\circ\)C for at least 10 min, followed by addition of several drops of the solution containing the nanoparticle/molecule/nanoparticle dimers. Grids with dimers were placed into a vacuum desiccator (~10⁻² Torr) overnight followed by ALD treatment. For these samples, TEM analysis was carried out with a JEOL 2010F high-resolution TEM operated at 200 kV using a Schottky field emitter in combination with electron energy loss spectroscopy (EELS).

Current-vs-Voltage Analysis.

For the dimers adsorbed onto the nanogap electrodes, the current–voltage measurements were performed in a vacuum-compatible probe station (Janis Research Co., Inc.) using a Keithley 2602 sourcemeter, and heating was carried out using a 331 temperature controller (LakeShore). When not being measured, samples were generally stored in the dark in a vacuum desiccator in the milli-Torr pressure range with no bias applied. Some samples were stored in lab ambient air, also without applied bias and isolated from visible light exposure. For each measurement, samples were transferred in air to the vacuum probe station. Unless specifically noted, current-vs-voltage measurements were performed under a vacuum of \(~5 \times 10^{-4}\) Torr. The total time for each sample analysis point, including sample
transfer, pumping, and multiple I–V measurements (typically three to five times for each sample) was ~1–2 h. After measurements, the samples were transferred in air to storage (in air or vacuum) until the next analysis point was collected.

8.4 Results and discussion

The nanoparticle/molecule/nanoparticle dimers were synthesized according to previously published methods\textsuperscript{16, 27} and utilized to form an electrical bridge across a planar nanogap electrode. We note that the dimer formation procedure\textsuperscript{16, 27} was performed under conditions in which the concentration of molecules and nanoparticles is controlled such that dimers were likely to contain only one or a small number of molecules. In fact, during the dimer formation process when a higher concentration of molecules was used, significant agglomeration of nanoparticles was observed, consistent with more than one molecule on each nanoparticle surface.\textsuperscript{15} Under conditions used for the dimer formation, the concentration of clusters of three or four nanoparticles was relatively low, further suggesting that many of the nanoparticle dimers contained only one or two molecules. An example transmission electron microscopic (TEM) image of an uncoated synthesized dimer, shown in Figure 8.1a, shows two nanoparticles with diameter of ~ 40 nm separated by the length of an OPE linker molecule (~2 nm). Figure 8.1b shows a plan-view scanning electron microscope image of a nano-scale Pd metal electrode gap of ~70 nm fabricated by oblique angled metal evaporation, which is used to trap and electrically contact the nanoparticle/molecule/nanoparticle dimers, as shown in the scaled schematic in Figure 8.1c.
Figure 8.1  (a) Example TEM image of an oligomeric phenylene ethynylene molecule (OPE)-linked nanoparticle dimer, consisting of two gold nanoparticles with a diameter of ~40 nm covalently connected by the molecule. The structure of the OPE molecule is also shown. (b) Plan-view SEM image of the nanogap electrode with a gap width of ~70 nm fabricated by oblique-angle metal evaporation with a tilt angle of 50° from the normal to the surface. (c) Schematic structure of the OPE-linked gold nanoparticle dimer trapped between the nanogap electrodes.
Typical current-vs-voltage curves measured for an example trapped molecular dimer are shown in Figure 8.2a, measured immediately after assembly in the nanogap, and after various exposure times to laboratory air. The shape of all the I–V curves collected is consistent with nonresonant charge tunneling, as shown previously for these structures. The current values measured between –0.2 and +0.2 V immediately after initial trapping correspond to a resistance of 4.8 ± 0.1 GΩ in the circuit. This value is within a factor of 2 of the value of ~2.8 GΩ previously reported by our group for similar trapped OPE-linked gold nanoparticle dimers and is also close to the value of 1.7 ± 0.4 GΩ reported at ± 0.1 V for a single molecule of OPE measured by scanning probe microscopy. Further evidence of the number of molecules present can be obtained from surface enhanced Raman spectroscopy (SERS). Analysis of nanoparticle/molecule dimers previously fabricated with the same methods used here showed temporal blinking in the concurrent SERS images, consistent with a single molecule between the nanoparticles. Other groups utilizing similarly prepared nanoparticle/molecule dimers also cited similar SERS results consistent with single-molecule behavior between the nanoparticles.

The stability of the current through several nanoparticle/OPE/nanoparticle structures was investigated in vacuum and in ambient air as shown in Figure 8.2. The stability under air exposure is shown in Figures 8.2a, d, and e. The data in Figure 8.2a shows results from a single dimer stored in lab air and measured in vacuum over a period of ~25 days. The current was observed to rise as a function of time, but the shape of the I–V curve did not significantly change.
Figure 8.2  Ambient stability of the OPE-linked gold nanoparticle dimer trapped in the nano-scale electrode gap. (a) Several I–V curves for a typical nanoparticle/molecule/nanoparticle sample after various times exposed to air. The general shape of the I–V curve does not change upon air exposure. Also shown are I–V traces for single large (80 nm diameter) nanoparticles adsorbed in the nanogap (i.e., with no OPE molecules), showing significantly lower resistance than the nanoparticle/molecule dimers. (b) I–V curves showing the data from (a) on a linear scale, before exposure to air, emphasizing the different shape for the curves with and without the molecule present. (c) A molecular dimer device kept in vacuum shows no significant current change over more than 13 days. (d) Upon continuous air exposure, current through two different dimers is observed to show a rapid initial decrease, followed by a rapid increase over the next several days before transitioning to a slower rate.
of increase (measured at 0.5 V in air). (e) The current measured through three different
dimers and one large nanoparticle (measured at 0.5 V in vacuum) exposed to ambient air for
various times shows exponential increase in the current. The dashed line corresponds to an
apparent change of the slope in log(current) versus time, delineating region I and region II.
The line marked with an asterisk (*) corresponds to the data in panel (a). All lines are drawn
as a guide to the eye.

Also shown in Figure 8.2a are I–V traces from a control experiment in which a relatively
large (~80 nm) gold nanoparticle was trapped between the nano-gap electrodes following the
same procedure used for dimer trapping. A much larger current was observed through the
single nanoparticle, and the shape of the I–V trace through single nanoparticle was more
linear than for the nanoparticle/molecule dimer, as shown in Figure 8.2b. The current
through the single nanoparticle was measured periodically over 18 days under lab air
exposure, and the current increased by approximately a factor of 2 during that period. The
gold nanoparticles are coated with a citrate capping layer, which may lead to some resistance
at the nanoparticle/electrode connections. However, compared with the nanoparticle dimers,
the much higher current through the single nanoparticle structures demonstrates that the
electrode contact resistance contributed minimally (~ 0.1 %) to the overall measured
resistance of the OPE-linked junction.

As another control experiment, Figure 8.2c shows the current measured at 0.5 V
applied bias for a single dimer sample held in vacuum over a period of 12 days. A current
near 1 nA was observed, and no measurable change in current was detected. The effect of
applied bias on the stability of the I–V measurements was also evaluated. Samples were
measured under vacuum for several hours with continuous bias of 0.5–1 V applied, and no significant change in the current was observed.

Under air exposure, the dimer samples generally showed both short-term (over several minutes) as well as long-term instability (over several days). Figure 8.2d shows the current measured through a dimer sample at 0.5V as a function of time exposed to air (and measured in air). The current showed a rapid initial decrease, followed by an increase over the next several days before transitioning to a slower rate of increase. Long et al.$^3$ analyzed the short-term ambient stability of conductance through thiol-terminated molecule ensembles using a magnetic microsphere bridge junction. They reported a rapid reversible decrease in conductance upon air exposure, and ascribed the change to hydration of the thiolate moiety, leading to a disruption of the gold/sulfur bond. The initial decrease in the current shown in Figure 8.2d is consistent with the results and mechanisms presented by Long et al.$^3$

The remaining results presented here address the issue of long-term stability. The short-term current change upon the transition from air to vacuum, or vacuum to air, was not typically recorded. Figure 8.2e shows the current measured at 0.5 V plotted versus air exposure time for two dimer samples prepared using identical fabrication procedures. In this figure, the data points at day 0 correspond to the first measurements of each sample, immediately after fabrication. Also shown in Figure 8.2e are results from the control experiment where the current through the single gold nanoparticle was monitored in air as a function of time. The current through the gold nanoparticle was stable (within a factor of 2) upon exposure to air for up to 18 days, further indicating that the time-dependent current observed in the nanoparticle/molecule dimer was dominated by changes in the overall
conductance through the molecular junction. We note that for the two example nanoparticle/molecule dimer structures in Figure 8.2e, the current measured immediately after junction formation exhibited some sample-to-sample variation. The data points shown represent the typical range of current values observed for the dimer samples we have measured to date. This variation likely reflects that some dimers may contain two or more molecules, that there is some variability in the metal/molecule contact structure within the dimer that affects the overall conductivity,\textsuperscript{30} or both. Larger current values were observed in some samples and ascribed to defects or other contamination.

For each sample measured in air, the current shown in Figure 8.2e was observed to increase by a factor of 4–15 within the first 8–12 days of air exposure, and then continue to increase more slowly. We note that some dimer samples with higher initial current also showed the same behavior of current change with exposure to air. The data marked with an asterisk in Figure 8.2e correspond to the example I–V data set shown in Figure 8.2a. The initial rate of current increase with time was similar for all the devices measured and found to be proportional to $\sim \exp (t/\tau)$, where $\tau \approx 4.3$ is the characteristic time constant (in days) for the current increase. A dashed line in Figure 8.2e is drawn to roughly delineate the regions for fast (region I) and slower (region II) current increase with time. We note that for the samples studied, the time required for the current to transition from fast to slower increase depends on the initial measured current such that devices with an initial smaller current require longer times for the current change to decrease, as compared to those with larger initial current values. The current stability was further evaluated by storing samples previously exposed to air in a desiccated vacuum ($\sim 10^{-2}$ Torr), then measuring the current after vacuum storage.
Results are shown in Figure 8.3. For devices initially exposed to air for only a few days (i.e., current change was still in region I of Figure 8.2e), storing the samples in vacuum for several days resulted in a partial recovery (i.e. decrease) of current back to the initial pre-exposure value. However, devices exposed to air for many days (in region II in Figure 8.2e) exhibited a much smaller decrease in current after vacuum storage. This suggests that the long-term change in conductivity is somewhat reversible within the first few days, whereas the change becomes fixed or less reversible after longer-term (10–15 days) air exposure.

Figure 8.3  Current measured after various times in air (solid arrows), and after returning to desiccated vacuum storage for several days (dotted arrows). The thicker dashed line corresponds to the transition from region I to region II as shown in Figure 8.2. For samples (■) exposed to air for relatively short times (i.e., still in region I) the current responds significantly to vacuum treatment, returning to nearly its original before-exposure value. Samples (●) exposed to air for a relatively long time (i.e., in region II) show less response to vacuum exposure. All lines are drawn as a guide to the eye.
Generally, a molecular junction involves mixing between discrete orbitals in a molecule and the continuum states in a metal, so that the metal/molecule/metal junction should be considered as a single unit. Instability mechanisms could include alterations of the molecule/metal linkage, the molecular electronic or physical configuration,\textsuperscript{31} or both. The current measured as a function of air exposure time observed in Figures 8.2 and 8.3 showed that the current change of the molecule/nanoparticle dimer junction is much larger than for the nanoparticle/metal contact. One possible explanation for the change in conductance in the molecular junction is that contaminant species in air (i.e., water) adsorb in the junction region and increase the current. Contaminant adsorption can be expected to affect the molecule/nanoparticle junction as well as the nanoparticle/electrode connections. Any mechanical force that decreases the junction length by a small amount will also increase the magnitude of the tunneling current. For example, for an electron decay constant of 0.2–0.4 Å\textsuperscript{-1}, a 4–6 Å change in junction length would change the resistance by a factor of \sim 5. Because of its large resistance, small modifications of the molecule junction will lead to a large change in measured conductivity, whereas small modification to the smaller resistance nanoparticle/electrode connections will show less change. The results in Figures 8.2 and 8.3 follow this trend. The partial reversibility and longer-term persistence of the instability upon subsequent vacuum exposure shown in Figure 8.3 are also consistent with contaminant condensation, where contaminant desorption from the nanoscale region between the nanoparticles becomes progressively more difficult with extended exposures.\textsuperscript{32} Results shown here are not sufficient to uniquely identify the detailed mechanisms associated with the current instability.
We hypothesized that the instability of the molecular junctions could be improved by encapsulating the nanoparticle/molecule/nanoparticle dimer with an inert coating of a barrier dielectric film, such as Al₂O₃. Atomic layer deposition was chosen for these tests because it can be deposited at low temperature with high conformality. The low temperature will also allow minimal disruption of the gold-thiol bonded nanoparticle/OPE junction. Initially, ALD Al₂O₃ was carried out on planar silicon substrates for a range of ALD cycle numbers between 30 and 100 °C. Thickness was observed to increase linearly with the number of ALD cycles with a growth rate that increased from 0.74 to 0.99 Å/cycle as temperature increased from 30 to 100 °C when sufficiently long purge times were used after water exposure. Groner et al.²⁴ reported that for ALD Al₂O₃ at temperatures less than 100 °C, the rate of water molecule desorption from the growth surface had a significant effect on the growth rate. The data in Figure 8.4 shows the effect of argon purge time following the water exposure cycle, on the growth rate of Al₂O₃ at temperatures between 30 and 100 °C. The results show that the growth rate of Al₂O₃ was nearly independent of temperature between 50 and 100 °C. At 30 °C, the growth was strongly influenced by the Ar purge time after the H₂O exposure step, whereas at temperatures > 50 °C, the growth rate was not significantly affected by the reactor purge time. For experiments performed here, long purge times were used and growth conditions were fixed to achieve a similar film thickness (~10 nm) at each temperature used.

To examine the conformality of the deposited coating, a nanoparticle dimer was placed on carbon support film and coated by the ALD method at 70 °C using 120 TMA/H₂O cycles, followed directly by evaluation with TEM. Figure 8.5a shows a TEM micrograph of
the dimer after ALD treatment, revealing an Al$_2$O$_3$ coating with a thickness of ~10 nm which is extremely uniform and conformal.

Figure 8.4 Atomic layer deposition growth rate of Al$_2$O$_3$ (in Å per ALD cycle) versus Ar purge time after the H$_2$O exposure step, at growth temperatures of 30–100 °C. At 30 °C, the growth rate of Al$_2$O$_3$ sharply decreased as the purge time increased from 20 to 120 s. All lines are drawn as a guide to the eye.

The growth rate of Al$_2$O$_3$ film on gold nanoparticle dimer was calculated ~0.83 Å/cycle, equivalent to that observed on a Si substrate exposed to the same deposition conditions. This is due to the facile nucleation of Al$_2$O$_3$ film on the hydroxyl groups of the citrate capping layer covering the gold nanoparticles. Figure 8.5b displays a high resolution TEM image acquired near the interface between a gold nanoparticle and the Al$_2$O$_3$ layer, showing a distinction between the amorphous Al$_2$O$_3$ film and the polycrystalline gold nanoparticle.
A series of current-versus-voltage measurements were carried out for samples coated with ALD Al₂O₃ immediately after coating and over several day of continuous air exposure, and results are shown in Figure 8.6. The data collection protocol followed the methods used for collecting data for uncoated samples in Figure 8.2. Figure 8.6a shows a set of I–V curves for one example junction coated at 50 °C, including an I–V trace made immediately after junction formation and before ALD coating, as well as traces collected over a range of times after coating. Generally, the shape of the I–V traces was not affected by the ALD coating procedure. The current at 0.5V measured for four dimer samples before and after ALD treatment at temperatures between 30°C and 100 °C is shown in Figure 8.6b.
Figure 8.6  (a) Typical I–V curves for a nanoparticle/molecule/nanoparticle dimer after coating with ALD Al₂O₃ at 50 °C using a deposition rate of ~0.8 Å/cycle.  (b) The current measured through four different devices (measured at 0.5 V in vacuum) exposed to ambient air for various times, with ALD Al₂O₃ encapsulation deposition performed at various temperatures. The data marked with an asterisk correspond to the data shown in panel (a). The data point at time=0 corresponds to the current measured in vacuum immediately after encapsulation. The samples with the low-temperature Al₂O₃ encapsulation layer showed stable current at a value similar to the precoating value. (c) Net current change of the encapsulated dimer (measured at 0.5 V in vacuum) as a function of Al₂O₃ deposition
Similar to the data in Figure 8.2e, the data from four dimer samples in Figure 8.6b show sample-to-sample variation in the conductivity measured immediately after junction formation. After coating, all samples were exposed to air, similarly to the samples shown in Figure 8.2, and the I–V data was collected at various times after air exposure. Samples measured immediately after coating showed conductivity values larger than the original precoating values, and the magnitude of change became more pronounced as the ALD temperature was increased. For all dimer samples, the current after coating decreased slowly over 1–2 days then stayed relatively stable during analysis as long as 19 days. The samples encapsulated at 30 and 50 °C show similar behavior in that the current after encapsulation stabilizes at a value within a factor of ~2 of the original value measured before encapsulation. The data points at 50 °C correspond to the data shown in Figure 8.6a.

It is important to note that when the current through these ALD encapsulated samples was measured in real-time during a vacuum-to-air or air-to-vacuum transition, the current remained unchanged, whereas uncoated samples observed by our group and by Long et al. showed a rapid decrease in current upon air exposure. The ALD process included exposing the samples to vacuum (~10⁻⁶ Torr) at the deposition temperature (30 to 100 °C) for approximately 30 min before deposition was initiated. When the ALD encapsulation was performed at higher temperatures, 70 and 100 °C, the current increased by a factor of 10 to 100 or more, and the current remained high after extended measurement times. In Figure 8.6c,
the net change in measured current is shown as a function of processing temperature. For all I–V traces collected from the dimer samples, the curves showed nonlinear I–V traces consistent with nonresonant charge tunneling before and after ALD treatment.

A few samples were treated with ALD at 200–230 °C, and after deposition the samples showed very high current that was linear with voltage, consistent with shorting of the nanoparticles and irreversible degradation of the molecular junction. Two samples with electrodes bridged by only one large nanoparticle (i.e., with no molecule junction) were also coated by ALD at 50 and 100 °C. In both samples, the current increased by a factor of 10 or more after deposition, indicating improved nanoparticle/electrode contact after ALD treatment.

As a further control experiment, the specific effects of the various ALD reactants and procedures on the current through the molecular junction were individually investigated in the ALD furnace at 30-100 °C and 0.5 Torr. Specifically, samples were exposed to one of three treatments: (i) water vapor and argon (consisting of 0.3 s H₂O followed by 120 s Ar for 20 cycles); (ii) trimethylaluminum vapor and argon (consisting of 1.0 s TMA followed by 20 s Ar for 20 cycles); or (iii) heating in vacuum for times equal to the duration of a typical ALD process. None of these exposure sequences resulted in film deposition under the conditions studied. Current-vs-voltage characteristics were measured, and the ratio of current (at 0.5 V) measured before and after treatment was plotted as shown in Figure 8.7. All treatments at T > 50 °C were observed to affect the current through the junction, whereas none of the treatments had significant affects on the junction properties when performed at T ≤ 50 °C.
Figure 8.7 Effect of H₂O and TMA exposure and vacuum thermal treatment at 30–100 °C on the current change (at 0.5 V) through twelve nanoparticle dimer samples. The ratio corresponds to the current after treatment divided by the current before treatment. All currents are measured after sample cooling to room temperature.

Samples exposed to heating in vacuum also showed relatively small changes. Although the results presented here cannot unambiguously determine the mechanisms associated with the observed current instability, the results in Figure 8.7 show clearly that exposing the junctions to TMA or water vapor under vacuum (0.5 Torr) and temperature conditions (30-50 °C) for short times (seconds) typical of low-temperature ALD does not significantly degrade molecular junction conductivity or tunneling performance. Trimethylaluminum is highly reactive, but the relative insensitivity of the junction to the TMA exposure under the conditions used may result from the geometrical constraints of the system. Specifically, a
molecule ~2 nm in length connected to two 40-nm-diameter nanoparticles creates a very small gap region between relatively large nanoparticles, and reactive species diffusing into this region are likely to collide and react with a partially oxidized or coated nanoparticle surface well before reaching the small molecule at the center of the junction. Moreover, Elam et al.\(^{33}\) report that aromatic molecules show relatively low reactivity to ALD Al\(_2\)O\(_3\) deposition reactions. Furthermore, any reaction between the citrate on the nanoparticle and TMA will help impede TMA from reaching the active molecule.

To confirm the presence of the molecular junction after ALD encapsulation, several experiments were performed; the results are shown in Figure 8.8. The junction before and after ALD coating measured up to 2\(\text{V}\) show similar behavior in Figure 8.8a. Another coated junction measured from 0 to 10\(\text{V}\) showed high current spikes near 5–6 \(\text{V}\), consistent with junction breakdown and a transition to current flow through the oxide coating.\(^{35}\) The same junction after the high-voltage treatment shows much lower current at low voltage, consistent with junction loss. AFM analysis of the nanogap region provides evidence that the dimers are still present in the gap after breakdown, giving credence that the molecule junction is present after ALD (before breakdown). Furthermore, the transition from direct to Fowler–Nordheim tunneling is characterized before and after ALD encapsulation, and the transition voltage, determined from the change in slope of a plot of \(\ln(I/V^2)\) vs 1/\(V\) (Figure 8.8b), is the same before and after encapsulation.\(^{16,34}\) Loss of the molecule junction is expected to lead to significant change in the tunnel junction barriers and a change in the transition voltage between direct and Fowler–Nordheim tunneling,\(^ {16,34}\) consistent with results in Figure 8.8b. These results support the presence of the OPE molecules after ALD Al\(_2\)O\(_3\) coating.
(a) I–V characteristics of molecular junctions. Including one sample measured before and after ALD between 0 and +2 V, and another sample measured up to 5 V applied bias. Up to 2 V applied bias, the I–V trace is generally reproducible for many measurement cycles. After exposure to high field, the I–V trace shows a significantly reduced current, consistent with loss of the molecular junction. (b) A plot of $\ln(I/V^2)$ vs $1/V$ shows the transition from direct to Fowler–Nordheim tunneling for uncoated and coated samples, and for a coated sample after high field treatment. The transition field does not change upon ALD encapsulation, but it changes significantly after high field treatment. Results indicate that the molecular junction is intact after ALD encapsulation, and is only lost during high field exposure.

Figure 8.8
Several mechanisms could account for the initial increase in current observed after ALD and the subsequent decrease in current during the first 1–2 days after encapsulation. Considering first the larger current measured after encapsulation, as shown above, the current through the junction is expected to increase upon exposure to laboratory air. The sample transfer from I-V measurement chamber to the ALD reactor proceeds through laboratory air. Therefore, exposure to laboratory air during sample transfer, loading and pump-down in the ALD reactor system could affect the junction conductivity. In addition, data in Figure 8.7 indicate that sample heating and water exposure during the ALD process will also increase junction conductance. Other mechanisms could account for the current decrease after ALD encapsulation. For example, the Al₂O₃ deposited at low temperature is not as dense as that deposited at high temperatures, so it is possible that water or other contaminants originating in the deposited film may be contributing to instability for 1–2 days after coating.

8.5 Conclusions

The data presented here shows that the current through a molecular junction containing a single or small number of molecules is sensitive to ambient exposure over short and long exposure times. While the results shown here cannot explicitly identify the mechanisms associated with the current instability, reasonable arguments can be made to account for the observed trends, including effects of ambient water or other contaminants. Results show that exposing molecular junctions to atomic layer deposition processes at low temperatures (≤50 °C) to form Al₂O₃ encapsulating layers around the molecule junctions, the
junction conductance is not significantly modified by the deposition process itself. Moreover, junctions coated at low temperature show significantly improved long-term stability, where the molecular conductance does not change during storage for more than 20 days in laboratory air. This encapsulation method can be used, for example, to stabilize junctions for extended analysis and functional evaluation. Further work can probe the detailed effects of the ALD process on the structure of the oligomeric phenylene ethynylene molecule or molecules in the dimer junction. Furthermore, this work provides a new route for gentle encapsulation and stabilization for a variety of synthetic molecule/nanoparticle structures and other engineered molecular nanosystems.

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8.6 References


Chapter 9

Role of gas doping sequence in surface reactions and dopant incorporation during atomic layer deposition of Al-doped ZnO*

Jeong-Seok Na, Qing Peng, Giovanna Scarel and Gregory N. Parsons 2009, submitted.

*My contributions to this work include developing the in situ quartz crystal microbalance and electrical conductance measurements during atomic layer deposition of Al₂O₃, ZnO and Al-doped ZnO. I also performed all the physical, chemical and electrical characterization and analysis of results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. While Dr. Gregory Parsons helped in experimental design, I worked independently to conceptualize and initiate the experiments. The measurements of angled Fourier transform Infrared spectroscopy and quartz crystal microbalance were performed by the help of Giovanna Scarel and Qing Peng, respectively.
9.1 Abstract

Aluminum incorporation into ZnO films during atomic layer deposition is investigated using \textit{in situ} quartz crystal microbalance and electrical conductance analysis. Chemical interactions between Zn– and Al– species during ZnO:Al ALD depend on the order of metal precursor exposure. Exposing the growing ZnO surface to trimethyl aluminum (TMA) impedes the subsequent ~4 monolayers of ZnO growth. However, the extent of interaction can be reduced by performing the TMA exposure immediately following a diethyl zinc step, without an intermediate water exposure step, consistent with increased surface mixing of Zn and Al species. Infrared spectroscopy analysis of heavily aluminum doped ZnO shows features consistent with the presence of amorphous ZnAl$_2$O$_4$ bonding units. For more lightly doped films, SIMS depth profiling confirms non-uniform aluminum distribution, even after annealing at 500°C. Film conductance measured during growth shows complex trends that are highly repeatable over multiple doping cycles, and values for \textit{in situ} conductance are consistent with post-deposition I–V characterization. Results are understood in terms of relative bonding energies of surface species, and expected reaction pathways for dopant atom incorporation.
9.2 Introduction

Multi-component oxide materials find applications in many fields including electronic insulators, optical components, and mechanical elements. Transparent conducting oxides for example, are useful in displays, sensors, light emitting diodes, photovoltaic cells, and transparent electronics.\(^\text{1-6}\) Improving device performance often requires decreasing film thickness, and this has driven research toward techniques such as atomic layer deposition (ALD) to attain a high degree of thickness control. Recently, zinc oxide (ZnO) and aluminum doped ZnO (ZnO:Al) have been fabricated by ALD and studied as a potential alternative transparent conductor to act in place of conventional tin-doped indium oxide (ITO), or fluorine-doped tin oxide (FTO) films.\(^\text{5-7}\) In addition to ALD, other fabrication methods including MBE and electrodeposition have been studied to achieve controlled extrinsic doping of ZnO by substitution of group III or IV elements (i.e., B, Al, Ga, In, Ga) for Zn, or group VII species (i.e., F, Cl, I) for oxygen.\(^\text{8-10}\)

The sequential reactant exposure used in atomic layer deposition\(^\text{11-16}\) allows the composition of multicomponent materials to be adjusted by changing the number of cycles used for each precursor material of interest.\(^\text{17-20}\) While many studies have addressed the properties of multicomponent and doped oxide materials, the surface reaction mechanisms associated with multicomponent film formation and dopant atom incorporation are less widely investigated.\(^\text{18,21,22}\) The work presented here probes surface reactions in ALD of ZnO:Al by correlating \textit{in situ} mass uptake\(^\text{18,21,23}\) and conductance analysis\(^\text{24-26}\) results with findings from post deposition characterization. In particular, the surface reactions are modulated using three different schemes for dopant species introduction, and results obtained
using these schemes are contrasted to expand insight into surface reactions that proceed during film growth.

9.3 Experimental methods

Atomic Layer Deposition of Zinc Oxide Films. ZnO ALD was performed using diethylzinc (DEZ, Zn(C₂H₅)₂), trimethylaluminum (TMA, Al(CH₃)₃), and deionized water (H₂O) as Zn, Al and oxidant precursor, respectively. Argon was used as a carrier and purge gas. The deposition was carried out in a custom made hot-wall stainless tube reactor with a diameter of 1.5 inches. DEZ and TMA were obtained from STREM Chemicals and used as received. The growth temperature was set at 125 °C and the operating pressure was maintained at 2 Torr with a total gas flow rate of 100 sccm. The pressure increase during each precursor exposure was set at ~0.1 Torr using metering valves. The general reaction sequence for ZnO ALD involves separate DEZ and H₂O exposures, and Al₂O₃ ALD utilizes separate TMA and H₂O exposures. The general overall reaction schemes for ZnO and Al₂O₃ are given as:

\[
\begin{align*}
\text{ZnO:} & \quad \text{ZnOH}^\ast + \text{Zn(C₂H₅)₂} \rightarrow \text{ZnOZnC₂H₅}^\ast + \text{C}_2\text{H}_6 \\
& \quad \text{(DEZ pulse)} \quad (1) \\
\text{ZnOZnC₂H₅}^\ast + \text{H}_2\text{O} \rightarrow \text{ZnOZnOH}^\ast + \text{C}_2\text{H}_6 \\
& \quad \text{(H}_₂\text{O pulse)} \quad (2) \\
\text{Al}_2\text{O}_3: & \quad \text{AlOH}^\ast + \text{Al(CH₃)₃} \rightarrow \text{AlOAl(CH₃)₂}^\ast + \text{CH}_₄ \\
& \quad \text{(TMA pulse)} \quad (3) \\
\text{AlOAl(CH₃)}^\ast + \text{H}_₂\text{O} \rightarrow \text{AlOAlOH}^\ast + \text{CH}_₄ \\
& \quad \text{(H}_₂\text{O pulse)} \quad (4)
\end{align*}
\]

For Al doping into ZnO, the Al–O layer was incorporated discretely into the growing ZnO film using three different doping sequences, shown in Figure 9.1.
Figure 9.1  Schematic diagram of the process sequences used to grow (a) undoped and (b)–(d) Al-doped ZnO films. The precursor pulse and Ar purge time is fixed at 1 s and 20 s, respectively. Three different doping sequences are classified as (b) case 1, (c) case 2, and (d) case 3.
Figure 9.1a shows a typical ALD reaction cycle for undoped ZnO using DEZ/Ar/H$_2$O/Ar exposure times of 1/20/1/20 s, respectively. Figure 9.1b–d display the gas pulsing sequences for deposition of ZnO:Al. “Case 1” corresponds to TMA/Ar/H$_2$O/Ar = (1/20/1/20 s), where the TMA/Ar/H$_2$O/Ar sequence replaces one DEZ/Ar/H$_2$O/Ar exposure during the ZnO ALD process. For “case 2” and “case 3” one DEZ/Ar/H$_2$O/Ar cycle is replace with TMA/Ar/DEZ/Ar/H$_2$O/Ar = (1/20/1/20/1/20 s), and DEZ/Ar/TMA/Ar/H$_2$O/Ar = (1/20/1/20/1/20 s), respectively. In cases 2 and 3, the water exposure in the doping step proceeds only after exposing the surface to both TMA and DEZ. For clarity, we refer to the doping sequences as:

Case 1: TMA/H$_2$O
Case 2: TMA/DEZ/H$_2$O
Case 3: DEZ/TMA/H$_2$O

The frequency of the dopant exposure sequence relative to the ZnO ALD cycle sequence, denoted as $R_{D/Z}$, can be readily adjusted by the ALD control software. When one dopant gas cycle occurs after 19 DEZ/H$_2$O cycles, the doping cycle ratio is given as: $R_{D/Z} = 1/19$.

**In situ Quartz Crystal Microbalance Measurements.** The *in situ* QCM was introduced into the ALD reactor, as shown in Figure 9.2a, to investigate the mass uptake occurring during the precursor and reactant exposure steps. The QCM sensor is a polished gold crystal with an oscillating frequency of 6 MHz. The crystal sensor was mounted in a Maxtek BSH–150 bakable sensor head attached to a 2.75 inch conflat flange. The sensor head was modified to supply an argon flow of ~10 standard cubic centimeters per minute to the back surface of the sensor crystal. This inert argon flow is needed to prevent the back of
the crystal sensor from film deposition. Signals from the crystal sensor were received every 0.1 s by a Maxtek thickness monitor (TM–400), which was interfaced to a computer. The QCM data were obtained after reaching the saturated mass uptake during ZnO ALD. The QCM mass uptake during ZnO ALD was compared with the film thickness measured by ellipsometry. Assuming that the bulk ZnO density is 5.675 g/cm$^3$, the QCM and ellipsometry results agree within a few percent. However, the QCM data is used here to observe changes in mass uptake, and it is not used to make quantitative comparisons of film growth.

**In situ Conductance Measurements.** To examine how the electrical conductance changes in real time during ZnO:Al ALD, an *in situ* conductance measurement device was attached to the ALD reactor as shown in Figure 9.2b. The current was measured in real time at an applied bias voltage of 0.1 V in the middle of Ar purge time after each precursor exposure during ZnO ALD using a Keithley 2602 Sourcemeter. Insulating spacers were used to electrically isolate the two wires which were connected to the electrical current–voltage (I–V) measurement tool. Figure 9.2c shows the cross–sectional schematic diagram of the device structure used for *in situ* conductance analysis. The patterned metal electrode was fabricated by thermal evaporation of Cr (13 nm) and Au (100 nm) onto a Si substrate with a thermally grown SiO$_2$ (100 nm) using a shadow mask. The copper tape was used to contact the electrical lead wires to the Au/Cr electrodes, and also acted to protect the electrical contact between the lead wire and the contact pad during film growth. Four point probe measurements performed ex-situ after deposition show values very similar to those measured in-situ. The analysis of the in situ conductance results was performed for data collected in the steady state deposition region, where any contact effects are minimized.
**Ex situ Characterization of Zinc Oxide Films.** After deposition of ZnO on a planar silicon substrate, the film thickness was measured using Auto EL ellipsometer (Rudolph Tech.) at an angle of incidence $\Phi = 70^\circ$ and a wavelength $\lambda = 632.8$ nm using a refractive index of 1.95.

![Schematic diagram of the experimental setup](image)

**Figure 9.2** Schematic diagram of the experimental setup for (a) *in situ* quartz crystal microbalance (QCM) measurements, (b) *in situ* conductance measurements and (c) cross-sectional view of the device structure used for (b).
The chemical bonding features in films were characterized using transmission Fourier transform infrared spectroscopy (FTIR), Nicolet Magna 750. Auger electron spectroscopy (AES) measurements were performed using a Physical Electronics AES in order to analyze the surface composition and compare the Al/Zn ratio among the ZnO:Al films with three different doping sequences. The Auger spectra were obtained with an electron beam generated at 5 keV and 20 mA. Dynamic secondary ion mass spectrometer (SIMS) depth profiling was also carried out to monitor the mass spectrum of the Al component at each depth using a CAMECA IMS–6F SIMS, where an O$_2^-$ was incident at 1.25 keV with an angle of 40° from normal to the surface. The electrical I–V characteristics were measured using a Keithley 2602 Sourcemeter.

9.4 Results and discussion

In situ QCM Analysis during ZnO, Al$_2$O$_3$, and ZnO:Al ALD. Figure 9.3a shows representative in situ QCM results collected during 100 cycles of independent ZnO and Al$_2$O$_3$ ALD film growth processes. The mass uptake is observed to increase linearly with time, exhibiting the growth rate of ZnO and Al$_2$O$_3$ film to be 115 ng/cm$^2$/cycle and 40 ng/cm$^2$/cycle, respectively. Figure 9.3b displays a more detailed view of the QCM results, showing mass uptake with time for 10 ZnO or Al$_2$O$_3$ ALD reaction cycles. The mass change takes place dominantly after exposure to the DEZ or TMA precursor, and the mass uptake traces indicate that the precursors undergo saturated chemisorption, as expected in ALD, followed by desorption of DEZ, TMA or product ligands during the Ar purge step.
Figure 9.3  (a) In situ QCM measurements of 100 cycles of undoped ZnO and Al$_2$O$_3$ ALD. (b) Representative in situ QCM trace curves for 10 reaction cycles. (c) Growth rate of undoped ZnO and Al$_2$O$_3$ film as a function of ALD cycle. The upper and lower dotted line represent the average growth rate of undoped ZnO and Al$_2$O$_3$, respectively, obtained from (a).
Figure 9.3c presents the growth rate versus ALD cycle obtained from Figure 9.3a, showing the growth rate remains constant with ALD cycle. The upper and lower dotted lines represent the average value of growth rate for ZnO and Al2O3 film, respectively.

In situ QCM measurements are performed to understand the influence of different doping sequences on the surface reaction (i.e., mass uptake and growth rate) in real time during ZnO:Al ALD. Figure 9.4 shows the in situ QCM data obtained during ALD of Al doped ZnO at a doping ratio (R_{D/Z}) of 1/19. For case 1 (Figure 9.4a), the TMA/H2O exposure cycle results in a mass uptake of ~40 ng/cm^2, similar to the value during Al2O3 ALD (Figure 9.3c), indicative of TMA reacting with available –OH groups. For case 2 (Figure 9.4b), the TMA/DEZ/H2O cycle shows QCM response that is very similar to the case 1 data, with evidence for DEZ adsorption and/or absorption followed by desorption during the Ar purge. The QCM response in case 2 suggests that the O–Al(CH3)2* surface remains relatively stable under DEZ exposure, consistent with the expected stronger bonding energy of Al–O relative to Zn–O species.27 For case 3, however, a different trend is observed in the QCM results (Figure 9.4c). The mass increases during DEZ exposure, then decreases upon introduction of TMA, which indicates replacement of Zn-alkyl species with Al-alkyl groups.28 The net mass uptake during the doping step in case 3 is 69 ± 5.5 ng/cm^2, which is larger than the ~40 ng/cm^2 measured after the doping sequence for cases 1 and 2.

Figure 9.4d–f show the growth rate obtained from the QCM data, plotted as a function of ALD cycle for doping cases 1, 2, and 3. For all cases, the growth rate of the first ZnO layer just after the Al doping cycle is in the range of 60–70 ng/cm^2/cycle.
Figure 9.4  (a)–(c) mass uptake versus time and (d)–(f) Growth rate versus ALD cycle for ZnO:Al films, which correspond to the doping sequences of case 1, 2, and 3, respectively, at the R_{D/Z} of 1/19 using in situ QCM measurements.
The ZnO growth rate then increases during the next 4–5 cycles back to a value somewhat larger than that of the steady state ZnO growth rate. This larger growth rate may result from an increased surface roughness and surface area during the initial stages of polycrystalline ZnO growth after the Al introduction.

The mass uptake trend for case 3 doping in Figure 9.4c is related to the relative stability of the Al and Zn related precursors, surface adsorbates, and metal oxides. The data is understood by considering that surface O–Zn(C₂H₅)* species formed during DEZ exposure can be replaced by Al-methyls, resulting in formation of volatile Zn-alkyls and surface O–Al–alkyl groups. Gas phase products in this reaction were previously explored using in situ quadrupole mass spectrometry, and the primary volatile desorbing species were identified as Zn(CH₃)₂. This is in contrast to case 2 mentioned above, where the O–Al(CH₃)₂* surface groups are relatively stable under exposure to DEZ. The magnitude of the net mass uptake in case 3 (~69 ng/cm²) falls between the steady state mass uptake values during ZnO (~115 ng/cm²) and Al₂O₃ ALD (~40 ng/cm²). It is likely that the mixing of –Zn(C₂H₅)* and –Al(CH₃)₂* surface species during case 3 doping will promote formation of Zn–O–Al bonding units, similar to those formed in the stable ZnAl₂O₄ spinel structure. This mixed Zn-O-Al bond formation will also occur in case 1 and case 2 doping. However, in case 3, the extent of Al incorporation during TMA exposure will be less than in case 1 and 2. This is because in case 3, most of the surface OH groups are consumed during the DEZ reaction step producing a high density of Zn(C₂H₅)* species. The subsequent reaction during TMA exposure is therefore controlled by the ligand exchange reaction, rather than the more favorable TMA/OH surface reaction. Moreover, in case 3, the –Zn(C₂H₅)* surface formed during DEZ
exposure acts as a “sacrificial” layer to isolate the underlying ZnO from reaction with the TMA precursor. Therefore, the DEZ exposure step in case 3 doping helps control Al dopant incorporation during the TMA exposure. The reduced mass uptake during case 3 doping, and the presence of Zn–O–Al bonding in the resulting films are confirmed by elemental and IR spectroscopic analyses presented below. Furthermore, the recovery period (~5 cycles) of the ZnO growth rate after introduction of the Al dopant can be understood in terms of monolayers (ML)/cycle. Based on film thickness measured by ellipsometry and the bulk density of ZnO, the growth rate is estimated to be ~0.97 ML/cycle during steady state ALD. During the 5-cycle transient period after TMA introduction, the total mass uptake corresponds to ~4 ML of ZnO growth. This suggests diffusion or mixing of the Al and Zn species during growth, and/or a process by which the Zn incorporation is influenced by the Al species at or near the surface.

The Al/Zn gas doping cycle ratio (RD/Z) also has a significant influence on mass uptake. Figure 9.5 shows the QCM data obtained using RD/Z = 1/4, with conditions otherwise unchanged from those used to collect data in Figure 9.4. TMA exposure in case 1 produces a net surface etching, (Figure 9.5a, Δm = −16.6 ± 2.5 ng/cm²). Etching also results for case 2 (Figure 9.5b) after the TMA/DEZ/H₂O exposure sequence. However, for case 3 (Figure 9.5c) a large mass increase is seen during DEZ exposure, followed by a decrease during TMA, with a net mass uptake of ~0 ng/cm². The growth rates obtained from the QCM data are also shown in Figure 9.5d–f.
Figure 9.5  (a)–(c) mass uptake versus time and (d)–(f) Growth rate versus ALD cycle for ZnO:Al films, which correspond to the doping sequences of case 1, 2, and 3, respectively, at the R_{D/Z} of 1/4 using in situ QCM measurements.
Deposition rate was also characterized using $R_{D/Z} = 1/9$, and the data is summarized in comparison with the data using $R_{D/Z} = 1/4$ and $1/19$ in Figure 9.6, for doping cases 1, 2, and 3. For all doping ratios studied, the case 3 sequence shows a larger net mass during the doping step than either case 1 or 2.

**Figure 9.6** Average mass change occurring during 3 different doping sequences at the $R_{D/Z}$ of 1/4, 1/9, and 1/19.
**In situ Conductance Analysis during ZnO and ZnO:Al ALD.** Figure 9.7 presents conductance data collected *in situ*, with one data point measured per cycle after the H₂O exposure step. The four data sets correspond to no doping, and to doping sequence cases 1, 2 and 3 (data for case 2 and 3 are shifted by +0.5 and +1.0 mS, respectively for improved visibility). The conductance during ZnO ALD displays a linear increase with ALD cycle, indicative of the resistance decrease with increasing film thickness. The conductance of the ZnO:Al films also generally increase with ALD cycle, but they show an additional reproducible characteristic variation upon introduction of Al doping cycle. The shape of the conductance trend is consistent from run-to-run for all gas doping ratios and doping sequences studied.

**Figure 9.7** Conductance measured as a function of ALD cycle in real time during ZnO and ZnO:Al growth with different doping cases at the R<sub>DZ</sub> of 1/19. Cases 2 and 3 were shifted up by +0.5 and +1 mS, respectively. Here (I) to (III) represent different slopes of conductance change after the doping sequence.
Figure 9.7 shows the conductance trend over 3 macro cycles (where for $R_{D/Z} = 1/19$, 1 macro cycle consists of 1 doping cycle + 19 ZnO cycles). Three regimes are identified: (I) conductance decreases after TMA exposure (up to ~4$^{th}$ DEZ/H$2$O cycle), (II) conductance increases slightly (from 4$^{th}$ to 11$^{th}$ cycle), and (III) conductance increases more significantly (from 11$^{th}$ to 19$^{th}$ cycle). The doped films show higher conductance than the ZnO. It is interesting to note that a decreased conductance is observed during the same 4–cycle period that a decrease in deposition rate is observed in QCM, suggesting a link between surface conductance and dopant incorporation.

The data in Figure 9.8 present a more magnified view of the thin film conductance results. Data points are shown for each step in the deposition cycle. The ZnO ALD process (Figure 9.8a) results in a regular conductance oscillation, with a decrease during DEZ exposure and an increase during H$2$O exposure.$2^4$ The conductance oscillation is ascribed to a change in conduction electron density during the ALD binary chemical adsorption/reaction sequence. Results in Figure 9.8b–d show the in situ conductance progression during ZnO:Al ALD process using the various Al doping sequences. The conductance change shows a complex trend after TMA introduction, but the results are highly reproducible over many macro–cycles. Moreover, the TMA/H$2$O introduction results in a reproducible characteristic variation in conductance even for different dopant series ratios. In all cases, the first exposure of TMA or DEZ during the doping step result in decreased conductance, with some recovery during the H$2$O exposure. Over the next 3–5 DEZ/H$2$O cycles, the conductance drops then resumes the oscillation pattern with increasing conductance associated with the undoped ZnO ALD. Similar trends are seen in all the doping sequence cases, however, a
larger relative increase in conductance occurs after DEZ/TMA/H₂O (case 3) as compared to TMA/DEZ/H₂O (case 2) or TMA/H₂O only (case 1). We also find that overall, the film conductance measured in air after deposition is larger for the case 3 films, probably due to a somewhat smaller Al content, closer to that resulting in the maximum ZnO:Al conductivity.

**Figure 9.8** Conductance measured versus time for (a) ZnO and ZnO:Al with different doping sequences of (b) case 1, (c) case 2 and (d) case 3. All the conductance data were obtained in the saturation region of ZnO film growth.
**Ex situ** Characterization for ZnO and ZnO:Al Films Grown by ALD. The different doping sequences affect the measured mass uptake observed using QCM. We expect, therefore, the doping sequence will influence the macroscopic film thickness, chemical composition and electrical I–V characteristics. Figure 9.9 displays the film thickness determined by ellipsometry for ZnO and ZnO:Al films grown for 220 cycles with \( R_{DZ} \) of 1/19. Case 3 doping shows a reduced film thickness relative to the undoped film, which is ascribed to a combination of film etching during dopant introduction and decreased ZnO growth rate after TMA exposure. Film thickness is further reduced for case 1 and 2, also consistent with the larger extent of etching obtained from QCM for those cases.

**Figure 9.9** Measured thickness obtained by ellipsometry of ZnO and ZnO:Al films grown with different Al doping sequences at the \( R_{DZ} \) of 1/19 for 220 cycles. For each data point, five measurements were made on one sample. The error bars represent one standard deviation.
Based on the QCM results over the 11 macrocycles used in film growth, the net deposition thickness is expected to be ~0.6 nm larger for the case 3 film compared to case 1, consistent with the difference of ~0.7 nm obtained by ellipsometry analysis.

The Al–O and Zn–O bonding features in the resulting films were characterized using FTIR, and results are given in Figure 9.10. The films were deposited on double–side polished high resistivity (> 10 $\Omega \cdot \text{cm}$) silicon substrates and were measured in transmission configuration with the IR beam incident at an angle of 60° with respect to the sample normal. The incident angle allows both the transverse (TO) and longitudinal optical (LO) modes to be observed. The peaks of the ZnO TO and LO, and the Al$_2$O$_3$ LO modes are indicated at 402, 576, and 950 cm$^{-1}$, respectively. Peaks denoted by asterisks (*, **) correspond to modes expected for materials containing Zn–O–Al bond units. As R$_D$/Z increases, features associated with Zn–O bonding decrease. Features related to Al–O bonding are not observed in any of the ZnO:Al films studied, but features are observed for Zn–O–Al. The films formed with R$_D$/Z = 1/4 show predominantly Zn–O–Al modes, without visible Zn–O or Al–O modes present. This suggests that the aluminum species readily mix with the ZnO over the thickness associated with 4 cycles of ZnO deposition. This is consistent with the QCM results that show that TMA affects the subsequent DEZ/H$_2$O mass uptake for ~4 ALD cycles. For the films deposited at R$_D$/Z = 1/19, no marked effect of doping sequence was observed in the IR analysis, indicating any differences were outside the experimental sensitivity limit (typically 0.5 atomic %).

Chemical composition and dopant distribution analysis of the deposited materials were performed using AES and SIMS depth profiling. Figure 9.11a shows a representative
AES spectra of a ZnO:Al film grown at R_{D/Z} = 1/19 using doping case 1. A small feature associated with aluminum is observed. Figure 9.11b shows the atomic Al/Zn ratio obtained from similar AES data from samples prepared using the three doping cases at R_{D/Z} = 1/19. The Al/Zn ratio for case 1 is similar to that in case 2, but larger than that in case 3, demonstrating less Al incorporation for case 3.

**Figure 9.10**  Infrared (IR) absorbance spectra of ZnO/Si, ZnO:Al/Si and Al$_2$O$_3$/Si measured in transmission configuration at an incident angle of 60°. The TO and LO peaks indicate the transverse and longitudinal optical modes, respectively. The TO (Zn–O) and LO (Zn–O) modes decrease from the pure ZnO to ZnO:Al (R_{D/Z} =1/9) and then disappear at the R_{D/Z} of 1/4 while a new LO mode (**) associated with a Zn–O–Al layer appears. The peaks corresponding to asterisks (*,**) are considered associated with Zn–O–Al bonding features. For comparison, an amorphous Al$_2$O$_3$ feature with the prominent LO mode at 950 cm$^{-1}$ is also shown.
Figure 9.11  (a) Representative Auger electron emission spectra (AES) of ZnO:Al film grown at $R_{D/Z}$ of 1/19 for the doping case 1. (b) Average Al/Zn composition ratio of ZnO:Al films grown at $R_{D/Z}$ of 1/19 with different doping sequences using AES surface analysis.
Figure 9.12a exhibits the SIMS profile results for the Al component from ZnO:Al films formed using $R_{D/Z} = 1/39$ for 240 cycles. The aluminum concentration oscillates as the film is profiled normal to the film surface, with six peaks observed (including the peak at the film surface). These peaks correspond spatially to the positions expected for the six dopant incorporation steps used in film growth (Figure 9.12c). Again, comparing the different doping sequences, the film deposited using case 3 shows less Al than for case 1. Annealing the case 1 film at 500 °C results in some Al redistribution (Figure 9.12b), but the concentration oscillation is still readily visible. These results are in contrast to previous doping profiles\textsuperscript{35} observed for Al doping in ALD TiO$_2$, where uniform aluminum atom distribution was observed in films deposited at 250 °C using a very low doping ratio of 1/119.

Current–voltage (I–V) characteristics were measured in air at room temperature using two evaporated metal electrodes (Au/Cr) on doped and undoped films. Results from layers formed using 220 cycles and $R_{D/Z} = 1/19$ for the three different doping sequences are shown in Figure 9.13. All the ZnO films show ohmic traces, and case 3 has a higher conductance than cases 1 and 2. The conductivity for the case 3 film is $\sim 740$ S/cm, which is less than the typical value of $1 \times 10^4$ S/cm for good quality tin-doped indium oxide (ITO) films.\textsuperscript{3} We find that films measured using 4-point probe typically show conductivity values 2-3 times lower than that obtained using the evaporated electrodes. The higher conductivity in the case 3 film is likely due to the smaller dopant concentration, resulting in film composition closer to the optimized maximum conductivity. Results therefore demonstrate that the DEZ exposure before dopant introduction acts to reduce the number of active Al dopant atoms introduced during the TMA dose.
Dynamic SIMS depth profiling of the $^{27}$Al component of the ZnO:Al films grown at the $R_{D/Z}$ of 1/39 for 240 cycles (a) for different doping sequences and (b) for the as grown at 125 °C and the annealed at 500 °C. (c) Schematic diagram of the deposited ZnO:Al film showing the spatial positions of the Al–O doping cycles within the ZnO layer.

Figure 9.12
9.5 Conclusions

Quartz crystal microbalance analysis revealed that chemical interactions during aluminum doping of ZnO:Al depend on dopant/ZnO ALD cycle ratio, and on the order of precursor exposure. Introduction of the aluminum dopant impedes the subsequent growth of ZnO layers for ~4 ALD cycles, and infrared transmission analysis confirms the formation of Zn–O–Al bonding. Depth profiling using SIMS also confirms non-uniform aluminum distribution through the deposited film.
Introducing the trimethyl aluminum dopant immediately after diethyl zinc results in less Al uptake than for doping sequences where TMA follows a water exposure step. When DEZ is introduced before the TMA, without water exposure, the zinc-organic surface species can act as a sacrificial layer which is partially removed during TMA exposure, resulting in less Al incorporation. *In situ* conductance shows complex but highly repeatable trends in current flow during ALD cycling, and the overall trend in conductance with doping sequence is confirmed by post-deposition I–V characterization. The combination of *in situ* QCM and conductance measurements could be readily applied to other multi-component ALD material processes, enabling improved understanding of multicomponent thin film deposition processes.

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9.6 References


Chapter 10

Correlation in charge transfer and mass uptake revealed by real-time conductance and quartz crystal microbalance analysis in low temperature atomic layer deposition of zinc oxide and aluminum-doped zinc oxide*


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*My contributions to this work include developing the in situ quartz crystal microbalance and electrical conductance measurements during atomic layer deposition of $\text{Al}_2\text{O}_3$, $\text{ZnO}$ and Al-doped $\text{ZnO}$. I also performed all the electrical and spectroscopic characterization and analysis of results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. While Dr. Gregory Parsons helped in experimental design, I worked independently to conceptualize and initiate the experiments. Giovanna Scarel helped me in understanding the surface states of adsorbed molecules on the growing film.
10.1 Abstract

In situ characterization of low temperature atomic layer deposition (ALD) of ZnO and aluminum doped ZnO (ZnO:Al) establishes a relationship between species adsorption, mass uptake, and surface electrical conductance during deposition and dopant atom incorporation. Conductance measured in situ during ZnO ALD is observed to oscillate with species surface adsorption, consistent with surface potential modulation and charge transfer during surface reaction. Dopant introduction using trimethyl aluminum results in a decreased growth rate and a decrease in the net material conductance, followed by growth rate recovery and conductance increase. The trends in growth and conductance are ascribed to excess surface Al–O bonding after TMA exposure, followed by doping development as dopants transition to the film bulk. A non–uniform dopant atom distribution in the direction of film growth is observed and supports the doping model. The results expand fundamental understanding of doping-associated changes in film deposition and conductivity.
10.2 Introduction

Low temperature transparent conducting thin films\textsuperscript{1-4} provide vital function in several emerging fields, such as displays, sensors, touch panels, light emitting diodes, photovoltaic cells, and transparent electronics.\textsuperscript{5-12} For many new uses, highly conformal coatings enable three dimensional designs that enhance function or performance over typical planar or semi–planar constructs.\textsuperscript{5-7,13} Atomic layer deposition (ALD) produces highly conformal coatings with monolayer precision at low temperatures, and has been studied for formation of several transparent conductors including ZnO and aluminum–doped ZnO (ZnO:Al).\textsuperscript{6,12,14,15} Extrinsic doping of ZnO by substitution of group III or IV elements, (i.e. B, Al, Ga, In, Ge) for Zn, or group VII species (F, Cl, I) for O are also well investigated.\textsuperscript{16,17} However, the mechanisms associated with dopant atom incorporation, and the surface reaction steps that lead to dopant atom assimilation and activation are not well known. Dopant activation is particularly important in applications where very thin conductive layers are desired. The work presented here exposes new relations between surface deposition reactions, dopant activation, and charge transfer that proceed during low temperature ALD of transparent conducting ZnO and ZnO:Al films. Results include a systematic combination of \textit{in situ} quartz crystal microbalance (QCM)\textsuperscript{18,19} and conductance measurements,\textsuperscript{20,21} to provide complementary \textit{in situ} reaction analysis of film formation and doping mechanisms.

Previously, Yousfi \textit{et al.}\textsuperscript{18} and Elam \textit{et al.}\textsuperscript{19} applied \textit{in situ} QCM to analyze ZnO and nanocomposite films. Also, Schuisky \textit{et al.}\textsuperscript{20} and our group\textsuperscript{21} used \textit{in situ} conductance to study steady–state ZnO and Al\textsubscript{2}O\textsubscript{3} ALD, respectively. However, \textit{in situ} QCM and conductance analysis have rarely been combined. We show here that their combination
provides a powerful means to observe direct links between surface reactions, surface transconductance and charge transfer. Specifically, we observe that conductance oscillations follow the ZnO ALD mass uptake cycle as the surface alternates between zinc hydroxide and zinc–alkyl termination. The addition of approximately one monolayer of aluminum dopant during ALD impedes ZnO mass uptake and disrupts transverse conductance oscillations for ~4–5 deposition cycles. By matching the conductance oscillations with the Al atom concentration profile obtained after deposition, we show that full dopant activation proceeds only after dopant atoms assimilate into the film bulk, several nanometers below the growing ZnO surface. These and other results provide a link between surface charge density, surface growth reactions, and dopant incorporation, adding new insight into growth mechanisms for low temperature thin film material deposition.

10.3 Experimental methods

Atomic Layer Deposition of Zinc Oxide Films: ZnO ALD was performed using diethylzinc (DEZ, Zn(C₂H₅)₂), trimethylaluminum (TMA, Al(CH₃)₃), and deionized water (H₂O) as Zn, Al and oxidant precursor, respectively. Argon was used as a carrier and purge gas. The deposition was carried out in a homebuilt hot-wall stainless steel tube reactor. The DEZ and TMA precursors were obtained from STREM Chemicals and used as received. The growth temperature was set at 125 °C, and the operating pressure was maintained at 2 Torr with a total gas flow rate of 100 standard cubic centimeters per minute (sccm). The pulsed amount (ΔP) of a precursor and oxidant gas was kept at ~0.1 Torr using metering valves. The
ZnO ALD was performed using separate DEZ and H₂O exposures, following the sequence: DEZ/Ar/H₂O/Ar (1/20/1/20 s), and the doping was performed by substituting TMA exposure for the DEZ, resulting in discrete Al–O layer incorporation into the ZnO film. Several DEZ/H₂O cycles (C_{ZnO}) followed by typically one TMA/H₂O cycle (C_{Dopant} = 1) constitutes one growth “macrocycle”. Several macrocycles are used in a typical film growth process, and the doping cycle ratio (C_{Dopant}/C_{ZnO} = R_{D/Z}) studied ranged from 1/4 to 1/39.

In situ Quartz Crystal Microbalance Measurements: The in situ QCM was attached to the ALD reactor to investigate the surface chemistry between each cycle. The QCM sensors were polished gold crystals with an oscillation frequency at 6 MHz. These sensors were mounted in a Maxtek BSH-150 bakeable sensor head attached to a 2.75 inch conflat flange. The sensor head was modified to supply an argon flow of ~10 sccm to the back surface of the sensor crystal. The inert argon flow is needed to prevent the back of the crystal sensor from film deposition. Signals from the crystal sensor were received by a Maxtek thickness monitor (TM-400) every 0.1 s, which was interfaced to a computer via a RS232 cable. In this study, the in situ QCM data were obtained after reaching steady state growth during ALD.

In situ Conductance Measurements: To investigate how conductance changes in real time during ZnO:Al film growth, an in situ conductance measurement tool was attached to the ALD reactor. The current was measured in real time at an applied bias voltage of 0.1V in the middle of Ar purge time after the dose of each reactant during ZnO growth using a Keithley 2602 Sourcemeter. Insulating spacers were used to electrically isolate between two wires, which were connected to the I–V measurement tool. The evaporated Au/Cr electrodes
were carefully shielded during probe assembly using conducting foil tape to isolate and screen them from the process gases. Also, because the ALD film readily deposits over the entire sample probe surface, conductance measurements were performed after deposition, after etching the film outside of the electrode region, with the sample disconnected from the probe housing. The current showed only minimal change, indicating that the \textit{in situ} conductance corresponded nearly completely to lateral charge flow, directly between the patterned electrodes.

\textit{Ex situ Characterization of Zinc Oxide Films:} To investigate Al dopants diffusion behavior in the following ZnO growth after the Al–O doping sequence, dynamic secondary ion mass spectrometry (SIMS) depth profiling was carried out to detect the mass spectrum of the Al and Zn component at each depth using a CAMECA IMS–6F SIMS, where an O\textsuperscript{2+} was incident at 1.25 keV with an angle of 40° from normal to the surface.

10.4 Results and discussion

\textbf{QCM results for ZnO, Al\textsubscript{2}O\textsubscript{3} and ZnO:Al ALD.} Figure 10.1a displays representative \textit{in situ} QCM results collected during independent ZnO and Al\textsubscript{2}O\textsubscript{3} ALD film growth processes. The primary mass change was observed during the 1 second precursor pulse, and the step shape indicates the precursors undergo chemisorption and some reversible physisorption, resulting in self-limiting monolayer–level saturation. The growth rate obtained from the QCM results is constant with time, as plotted in Figure 10.1b.
Figures 10.1c and 1d present the QCM results obtained during steady-state deposition, when each 20th DEZ pulse is replaced with one TMA exposure (i.e. gas pulse doping ratio Al/Zn, $R_{D/Z} = 1/19$). Under the conditions used here, the mass uptake after the TMA/H$_2$O cycle is approximately the same as during Al$_2$O$_3$ deposition (~40 ng/cm$^2$ in Figure 10.1b). However, data obtained using other doping ratios demonstrate that the TMA mass uptake depends dramatically on the number of Zn–O ALD cycles between TMA exposures. For example, when $R_{D/Z}$ was maintained at 1/4, a negative mass uptake was observed during TMA exposure, indicating surface etching reactions, consistent with the report of Elam et al.$^{19}$ Using $R_{D/Z} = 1/19$, the mass uptake during TMA exposure likely proceeds from a balance of Al– species deposition and Zn– species etching. After the subsequent water exposure, the surface will roughen and contain a mix of Al– and Zn– hydroxyls. It is interesting to note that the mass uptake data obtained in our experiments, including points for $R_{D/Z} = 1/19$ in Figure 10.1c–d, and other $R_{D/Z}$ values studied, are strikingly similar to the data of Elam et al.$^{19}$ illustrating the extraordinary repeatability of the surface saturating ALD process. The mass uptake during the next several DEZ/H$_2$O cycles (Figure 10.1d) is less than that observed during steady-state ZnO ALD, and after 4–5 cycles, the mass uptake increases to ~125 ng/cm$^2$ which is higher than the ~115 ng/cm$^2$ observed for undoped ZnO in Figure 10.1a and b. A proposed mechanism for the decreased mass uptake during DEZ exposure after the TMA/H$_2$O step involves a proton exchange reaction to form Zn–OH$^2$–AlO$^-$ surface complexes that reduce the number of hydroxyl surface groups available for surface reaction.$^{19}$ The in situ conductance results discussed below provides further insight into this surface passivation mechanism.
Figure 10.1  (a) Representative *in situ* QCM curves vs time and (b) growth rate vs ALD cycle number for the undoped ZnO and Al₂O₃ ALD. (c) Change of the mass uptake vs time and (d) growth rate vs ALD cycle number for the ZnO:Al film at the doping ratio of 1/19 using *in situ* QCM measurements.
In situ conductance during ZnO ALD. Figure 10.2 shows a cross-sectional schematic of the device structure used for the in situ conductance analysis, and the inset displays a sketch of a typical reaction cycle for ZnO ALD. To achieve low contact resistance and high current sensitivity, patterned metal electrodes are fabricated by thermal evaporation of Cr (13 nm) and Au (100 nm) through a shadow mask onto a Si substrate coated with 100 nm of thermally grown SiO$_2$. Figure 10.3 shows the overall trend in conductance ($G$) vs. time during ZnO and ZnO:Al ALD, where data is collected once per cycle, after the H$_2$O exposure step. Conductance is low during film nucleation, and then increases rapidly during film coalescence. Steady state deposition results in a slower rate of conductance increase. The repeating inflection points in the data set in Figure 10.3b correspond to the dopant atom incorporation steps. The data sets in Figure 10.4a and b present a more magnified view of the thin film conductance results. Shown are two data points per cycle, collected after precursor and H$_2$O exposure steps. The ZnO ALD process (Figure 10.4a) results in regular conductance oscillations, with a decrease during DEZ exposure and an increase during H$_2$O exposure. The conductance increases linearly during steady state growth, and data collected after the H$_2$O exposure over 80 deposition cycles is shown in Figure 10.4c.

ZnO is a well-known chemi–resistive sensor material, displaying a marked conductance change upon adsorption of surface species. The conductance change is generally ascribed to a change in surface chemical potential (band bending) due to modulation of surface state charge.$^{22-24}$ The in situ conductance measures the change in
conduction electron density that occurs upon surface charge transfer due to adsorption of chemical species.

Figure 10.2  Cross-sectional schematic illustration of the device structure used for in situ conductance measurements. The inset presents a schematic view of one reaction cycle, including charge transport steps, during ZnO ALD on the exposed ZnO surface layer contacted by the metal electrodes.
Figure 10.3  Overall trend in electrical conductance vs. ALD process time for (a) undoped ZnO and (b) ZnO:Al films with a doping ratio of 1/19 at 125 °C using the device structure shown in Figure 10.2.
Figure 10.4  Conductance change with exposure of each reactant for (a) the ZnO and (b) the ZnO:Al ALD. (c) Conductance of the ZnO and ZnO:Al film with a R_{DZ} of 1/19 measured in real time as a function of ALD cycle number. (d) Comparison of conductance change for the ZnO:Al film grown at the R_{DZ} of 1/19 and 1/39. Here (I)–(IV) indicate different slope of conductance change after the Al doping sequence.
Water adsorption and dissociation on ZnO and other transition metal oxides involves a series of neutral and charged physi– and chemisorbed OH and H₂O species, with the lowest energy charge state determined by the acid/base character of the particular oxide surface.²³,²⁵,²⁶ At temperatures <100 °C, water molecular physisorption can also play a significant role in surface charge screening. For example, in situ conductance measured during ZnO ALD at 90 °C (data not shown), results in conductance decrease upon exposure to H₂O and increase during DEZ exposure, which is opposite to that shown in Figure 10.4a.

The number of charge carriers needed to produce the observed change in conductance during each water exposure step in Figure 10.4a can be estimated as follows. Using Ohm’s law, and conductivity \( \sigma = ne\mu \) (where \( n \) is the volume density of charge carriers, \( e \) is the fundamental charge and \( \mu \) is carrier mobility), the charge transfer density (\( \Delta n_e \), charge/cm²) is given by:

\[
\Delta n_e = \Delta G \frac{L}{e\mu W}
\]

where \( \Delta G \) is the measured conductance change (\( \Omega^{-1} \)), and \( L \) and \( W \) are the separation and length of the electrodes, respectively. This relation does not include, for example, effects of fringing fields. A reasonable value for mobility is \( \mu = 1 \) cm²/Vs, which is within the range of transconductance mobility values for ALD ZnO thin film transistors,²⁷,²⁸ but not as large as the most optimized materials. Using the geometric electrode gap of 0.3 cm and length of 1.0 cm, and the \( \Delta G \) values from Figure 10.4a, we obtain \( \Delta n_e = \sim 6.4\times10^{14} \) charges/cm². This value is in the same order of magnitude as the density of surface growth sites, \( \sim 8.6\times10^{14} \) cm⁻², obtained from mass uptake results in Figure 10.1, and the estimated OH group density.
$1.06 \times 10^{15}$ cm$^{-2}$, on the ZnO ALD surface at low temperature.$^{19}$ This correlation indicates that a significant fraction of the reaction sites involved in deposition are also engaged in charge transfer between the surface and film bulk.

The surface of zinc oxide is known to be an active heterogeneous basic catalyst,$^{29}$ with an isoelectric point (IEP) in water of $\sim 8.1 - 9.8$. Upon water exposure during ALD, surface basic sites, including surface hydroxyls or lattice oxygen, can bind a proton which will release charge to the film bulk, resulting in charge accumulation and surface band bending. The charge transfer is shown schematically in Figure 10.5b. Analogous processes occur on the more acidic SnO$_2$ surface, leading to increased conductance upon exposure to water vapor at elevated temperature.$^{23,24}$ For example, OH groups can bond to metal Lewis acid site through lone-pair donation, leaving a hydrogen atom to bond to a lattice oxygen, promoting charge donation to the film bulk.$^{23,24}$ In SnO$_2$, this process also promotes formation of oxygen vacancy states which are readily ionized.$^{23}$ After the water exposure step in the ALD ZnO process, the subsequent DEZ exposure will revert the surface basic sites back to a more neutral ethyl termination, decreasing net conductance (Figure 10.5c). The smaller steady increase in film conductance (Figure 10.4a, c) is due to the net increase in film thickness.

The space charge resulting from the surface adsorption and charge transfer occurs within a surface layer with a thickness corresponding to the Debye length,$^{26,31}$ given by:

$$\lambda_D = (\varepsilon kT/q^2 n)^{1/2}$$

(2)

where $\varepsilon$ is the static dielectric constant, $k$ is Boltzmann’s constant, $T$ is an absolute temperature, $q$ is the electrical charge of carrier, and $n$ is the charge carrier concentration.
Figure 10.5  Effect of surface states of adsorbed molecules on the Fermi level ($E_F$) in the bulk. (a) Flat band before interaction of adsorbed DEZ and H$_2$O species with the n-type ZnO semiconductor. (b) After exposure to water precursor, the surface states might be higher relative to the Fermi level in the bulk. Electrons are donated to the conduction band ($E_c$) to form an accumulation layer within a surface layer of the bulk ZnO, resulting in the conductance increase. (c) After exposure to DEZ precursor, the surface states might be lower with respect to the Fermi level in the bulk. Electrons are captured from the conduction band to form a depletion layer within a surface layer of the bulk ZnO, resulting in the conductance decrease. Here $E_v$ indicates the valence band.

For a carrier concentration of $10^{18} - 10^{19}$ cm$^{-3}$ at 125 °C, the Debye length is ~ 1–3 nm, which is a small fraction of the 20–40 nm film thickness studied here. Transmission electron micrographs of ZnO ALD films deposited under similar conditions in our lab$^{32}$ demonstrate the material is a dense solid, without significant porosity to allow penetration of the reactants into the film. The conduction mechanism is therefore dominated by charge flow through the
film bulk, with charge density modulated by the presence or absence of a depletion or accumulation layer at the film/vapor surface.23

In situ conductance and film structure for ZnO:Al ALD. The in situ conductance progression upon TMA doping is shown in Figure 10.4b. While the ZnO ALD process shows constant conductance oscillations, the Al-doping process shows a reproducible characteristic variation upon introduction of the TMA and H2O, with consistent shape and magnitude from run-to-run, even for different gas dopant ratios. The conductance trend over 4 macro cycles (where 1 macro cycle consists of 1 TMA/H2O + 19 DEZ/H2O cycles) obtained during steady-state growth is shown in Figure 10.4c. Three regimes are identified: (I) conductance decrease (~ up to 4th DEZ/H2O cycle), (II) small conductance increase (from 4th to 11th cycle), and (III) more enhanced conductance increase (~11th to 19th cycle). With less frequent TMA/H2O doses (RD/Z = 1/39, Figure 10.4d) an additional regime (IV) appears, indicating slower conductance increase between the ~27th and 39th cycle. Using more frequent TMA/H2O doses (e.g. RD/Z of 1/9, not shown) the conductance drops for ~4 cycles (regime I), then increases slowly for cycles 5 to 9 (regime II), repeating again after the TMA/H2O step.

Dynamic secondary ion mass spectroscopy (SIMS) results in Figure 10.6a show the doping profile for the ZnO:Al with RD/Z = 1/39 for 240 total cycles (6 macro cycles) at 120 °C, where the process was finished with a TMA/H2O cycle. Also shown (Figure 10.6b) is a schematic of the deposited film, identifying the spatial positions of the TMA/H2O cycles within the ZnO layer. The 27Al signal in the SIMS data shows peak intensity corresponding to the points of TMA/H2O exposure, and oscillating signal pattern demonstrates that the Al
dopants are non-uniformly distributed through the ZnO film. The corresponding oscillations in intensity of the $^{64}$Zn signal may be associated with an enhanced Zn detection in the presence of the Al–O layer during SIMS measurement. A recent report by Kim et al. shows a more uniform dopant atom distribution in Al-doped TiO$_2$ formed by ALD at 250 °C. However, preliminary SIMS data from ZnO:Al deposited or annealed at 250 °C in our lab show a non-uniform Al atom distribution, similar to the data shown in Figure 10.6.

Figure 10.6 (a) Dynamic secondary ion mass spectroscopy depth profiling of the ZnO:Al films grown at the $R_{D/Z}$ of 1/39 for 240 cycles. Here Al and Zn components were detected during measurement. (b) Schematic diagram to show the ZnO film structure corresponding to (a).
The conductance measured *in situ* during processing (at 125 °C), and measured *ex situ* in air at room temperature, are shown in Figure 10.7. The peak conductance at $R_{D/Z} = 1/19$ is in good agreement with results reported by Elam *et al.* The ZnO films without added Al exhibit the largest change in conductivity upon the transition from vacuum at elevated temperature to air at room temperature. The changes in temperature reduce the concentration of thermally generated carriers, and the adsorption of oxygen onto ZnO will extract electrons from the surface, also decreasing the conductance. The maximum conductivity observed was $\sim 1.3 \times 10^3$ S/cm at $R_{D/Z} = 1/19$, which is less than the typical conductivity of indium doped tin oxide ($\sim 1 \times 10^4$ S/cm).

![Figure 10.7](image.png)

**Figure 10.7** Conductivity for ZnO films for various doping ratio values measured *in situ* during deposition and *ex situ* under ambient conditions. All the samples were grown at 125 °C for 240 cycles. The *ex situ* measurements were performed in lab air at room temperature after unloading the *in situ* measured samples using the same electrical characterization tool.
The introduction of TMA in the ZnO ALD process results in a change in surface conductance and a change in mass uptake, suggesting a correlation between these outcomes. As in the DEZ/H₂O case, the TMA dose results in a conductance drop, followed by a conductance gain during the next H₂O dose. The magnitude of the drop during TMA is consistent with that seen during the previous DEZ dose. However, the conductance gain during the next H₂O step is ~40% the magnitude of that of the previous H₂O dose (after DEZ). The changes during the next DEZ and H₂O steps are even smaller, both showing positive conductance change. The following 3 DEZ/H₂O cycles produce a transition to a period of net conductance decrease before returning to obvious oscillations and net conductance increase.

To understand the trends in conductance change, we can consider, as mentioned earlier, that the TMA exposure step likely results in a roughened surface with a distribution of surface Al– and Zn–alkyl sites. The conductance drop during TMA treatment coincides with surface alkylation and neutralization of the surface charge, similar to the previous DEZ exposure. However, during the subsequent H₂O exposure, the surface will form Al–OH groups, which are more acidic and have higher electron affinity than the basic Zn–OH species, resulting in less charge transfer and a smaller conductance increase. This is consistent with data in Figure 10.4b showing 60% less charge transfer after the TMA/H₂O step. The next DEZ pulse produces a mass uptake that is only 60% of that of a typical steady-state DEZ pulse (Figure 10.1d), and a small positive conductance change. A possible relationship between the mechanisms for surface reaction passivation and charge transfer can be inferred. Proton exchange reactions on the mixed oxide surface forming Zn–OH^{2+}⋯AlO⁻
complexes could simultaneously act to eliminate available OH sites needed for subsequent DEZ reaction and impede charge transfer to the film bulk. Further, isolated ZnOH sites that are active for protonation and subsequent charge transfer would remain available to react with DEZ. This is also consistent with the charge balance analysis given above, wherein during ZnO ALD, the reactive site density is approximately balanced with the charge transfer density. While enough data is not available to make a full detailed charge and site balance, charge transfer through 40 % of surface sites observed in the ZnO:Al case could correlate with growth at 60 % of the surface sites, if some of the complexed Zn–OH$_2^+$...AlO$^-$ sites provide Zn–OH sites for DEZ reaction, while not participating in charge transfer. This identifies a possible quantitative link between surface charge transfer and mass uptake during thin film materials deposition reactions.

Another puzzling observation is that upon TMA introduction, the conductance oscillations are nearly eliminated, and the conductance gradually drops during the 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ DEZ/H$_2$O cycles after the TMA/H$_2$O exposure. The substitution of Al$^{3+}$ into Zn$^{2+}$ sites in wurtzite ZnO could be expected to result in charge donation and an immediate increase in the conductance, which is clearly not observed. The SIMS data shows regions of enhanced Al concentration, and Al–O clusters are typically accompanied by bulk electron trapping. A large density of trap states in the forbidden energy gap at the growth surface could pin the Fermi level and impede the surface potential oscillations. Alternately, one could consider that the more strongly bound Al–O layer will produce higher energy conduction states at the surface, producing a local potential barrier for charge transfer to the bulk. In either case, the Al–O layer near the surface inhibits charge transfer. As the layer becomes buried in the
depositing ZnO, it will interact less with the surface. When the thickness of the ZnO layer over the thin buried Al–O region exceeds the Debye length (~2–3 nm), the trap layer will be effectively screened, and the surface will resume its previous charge transfer and conduction oscillation characteristics. This 2–3 nm thickness corresponds well with the ZnO film thickness deposited within regions I and II in the conductance oscillation plots. Within region III, the rapid increase in conductance then corresponds to fully buried Al–O regions, with full contribution from Al bulk doping, and minimal contribution from surface Fermi level pinning.

10.5 Conclusions

In summary, by exploiting the combination of in situ quartz crystal microbalance and conductance analysis, new insight is developed into the relation between reactant adsorption, mass uptake, and surface charge transfer behavior during ZnO and ZnO:Al atomic layer deposition. During ZnO ALD, conductance oscillations follow the ZnO ALD mass uptake cycle as the surface alternates between a basic (charged) zinc hydroxide surface, and a low energy (neutral) zinc–alkyl terminated surface, producing in charge transfer during species adsorption and reaction. Dopant introduction using one TMA/H_{2}O cycle in the DEZ/H_{2}O sequence decreases the extent of charge transfer and the total mass uptake, suggesting a correlation between the two mechanisms. We propose that the presence of more acidic Al–OH sites on the basic ZnO–H surface will decrease the net surface charge density, which diminishes the extent of charge transfer and conductance oscillation. Acid/base interactions
between the surface sites forming, for example, proton exchange complexes may also
decrease the availability of hydroxyl groups and account for the observed decrease in mass
uptake after dopant atom surface exposure. More exploration of relations between charge
transfer and surface mass uptake mechanisms, such as that shown here, will be helpful to
understand formation and function of a range of binary and doped materials, and will also be
important to evaluate low temperature formation of polar materials interfaces, including
organic/inorganic junctions.

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10.6 References


Chapter 11

Surface polarity Shielding and Hierarchical ZnO Nano-Architecture Engineering using Sequential Hydrothermal Crystal Synthesis and Thin Film Atomic Layer Deposition*

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*My contributions to this work include developing the sequential hydrothermal crystal synthesis and atomic layer deposition of Al₂O₃ and ZnO. I also performed all the microscopic and X-ray diffraction measurements and analysis of results. I took primary lead in writing the article and Dr. Gregory Parsons worked to modify the text. While Dr. Gregory Parsons helped in experimental design, I worked independently to conceptualize and initiate the experiments. The hydrothermal synthesis was performed initially by the help of Bo Gong.
11.1 Abstract

Engineered three dimensional nanoscale constructs are finding applications in many emerging fields, including energy generation and storage, advanced water and air purification and filtration strategies, as well as photocatalytic and bio-chemical separations systems. Progress in these important technologies will benefit from improved understanding of fundamental principles underlying nanostructure integration and bottom-up growth processes. While previous work has identified hydrothermal synthesis conditions to produce nanoscale ZnO rods, sheets and plates, strategies to systematically integrate these elements into more complex nano-architectures are not previously described. This article illustrates that amorphous nanoscale coatings formed by atomic layer deposition (ALD) are a viable means to modulate and screen the surface polarity of ZnO crystal faces, and thereby regulate the growth morphology during successive hydrothermal nano-crystal synthesis. Using this new strategy, this work demonstrates direct integration and sequential assembly of nano-crystalline rods and sheets, to produce complex three dimensional geometric forms, where structure evolution is achieved by modifying the surface growth condition, keeping the hydrothermal growth chemistry unchanged. Therefore, rational planning of seed layer and feature spacing geometries can allow researchers to engineer, at the nanoscale, complex three dimensional crystalline and semi-crystalline constructs for a wide range of future applications.
11.2 Introduction

Manipulating the growth of multi-dimensional nanostructures via bottom-up processes is important to advance fundamental understanding of nanomaterials and for engineering novel functional devices.\textsuperscript{1} Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 mV) and one of the most widely used and studied functional oxides. Zinc oxide readily forms into non-central symmetric wurtzite nanocrystal structures with self-polarized crystal surfaces. The thermodynamically stable crystallographic faces of ZnO include a polar-terminated (001) face and non-polar low-symmetry (100) faces.\textsuperscript{2} The low symmetry surfaces are more stable than the polar face, leading to faster growth along the polar surface. As a result, a variety of one-dimensional (1D) ZnO nanostructures including nanorods/nanowires, nanobelts, nanorings, and other hierarchical nanostructures can be readily synthesized, and these materials have been examined for applications in photovoltaic energy conversion, optics, optoelectronics, catalysis and piezoelectric systems.\textsuperscript{3-9} In addition, two-dimensional (2D) ZnO nanowalls, nanosheets and nanoplates have also attracted attention due to their nanometer-scale thickness, high surface-to-volume ratio and interesting optical and photocatalytic properties for applications in energy storage and conversion, electronic memory, and as chemical sensing elements.\textsuperscript{10} Primary routes for 2D ZnO nanostructure synthesis include vapor-liquid-solid (VLS) growth and metal-organic chemical vapor deposition (MOCVD) at relatively high temperatures (400–800 °C).\textsuperscript{10-15} A smaller number of researchers have also reported the formation of 2D ZnO nanostructures using solution-based hydrothermal or chemical bath
methods.\textsuperscript{16, 18-21} These methods are appealing because they proceed at low processing temperature (<100 °C), and allow for low cost and ready extension to large scale fabrication.\textsuperscript{17}

Previously, the morphology of 2D ZnO nanostructures has been controlled to some extent by adjusting the solution growth conditions, including pH, precursor concentration and temperature.\textsuperscript{18-21} For example, in aqueous processing under strong alkaline conditions (i.e., low Zn\textsuperscript{2+}/OH\textsuperscript{-} ratio) excess OH\textsuperscript{-} ions adsorb and inhibit growth on the positively charged (001) surface, promoting a morphology transition. Due to the inherent crystalline surface polarity, and the related thermodynamic restriction of ZnO growth, controlling the morphology of solution-based synthesis of ZnO nanostructures remains an important challenge in materials synthesis. New schemes to influence surface polarity and crystal nucleation will promote new methods and applications for low temperature solution-based materials synthesis.

In this article, we establish that amorphous nanoscale coatings formed by atomic layer deposition (ALD) are a viable means to modulate and screen the surface polarity of ZnO crystal faces, and thereby regulate the growth morphology during successive hydrothermal process steps. Atomic layer deposition proceeds through sequential exposures of a sample surface to a binary sequence of self-limiting surface reactions. On a reactive surface, when a monolayer-scale self-limiting heterogeneous surface reaction “A” is followed by another self-limiting reaction “B”, a uniform monolayer of product is formed. Repeating the A/B reaction sequence allows the product to be deposited conformally and uniformly over the entire available reactive surface. Many atomic layer deposition processes, including
those for Al₂O₃ and ZnO utilized in this work, are readily extendable to large-scale using temperatures less than ~150 °C.²²⁻²⁷ For Al₂O₃ ALD, the A/B reaction cycle consists of alternate exposures of trimethyl aluminum and water vapor at 125 °C, separated by Ar purge. Zinc oxide ALD is performed under similar conditions, with an A/B sequence of diethylzinc and water vapor.

In addition to surface charge screening, we show that highly conformal atomic layer deposition of polycrystalline ZnO can promote uniform nucleation during hydrothermal ZnO deposition, allowing hierarchical morphology evolution of 1D ZnO nanorods, 2D nanosheets (NSs) and complex three-dimensional ZnO nanosheet/nanorod constructs. For this work, the hydrothermal growth is performed under fixed conditions without changing pH or precursor concentration. The morphology control is fully enabled, therefore, by adjusting composition and thickness of the screening and nucleation layers formed using ALD. Specifically, covering hydrothermal ZnO nanorods with a bi-layer ALD nano-coating of amorphous Al₂O₃ followed by ZnO (denoted as Al₂O₃ + ZnO), enables facile screening of the polar surface of ZnO NRs and isotropic film growth during subsequent ZnO ALD.

Work shown here employs a multi-step synthesis of ZnO nanostructure, using sequential ALD and hydrothermal ZnO growth. The first hydrothermal growth produces ZnO NRs on the ZnO ALD-coated Si substrates. Then, ZnO or Al₂O₃+ZnO ALD coating is performed to tune the surface polarity of the 1st ZnO NRs, and a 2nd ZnO hydrothermal step is performed. The 2nd ZnO crystal synthesis process results in dramatic crystal morphology evolution that depends strongly on the substrate shielding, which is determined by the thickness of the aluminum oxide ALD layer. The substrate feature spacing, which is also
tuned by ALD, is also shown to have a notable influence on the resulting morphology. Mechanisms to account for the observed morphology evolution are proposed, and an effective “phase space” diagram is developed to organize and coordinate the resulting nano-structures. We further demonstrate the flexibility of the combined ALD and hydrothermal synthesis approach by systematical assembly of complex hierarchical nano-architectures, built up using sequential nanosheet on nanorod, and nanorod on nanosheet construction.

11.3 Experimental methods

Atomic Layer Deposition of ZnO and Al$_2$O$_3$ Films. Atomic layer deposition of ZnO and Al$_2$O$_3$ was performed using diethylzinc (DEZ, Zn(CH$_2$CH$_3$)$_2$), trimethylaluminum (TMA, Al(CH$_3$)$_3$), and deionized water (H$_2$O) as Zn, Al and oxidant precursors, respectively. Argon was used as a carrier and purge gas. The deposition was carried out in a custom made hot-wall two-inch diameter flow-tube reactor. Diethyl zinc and trimethyl aluminum were obtained from STREM Chemicals and used as received. The growth temperature was set at 125 °C and the operating pressure was maintained at 2 Torr with a total gas flow rate of 100 standard cubic centimeters per minute. Using in-line gas flow metering valves, the pressure increase during each precursor exposure was set at ~0.1 Torr during a typical 1 second exposure time. During ALD of Al$_2$O$_3$ (or ZnO), the TMA (or DEZ) and H$_2$O reactive precursor gases are injected into the ALD reactor in an ABAB… exposure sequence. When ZnO ALD is used alone to form nucleation layers on planar surfaces, a reaction cycle consists of 1s long precursor exposure and 20s long Ar purge. When ALD ZnO or
Al$_2$O$_3$+ZnO is formed on more complex surface structures, a longer process time is used with 2s long precursor exposure and 40s long Ar purge during each cycle, to more fully infiltrate the precursors into the ZnO nanostructures.

**Hydrothermal Growth of ZnO nanostructures.** After coating silicon substrates by ZnO or Al$_2$O$_3$+ZnO ALD, hydrothermal growth of ZnO nanorods or nanosheets was performed by suspending the sample upside-down in a teflon beaker filled with an equimolar aqueous solution (20mM) of zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O, Fluka, 99.0% purity] and hexamethylenetetramine (HMT) [C$_6$H$_{12}$N$_4$, Fluka, 99.0 % purity]. Before introducing the substrate into the growth solution, the teflon beaker containing the precursor solution was maintained in a laboratory oven at 80 °C for 1h to reduce the density of free-floating ZnO nanoparticulates. The substrate was then placed in the heated solution and held at the same temperature for 6 h. At the end of the growth period, the sample was removed from the solution, then immediately rinsed with deionized water to remove any residual salt from the surface. Finally, the sample was dried naturally in laboratory air at room temperature. The hydrothermal synthesis conditions used in this study were fixed for all growth steps. The morphologies observed, therefore, were related only to the changes in the substrate surface produced by the various ALD conditions studied.

**Characterization of ZnO Nanostructures.** After deposition of a ZnO seed layer by ALD on a planar silicon substrate, the film thickness was measured using Auto EL ellipsometer (Rudolph Tech.) at an angle of incidence $\Phi = 70^\circ$ and a wavelength $\lambda = 632.8$ nm. The morphology and chemical composition of the hydrothermal and ALD ZnO
nanostructures were characterized using a field emission scanning electron microscope (FESEM, JEOL 6400F) coupled with an energy dispersive x-ray spectroscopy (EDS) at 5 kV and 20 kV, respectively. Also high resolution transmission electron microscopy (TEM) images of ZnO NRs were collected with a Hitachi HF 2000 TEM at 200 kV. The crystal structures were determined by x-ray diffraction (XRD, Bruker AXS) with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ nm}\)).

11.4 Results and discussion

First Hydrothermal Growth of ZnO Nanorods (NRs) on ZnO ALD Surfaces.

Figure 11.1 shows typical FESEM and HRTEM images of ZnO NRs synthesized by hydrothermal growth on planar ALD ZnO formed on silicon substrates. For all samples studied on planar surfaces, the ZnO seed layer is formed at 125 °C using 60 A/B reaction cycles, resulting in \(~\)11 nm of deposited film, close to the expected deposition rate of 0.18 nm/cycle.\(^{25}\) It can be seen in Figure 11.1a that ZnO NRs are well aligned vertically with an average diameter of \(~\)27 nm and a length of \(~\)450 nm, leading to an aspect ratio (length/diameter) of \(~\)17. Figure 11.1b displays a HRTEM image of the lattice spacing between adjacent lattice planes in the resulting ZnO nanorods. The d-spacing of the (0001) planes is 0.26 nm, confirming anisotropic hydrothermal growth of crystalline ZnO NRs in a c-axis orientation. Nanorods grown on ALD ZnO seed layers appear equivalent to those deposited on seeds formed by sol-gel, sputtering or pulsed laser deposition.\(^{28-30}\) This demonstrates that the ALD method provides good quality seed layers at low temperature for
hydrothermal ZnO nanorod synthesis. Moreover, as presented below, ALD provides additional unique capability for seed layers that are highly conformal with uniform thickness, facilitating hydrothermal growth initiation on highly complex surface structures.

Figure 11.1  (a) FESEM image (60° tilt view) of 1st ZnO NRs grown on a ZnO ALD-coated Si substrate using hydrothermal method. (b) High resolution TEM image of the 1st ZnO NR shown in (a).
**Al₂O₃ and ZnO ALD on ZnO Nanorods.** Field emission SEM images of ZnO nanorod samples coated with: (a) ALD ZnO (300 cycles); and (b) ALD Al₂O₃ (20 cycles) followed by ZnO (300 cycles) are presented in Figure 11.2. Protuberances larger than the original nanorods are observed after each process. After the ZnO coating step, the features maintain a hexagonal-shape, whereas the Al₂O₃ + ZnO sequence results in features that are more spherical in shape. The EDS results that accompany the FESEM data in Figure 11.2 show the surfaces have the expected composition of Zn and O, or Zn, O, and Al.

Figure 11.3 presents x-ray diffraction (XRD) results obtained from the samples shown in Figure 11.2. The diffraction peaks positioned at \(2\theta = 31.77^\circ, 34.42^\circ, \text{ and } 36.25^\circ\) are indexed to the hexagonal wurtzite phase of ZnO (JCPDS card no. 36-1451). Figure 11.3a shows the sample after ZnO NR growth, and XRD exhibits a strong alignment toward the (002) orientation, consistent with data in Figure 11.1b showing ZnO preferential growth along the c-axis. The NR sample coated with 300 A/B cycles of ZnO shows a dramatic ~3× increase in the (002) reflection, indicating continued anisotropic crystal growth. The NR sample coated with Al₂O₃ + ZnO (20 + 300 A/B cycles) show new peaks associated with (100) and (101) planes, consistent with nonpolar surface orientation. Furthermore, as shown in Figure 11.3b, after 20 cycles of Al₂O₃ deposition, increasing the ZnO layer thickness from 100 to 300 cycles has a minimal effect on the (002) peak intensity, whereas the (100) and (101) peak intensities both increase, again consistent with non-preferential ZnO film growth.

The data presented in Figures 11.2 and 11.3 indicate that deposition of a very thin (~2 nm) amorphous Al₂O₃ layer disrupts the crystalline continuity of the subsequent ZnO ALD. This thin amorphous layer appears to be sufficiently uniform and conformal to effectively
screen the inherent surface polarity of the ZnO NRs and hinder the crystalline registry during the next ZnO deposition step.

**Figure 11.2** FESEM images (60° tilt view) and selective area EDS analysis for samples coated with (a) ZnO (300 cycles) and (b) Al₂O₃+ZnO (20+300 cycles) onto the 1st ZnO NRs.
Figure 11.3  XRD spectra of samples with ZnO or Al\textsubscript{2}O\textsubscript{3}+ZnO ALD coating onto the 1\textsuperscript{st} ZnO NRs. (a) The effect of the presence of intermediate amorphous Al\textsubscript{2}O\textsubscript{3} layer on the crystallinity of subsequent ZnO films on the 1\textsuperscript{st} ZnO NRs. The inset drawing shows the typical crystal structure of ZnO. (b) The effect of intermediate Al\textsubscript{2}O\textsubscript{3} layer on the lateral growth of subsequent ZnO films on the 1\textsuperscript{st} ZnO NRs.

Furthermore, field emission SEM results in Figure 11.4 demonstrate that the Al\textsubscript{2}O\textsubscript{3} + ZnO ALD bi-layer step results in lateral film growth, producing larger diameter rods that are more closely packed. The diameter of the rods scales with ALD film thickness. The average diameter increases from ~75 nm (Figure 11.4a) to ~150 nm (Figure 11.4d) as the ZnO ALD cycles increase from 100 to 300, consistent with a growth rate of ~0.18 nm/cycle during the ZnO ALD. The image in Figure 11.4d shows the nanorods merged into a near fully-covered surface.
Figure 11.4  FESEM images (top views) of samples obtained from different ALD coating on the 1st ZnO NRs with (a) Al₂O₃+ZnO (20+100 cycles), (b) Al₂O₃+ZnO (100+100 cycles), (c) Al₂O₃+ZnO (200+100 cycles) and (d) Al₂O₃+ZnO (20+300 cycles). The scale bar denotes 500 nm.
Second ZnO Hydrothermal Growth and Morphology Evolution on ALD Al\textsubscript{2}O\textsubscript{3} + ZnO-coated NRs. Data presented above indicate that a ZnO ALD coating on ZnO nanorods allows the surface polarity to be maintained, whereas polarity is lost when an intermediate Al\textsubscript{2}O\textsubscript{3} layer is deposited onto the NRs before the ZnO ALD step. To understand the influence of surface structure on subsequent hydrothermal ZnO growth, a series of samples was prepared with Al\textsubscript{2}O\textsubscript{3} + ZnO ALD layers on ZnO nanorods, where the thickness of the intermediate Al\textsubscript{2}O\textsubscript{3} ALD layer was set at 0, 20, and 100 Al\textsubscript{2}O\textsubscript{3} A/B cycles. These samples were then used as substrates for a second ZnO hydrothermal growth step, under the same conditions as for the first growth on the planar ZnO surface. The results are summarized in Figure 11.5. The panels on the left show the surface before hydrothermal growth, consisting of Al\textsubscript{2}O\textsubscript{3} + ZnO = (a) 0 + 100 cycles; (d) 20 + 100 cycles; and (g) 100 + 100 cycles. The remaining panels display images of the corresponding surfaces after hydrothermal growth.

Considering the substrate sample with only ZnO ALD coating (panel 5a), the hydrothermal step (panel b and c) results in continued growth of 1D ZnO NRs, where the rods have a relatively large diameter and low density. The cross-section image in panel (c) shows the nanorod layer formed during the 2\textsuperscript{nd} hydrothermal step is thicker, but less dense, than the underlying NR layer from the 1\textsuperscript{st} hydrothermal step. The resulting morphology indicates that growth proceeds almost exclusively in the vertical direction, and that the NR substrate presents a smaller number of successful nucleation sites for the 2\textsuperscript{nd} hydrothermal growth, as compared to the planar ZnO used for the 1\textsuperscript{st} hydrothermal step.

For the sample substrate with Al\textsubscript{2}O\textsubscript{3} + ZnO = 20 + 100 cycles (panel 5d), results after hydrothermal growth in panels e and f show that the intermediate Al\textsubscript{2}O\textsubscript{3} layer has a dramatic
effect on the growth morphology. The surface shows two dimensional “nanosheets”, mixed with one-dimensional nanorods. We note that the nanorods are now directed more randomly than for the substrate without the Al₂O₃ layer, consistent with a different NR nucleation process in this case. The nanosheets (NSs) appear to have uniform thickness, and height similar to the longest NRs.

Further increasing the intermediate Al₂O₃ layer thickness continues to influence the ZnO hydrothermal growth morphology, as shown in panels 11.5h and i. Hydrothermal growth on the substrate with Al₂O₃ + ZnO = 100 + 100 cycles, results in uniform 2D ZnO nanosheets, with no evidence for nanorod growth. The nanosheets are nearly 5× taller than the nanowires (panel c) and nearly 3× taller than the previous nanosheets (panel f) grown under the same conditions.²⁰ The wall thickness of the ZnO nanosheets is ~ 20 nm, consistent with similar ZnO structures formed previously by Jing et al.¹² Results from EDS analysis (not shown) indicate the sample has the expected composition of Zn and O, with some Al present from the ALD layer. The three different nanostructure types displayed in Figure 11.5 were readily reproduced. Each type was replicated in separate experiments at least two different times, consistent with the expected reproducibility of atomic layer deposition.

X-ray diffraction results from the samples in Figure 11.5c, f, and i are shown in Figure 11.6. The sample without the Al₂O₃ interlayer shows a strong c-axis (002) reflection. The samples with an Al₂O₃ layer show a much smaller (002) reflection intensity, along with new small peaks associated with (100), (101) and (102) orientations.
Figure 11.5  FESEM images (top and cross-sectional views) of samples with morphology evolution from ZnO nanorods (NRs) to ZnO nanosheets (NSs). The left panels present the surface before the 2nd hydrothermal growth consisting of Al₂O₃ + ZnO =: (a) 0 + 100 cycles; (d) 20 + 100 cycles; and (g) 100 + 100 cycles. The remaining panels of (b)-(c), (e)-(f) and (h)-(i) display images of the corresponding surfaces after the 2nd hydrothermal growth.
Figure 11.6  XRD spectra of samples with Al$_2$O$_3$ + ZnO ALD and subsequent ZnO hydrothermal growth on the 1$^{st}$ ZnO NRs. With introduction of amorphous Al$_2$O$_3$ layer, the ZnO growth along the polar (002) orientation is remarkably suppressed and new peaks of (100), (101), and (102) are generated, which is consistent with results for only ALD coating on ZnO NRs (Figure 11.3).
Mechanisms to account for the observed results are now proposed, and are illustrated schematically in Figure 11.7. The sample with ZnO nanorods on planar ZnO, depicted in the upper left of Figure 11.7 (and in the FESEM image in Figure 11.1) is the starting surface for all subsequent samples. Coating these nanorods with 100 cycles (~18 nm) of ALD ZnO slightly reduces the spacing between the NRs, but does not disturb the surface polarity of the ZnO NRs, allowing NR growth to readily proceed during hydrothermal growth. Similar behavior was observed previously in the multi-step hydrothermal growth of ZnO NRs, where stepwise continuous growth of ZnO NRs was exhibited.31 As displayed in the second row in Figure 11.7, a thin Al₂O₃ layer on the starting ZnO NRs impedes, but does not completely eliminate ZnO NR nucleation. On this surface, random growth of ZnO nanorods proceeds, including vertical growth, and some horizontal growth in the small gaps on the surface. The random intersection of growing crystals produces a high density of grain boundaries, which can provide thermodynamically favorable sites for Zn precipitation.10 We hypothesize that these grain boundaries thereby act to facilitate nucleation of the observed 2D nanosheets. The third row in Figure 11.7 shows the effect of a thicker Al₂O₃ layer, with additional surface polarity shielding. In this case, isotropic ZnO growth dominates, more efficiently filling the space between surface NRs, allowing nanosheets to more rapidly nucleate and grow. The increase in layer thickness upon progression from nanorods to nanosheets reflects the decrease in layer density and the mass uptake limitation by precursor depletion and consumption in the hydrothermal process.20
Figure 11.7 Growth mechanisms of ZnO nanostructures proposed for the morphology evolution of 1D ZnO nanorods to 2D ZnO nanosheets, which is determined by shielding the inherent surface polarity through ZnO or Al$_2$O$_3$ + ZnO ALD coating onto the 1st ZnO NRs.
The proposed mechanism for the transition from nanorod to nanosheet growth indicates that the initial spacing of substrate features has a strong influence on the resulting growth morphology. Results in Figures 11.4 and 11.5 show that this spacing can be tuned using ALD processing. To examine the effect of feature spacing more explicitly, two extreme cases are studied, where the feature spacing is very large (Figure 11.8) and where the starting surface feature spacing is very small (Figure 11.9). Figure 11.8a shows the case for large separation of surface features, where a set of vertically aligned silicon nitride-coated carbon nanofibers, separated by spaces of ~5 micrometers, were grown by plasma enhanced chemical vapor deposition on an regular array of Ni catalyst particles. The resulting rods were then coated by ALD Al$_2$O$_3$ + ZnO (10 + 200 cycles). A magnified view of one fiber, with exposed cross section, is presented in Figure 11.8b, demonstrating the conformal Al$_2$O$_3$ + ZnO ALD coating. Similarly prepared substrates are shown in panels c and d in Figure 11.8, after exposure to ZnO hydrothermal deposition. ZnO nanorods grow uniformly over the entire substrate area, and are directed normal to the growth surface, along the planar substrate bottom, and along the vertical length of the rod. In this case, the features are far enough apart that adjacent fibers do not interact.

Figure 11.9 shows another case, where ZnO nanorods formed by hydrothermal growth (similar to those shown in Figure 11.1a) are further coated with a thick layer of Al$_2$O$_3$ + ZnO ALD (= 20 + 300 cycles) before being exposed to hydrothermal ZnO deposition. The net ALD film coating thickness is ~60 nm, which is comparable to the distance between the starting nanorods. After ALD, therefore, the spacing between the surface features is very small (see Figure 11.4d).
Figure 11.8  (a) FESEM images of Al$_2$O$_3$ + ZnO (10+200 cycles) ALD-coated vertically aligned carbon nanofibers, which are grown on the patterned Ni nucleation sites with a distance of ~5 $\mu$m. (b) Magnified image of a carbon nanofiber with exposed cross-section in (a). (c) Carbon nanofibers covered with vertically aligned ZnO NRs formed during hydrothermal growth on (a) sample. (d) Magnified image of a carbon fiber covered with ZnO NRs in (c).
Figure 11.9 FESEM images (top and 60° tilt views) of a sample with Al₂O₃ + ZnO ALD (20 + 300 cycles) and subsequent hydrothermal growth onto the 1st ZnO NRs.

ZnO + 1st HT + Al₂O₃ (20) + ZnO (300) + 2nd HT
When this surface is used as a substrate for hydrothermal deposition, any structural registry between the initial nanorods and the 2nd hydrothermal growth layer is lost, and new ZnO nanorods are formed. The final structure is closely analogous to that obtained for hydrothermal growth on planar ZnO ALD layers, shown in Figure 11.1.

Based on the results in Figures 11.8 and 11.9, the effect of starting surface geometry can be summarized in the proposed scheme shown in Figure 11.10. The gap distance between ZnO nanorods are classified as wide, narrow, or negligible. When the gap is wide, new ZnO NRs emanate normal to the growth surface, as shown in Figure 11.8. As the gap becomes narrow, but not zero, 2D ZnO nanosheets are formed (Figure 11.5). Finally, when the gap becomes negligible, new ZnO nanorods, structurally isolated from the starting nanorods, are formed on top of the merged surface (Figure 11.9). If no polarity shielding layer is present, the gap width is expected to have minimal effect; the 2nd hydrothermal step simply continues the growth of the vertical nanorods.

**Third ZnO Hydrothermal Growth: Nanorod Growth on Nanosheets.** The results presented above reveal that surface polarity and feature separation both contribute to the nanoscale morphology of ZnO features formed during hydrothermal synthesis. As a further demonstration of the versatility of the ALD process to alter surface polarity, samples comprised of 2D nanosheets (formed during the 2nd hydrothermal step) grown on dense nanorods (1st hydrothermal step) were treated to Al2O3 + ZnO (100 + 200 cycles) ALD coating. This ALD sequence will act to shield the underlying ZnO crystal structure, but provide a stable and uniform nucleation layer for a 3rd ZnO hydrothermal growth treatment.
Figure 11.10 Illustration of the proposed growth mechanism of the ZnO nanostructures demonstrating the substrate geometrical effect of $\text{Al}_2\text{O}_3 + \text{ZnO}$ ALD coated ZnO NRs on the ZnO morphology evolution during hydrothermal growth.
The hydrothermal process then resulted, as expected, in uniform growth of nanorods, normal to the nanosheet surfaces, over the entire exposed surface area. Images of the resulting hierarchical nanorod/nanosheet/nanorod structures are shown in Figure 11.11. The density and net length of the new nanorods are similar to the nanorods that grew during the 1st hydrothermal step. A higher resolution image of a fractured nanosheet covered with nanowires is shown in panel 11d. The thin ALD nucleation layer is visible conformally covering the nanosheet, with nanorods extending out from the nucleation layer surface. Atomic layer deposition is a unique approach for crystal surface polarity shielding and conformal hydrothermal nucleation layer formation, thereby permitting rational hierarchical integration of one dimensional nanorods, two dimensional nanosheets, and mixtures of nanosheets and nanorods, with significant complexity. Nanostructure evolution is thereby controlled by combining surface polarity transitions, surface feature spacing and crystal seed layer conformality. The complex nanostructured geometries demonstrated here can be collected and sorted into a practical “phase space” diagram, constructed using substrate feature spacing and effective polarity shielding as controllable parameters. The resulting “phase diagram” is shown in Figure 11.12. It shows, for example, that with little or no polarity shielding, a change in the feature spacing provides little change in the hydrothermal growth morphology, whereas morphology is highly sensitive to feature spacing under heavy polarity shielding conditions.
Figure 11.11 FESEM images of a sample with additional Al$_2$O$_3$+ZnO (100+200 cycles) ALD coating on ZnO nanosheets (Figure 11.5e and f) and subsequent hydrothermal growth. (a) A plane- and (c) titled-view SEM images of three-dimensional ZnO nanostructure with ZnO nanorods grown on ZnO nanosheets (NS). (b) and (d) are the magnified images corresponding to (a) and (c), respectively.
Figure 11.12 Schematic illustration of the phase diagram showing the dependence of ZnO nanostructures on the surface polarity shielding and surface feature spacing during ALD coating and subsequent ZnO hydrothermal growth on the 1st ZnO NRs.
11.5 Conclusions

The sequential application of atomic layer deposition of \( \text{Al}_2\text{O}_3 \) and ZnO, integrated with low temperature hydrothermal synthesis of ZnO nanocrystals enables hierarchical assembly of ZnO nanorods and nanosheets into complex three dimensional constructs. Atomic layer deposition of ultra-thin highly conformal amorphous aluminum oxide layers onto ZnO crystals interrupts surface polarity effects that commonly guide the preferential growth of favored crystal faces. The uniform and conformal atomic layer deposition of ZnO nucleation layers on complex surfaces then permits homogeneous nanocrystal growth using hydrothermal synthesis techniques.

Substrate surface polarity shielding and substrate nanostructure spacing are shown to be critical independent parameters that define if hydrothermal growth will result in nanocrystal enlargement, nanocrystal overgrowth, formation of nanosheets, or formation of combined nanosheet/nanopillared structures. A practical “phase” diagram is proposed to help guide the understanding of nanostructure formation and propagation. Using the tools of polarity shielding and substrate geometric patterning described here, rational planning of seed layer and feature spacing geometries can be envisioned to allow researchers to engineer, at the nanoscale, complex three dimensional crystalline and semi-crystalline constructs for a wide range of future applications, including energy conversion and storage, sensing, and advanced nanoencapsulation architectures.
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11.6 References


