ABSTRACT

QIN, QINGQUAN. Investigation of Mechanical Properties and Interfacial Mechanics of Crystalline Nanomaterials. (Under the direction of Dr. Yong Zhu).

Nanowires (NWs) and nanotubes (NTs) are critical building blocks of nanotechnologies. The operation and reliability of these nanomaterials based devices depend on their mechanical properties of the nanomaterials, which is therefore important to accurately measure the mechanical properties. Besides, the NW–substrate interfaces also play a critical role in both mechanical reliability and electrical performance of these nanodevices, especially when the size of the NW is small. In this thesis, we focus on the mechanical properties and interface mechanics of three important one dimensional (1D) nanomaterials: ZnO NWs, Ag NWs and Si NWs.

For the size effect study, this thesis presents a systematic experimental investigation on the elastic and failure properties of ZnO NWs under different loading modes: tension and buckling. Both tensile modulus (from tension) and bending modulus (from buckling) were found to increase as the NW diameter decreased from 80 to 20 nm. The elastic modulus also shows loading mode dependent; the bending modulus increases more rapidly than the tensile modulus. The tension experiments showed that fracture strain and strength of ZnO NWs increase as the NW diameter decrease. A resonance testing setup was developed to measure elastic modulus of ZnO NWs to confirm the loading mode dependent effect. A systematic study was conducted on the effect of clamping on resonance frequency and thus measured Young’s modulus of NWs via a combined experiment and simulation approach. A simple scaling law was provided as guidelines for future designs to accurate measure elastic modulus of a cantilevered NW using the resonance method.
This thesis reports the first quantitative measurement of a full spectrum of mechanical properties of five-fold twinned Ag NWs including Young’s modulus, yield strength and ultimate tensile strength. *In situ* tensile testing of Ag NWs with diameters between 34 and 130 nm was carried out inside a SEM. Young’s modulus, yield strength and ultimate tensile strength were found to all increased as the NW diameter decreased.

For the temperature effect study, a brief review on brittle-to-ductile transition (BDT) of silicon (Si) is presented. BDT temperature shows decreasing trend as size of the sample decrease. However, controversial results have been reported in terms of brittle or ductile behaviors for Si NWs at room temperature. A microelectromechanical systems (MEMS) thermal actuator (ETA) was designed to test NW without involving external heating. To circumvent undesired heating of the end effector, heat sink beams that can be co-fabricated with the thermal actuator were introduced. A combined modeling and experimental study was conducted to access the effect of such heat sink beams. Temperature distribution was measured and simulated using Raman scattering and multiphysics finite element method, respectively. Our results demonstrated that heat sink beams are effective in reducing the temperature of the thermal actuator. To get elevated temperature in a controllable fashion, a comb drive actuator was designed with separating actuation and heating mechanisms. Multiphysics finite element analysis (coupled electrical-thermal-mechanical) was used to optimize structure design and minimize undesired thermal loading/unloading. A Si NW with diameter of 50 nm was tested on the device under different temperatures. Stress strain curves at different temperatures revealed that plastic deformation occurs at temperature of 55 °C.

For interfacial mechanics, we report an experimental study on the friction between Ag and ZnO NW tips (ends) and a gold substrate. An innovative experimental method based
on column buckling theory was developed for the friction measurements. Direct measurements of the static friction force and interfacial shear strength between Si NWs and poly(dimethylsiloxane) (PDMS) is reported. The static friction and shear strength were found to increase rapidly and then decrease with the increasing ultraviolet/ozone (UVO) treatment of PDMS.
Investigation of Mechanical Properties and Interfacial Mechanics of Crystalline Nanomaterials

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Mechanical Engineering

Raleigh, North Carolina
2013

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DEDICATION

To my family
BIOGRAPHY

Qingquan Qin was born in Liuzhou, Guangxi, in the south of China. He graduated from Liuzhou Minzu High School in 2002 and started his college in Tsinghua University. He received his bachelor degree in engineering mechanics in 2006. He continued his study and research in Tsinghua University in the Institute of Nuclear and New Energy Technology, where he received his master degree in 2008 with research focus on increasing safety and reliability of protection bearing in a magnetic bearing system. In the following fall, he started his PhD program at NC State under the advisory of Dr. Yong Zhu. His PhD research focuses on mechanical properties characterization of one dimensional nanomaterials and interfacial mechanics between nanomaterials and substrates.
ACKNOWLEDGMENTS

First and foremost, I would like to express my sincere gratitude to my advisor Dr. Yong Zhu, who introduced me into the area of nanomechanics and nanotechnology, and shared with me his knowledge in this area. This work would not have been possible without his guidance and support.

I would like to thank my committee members, Dr. Fuh-Gwo Yuan, Dr. Mohammed A. Zikry and Dr. Yuntian Zhu for their insightful thoughts and suggestions on my research. The guidance and effort from all committee members are indispensible and greatly appreciated.

Many thanks to Dr. Wei Lu University of Michigan for providing Si NWs, Dr. Yi Gu at Washington State University for providing ZnO NWs, Dr. Zhong Lin Wang at Georgia Institute of Technology and Dr. Wiley at Duke for providing Ag NWs, Dr. Xiaoning Jiang at NCSU for providing piezoelectric sheet, AIF at NCSU and Oak Ridge National Lab for allowing me to use their instrument and providing technique support.

I would like to thank my colleagues in our research group, Dr. Feng Xu, Changhong Guan, Jing Ouyang, Dr. Tao Jiang, John Durham, Tzu-Hsuan Chang, Shanshan Yao and Amanda Myers. I am lucky to be in a lab with great people like you and I enjoyed the time with you all. Special thanks to Dr. Feng Xu, I am going to miss all the hard time and pleasant time we went through in the experiments we did together.

Last but not least, I would like to thank my family for their unconditional love and support. Thanks from the bottom of my heart to my wife, Li Wei. I could never have accomplished this without her.
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Chapter 1

Introduction

1.1 One Dimensional Nanomaterials

One dimensional (1D) nanostructures such as nanowires (NWs) and nanotubes (NTs) are critical building blocks of nanotechnologies.\textsuperscript{[1, 2]} They exhibit outstanding mechanical properties in addition to electrical, thermal and optical properties.\textsuperscript{[3-5]} As such, they have been demonstrated in a broad range of applications including flexible/stretchable electronics,\textsuperscript{[6]} nanosensors,\textsuperscript{[7]} nanoelectromechanical systems\textsuperscript{[8]} and nanoscale energy harvesting/storage.\textsuperscript{[9, 10]} The operation and reliability of these nanodevices depend on the mechanical properties of the nanomaterials. Therefore, it is important to accurately measure their mechanical properties, which is the key to gaining fundamental understanding of surface effects on these properties. Surface effects are dominant for these small volume materials. It has been reported that size dependent mechanical properties arise as the characteristic dimension approaches sub-100 nm.\textsuperscript{[11-13]} The activation volume of surface dislocation nucleation for these small volume materials is in the range of 1–10$b^3$, which is relatively small compared to that of bulk nucleation source. The small activation volume leads to sensitivity of temperature and strain rate.\textsuperscript{[14]}

In nanodevices, NWs are typically integrated to larger structures. The NW–substrate interfaces therefore play a critical role in both mechanical reliability and electrical performance of these nanodevices, especially when the size of the NW is small.\textsuperscript{[2, 15]} The
friction and shear strength of NW–substrate interfaces critically influence the electrical, mechanical performance and life time of NW-based nanodevices. Yet, very few reports on this subject are available in the literature because of the experimental challenges involved.

In this thesis, we focus on the mechanical properties of three important 1D nanomaterials: zinc oxide (ZnO) NWs, silver (Ag) NWs and silicon (Si) NWs. And emphasize on the size and temperature effects on the mechanical properties of these nanomaterials. We also present the interfacial mechanics study of these NWs.

1.1.1 Zinc oxide nanowires

ZnO is an important semiconducting and piezoelectric material with a large exciton binding energy and a wide band gap.\cite{16} ZnO NWs have found broad applications ranging from nanoelectromechanical systems (NEMS)\cite{17} to nanosensors\cite{18, 19} to nanogenerators.\cite{9, 20} 1D ZnO nanomaterials can be synthesized by different methods. Most of them are bottom-up methods like wet chemical method,\cite{21-23} chemical or physical vapor deposition,\cite{24-26} pulsed laser deposition and molecular beam epitaxy.\cite{27-29} There is also a top-down approach to fabricate ZnO nanostructures.\cite{30} Among these methods, ZnO nanostructures synthesized via vapor–liquid–solid growth mechanism can be well controlled on orientation, position, size, morphology and density.\cite{31} Figure 1.1 shows a schematic of this growth mechanism and several SEM images of ZnO NWs grown using this method.

ZnO NWs are among the most extensively characterized nanostructures. A number of methods have been developed for mechanical testing of ZnO NWs including resonance in scanning or transmission electron microscopes (SEM/TEM),\cite{11, 32} bending or contact
resonance using atomic force microscopy (AFM),\textsuperscript{33-35} uniaxial tension in SEM or TEM,\textsuperscript{13, 36} and nanoindentation.\textsuperscript{37} A Majority of the reported studies focused only on the elastic property (i.e., Young’s modulus) of ZnO NWs.

\textbf{Figure 1.1.} (a) Schematic showing the growth mechanism of ZnO NWs, (b) SEM image of ZnO NWs grown on Si (100) substrate, (c) SEM images of a patterned ZnO NWs network on Si substrate.\textsuperscript{31}
In Chapter 2, we used both tensile and buckling test techniques to investigate size effect on not only the elastic properties also fracture properties of ZnO NWs. An improved resonance method was developed to evaluate the accuracy of elastic modulus measurement. A general experimental guideline was introduced to measure true Young’s modulus of a cantilevered NW. The static friction measurement between ZnO NWs and gold substrate was performed in situ a SEM as described in Chapter 4.

1.1.2 Silver nanowires

Ag NW is an important class of metallic NWs because of its potential use as interconnects in view that bulk silver exhibits the highest electric and thermal conductivity among metals. Ag NWs have found broad applications in flexible/stretchable electronics as conductors or electrodes.\[^{38-41}\] Ag is also recognized for its unique optical properties. An interesting property of Ag NW is the surface plasmon resonance which refers to the collective oscillation of conduction electrons in resonance with incident radiation.\[^{42}\] The plasmonic properties of Ag NWs have been used in a wealth of applications including biosensing and plasmonic waveguiding.\[^{43}\]

Various methods have been developed to synthesize Ag NWs. For example, using various types of 1D structures, like channels in alumina or other membranes, to control the growth of anisotropic Ag particles.\[^{44}\] A CVD method has recently been developed to grow single crystal Ag NWs on sapphire substrate.\[^{45}\] Xia’s group has demonstrated a hot-solution approach based on the polyol process for the large-scale synthesis of silver NWs.\[^{46, 47}\] It has become the most commonly used method to synthesize Ag NWs. In this method, Ag NWs
are produced when AgNO$_3$ is reduced in the presence of the capping/directing agent poly(vinylpyrrolidone) (PVP) by ethylene glycol. Five-fold twinned Ag NWs were obtained by carefully controlling the synthesis conditions, including the temperature, the concentrations of AgNO$_3$ and PVP as well as the presence of trace contaminants such as iron and chloride ions. Figure 1.2 shows the images of Ag NWs synthesized by different methods.

![Figure 1.2](image)

**Figure 1.2.** (a) TEM image of Ag NWs within the framework of SBA-15,[48] (b) SEM image of Ag NWs synthesized by soft solution process.[47]

Previous experimental studies on mechanical properties of Ag NWs have focused on elasticity using testing methods such as three-point bending[49, 50] and nanoindentation.[51, 52] In Chapter 2, we used in situ tensile testing technique to quantitatively measure a full spectrum of mechanical properties of five-fold twinned Ag NWs, including Young’s modulus, yield strength, and ultimate tensile strength. In Chapter 4, we presented the static friction and shear strength measurement between Ag NWs and gold substrate.
1.1.3 Silicon nanowires

Si is an important material in semiconductor industry, in electronics and in some high-cost and high-efficiency photovoltaic applications. In the micrometer scale, single-crystal silicon is the most commonly used material in MEMS devices. In the nanometer scale, Si NWs are one of the key building blocks for nanoelectronic and nanoelectromechanical devices.\(^2\) They exhibit excellent mechanical,\(^4, 5\) electrical,\(^5\) and optical properties,\(^5, 4\) in addition to interesting multifunctional properties such as piezoresistivity\(^5, 5\) and thermoelectricity.\(^5, 6\)

Si NWs can be synthesized using top–down or bottom–up approach. Sequences of lithography and etching steps are used for top–down approach.\(^5, 7\) The most extensively explored approach for bottom–up synthesis of 1D nanomaterials is probably vapor–phase synthesis. VLS mechanism is the most successful mechanism among all vapor based methods to generate large quantities of NWs with single crystalline structure. Wagner & Ellis first used this process to produce micrometer-sized whiskers in the 1960s.\(^5, 8\) The diameter of grown NWs is largely determined by the size of catalyst particle,\(^5, 9\) and the length of NWs can be controlled by controlling growth time.\(^6, 0\) Lu and Lieber found that Si NWs with diameter larger than 20 nm grow primarily along \(<111>\) direction, whereas the NWs with smaller diameter could have three growth directions: \(<110>\), \(<112>\) and \(<111>\).\(^2, 6\) Figure 1.3 shows the growth process of a Si NW using VLS method.

Because of its economic importance and the availability of large dislocation-free single crystalline material from bulk to nanoscale, Si has been extensively studied as a model material for understanding the brittle-ductile transition behavior of solids. Controversial
results have been reported in terms of brittle or ductile for Si NWs at room temperature. In Chapter 3, we conducted in situ thermal-mechanical testing on a Si NW under different temperatures to study the temperature effect on mechanical properties. In Chapter 4, we studied the static friction and shear strength between Si NWs and PDMS substrate for different ultraviolet/ozone (UVO) treatment time.

Figure 1.3. (a) Schematic showing the growth mechanism of Si NW.\textsuperscript{[2]} (b) SEM image showing the grown Si NWs.\textsuperscript{[62]}
1.2 In situ SEM Mechanical Testing Techniques for One Dimensional Nanomaterials

As mentioned above, the emergence of 1D nanomaterials as building blocks in the development of novel nanoscale devices has increased the need for the characterization of their mechanical properties. The development of 1D nanomaterials fabrication methods, especially bottom-up synthesis method, provides high quality 1D nanomaterials with controllable growth direction and nanostructure for mechanical testing. Mechanical properties studies can also reveal insight into fundamental mechanisms of a material’s deformation and failure. Therefore, more and more projects have been initiated by the mechanics community to investigate nanoscale mechanical behaviors from both experimental and computational perspectives.

The major challenge of conducting quantitative mechanical testing on 1D nanomaterials comes from the size of the specimen under study. The characteristic size of the sample ranges from less than 10 nanometers to several hundred nanometers. This leads to extreme challenges in manipulation and positioning of the sample, which is one of the key steps in testing individual sample in nanoscale. The very small size of the sample also leads to challenges in precise stress and strain measurement.

In this section, we review recent advances in experimental techniques for mechanical testing on 1D nanomaterials, mainly focusing on in situ SEM testing technique. Because, in situ SEM technique allows real time observation of the sample and also can reach nanometer resolution. In addition, the size of SEM chamber and the availability of ports which connect
vacuum side and air side of the chamber provide great space for user to put in a customized testing setup and connect with outside control or measuring components. In situ SEM manipulation of 1D nanomaterials is also an important technique to prepare samples for in situ TEM mechanical testing, which has higher resolution but might introduce unexpected effects (e.g. temperature) due to high energy electrons and is more time consuming than in situ SEM technique. From the testing setup view point, we divide previously developed techniques into three categories: nanoindenter and AFM based technique, manipulator and sensor based technique and MEMS based technique.

### 1.2.1 Nanoindenter and AFM based technique

Nanoindenter is designed to do indentation experiments on the nanoscale level. It can continuously record contact load and position with a resolution of nano-newton and nanometer, respectively. It can perform both load and displacement control experiments. The elastic modulus and hardness of thin films have been widely studied using this technique. Nanoindentation has also been utilized to test 1D nanomaterials. Li reported elastic modulus and hardness of Ag NW for the first time by conducting indentation test on a NW with a diameter of 42 nm, as shown in Figure 1.4a. Lucas later did indentation test on a Ag NW and obtained not only the elastic properties but also plastic deformation information, as shown in Figure 1.4b.
AFM was originally designed to acquire surface topographical information by using a very sharp probe of a micro cantilever to scan the surface. Force interaction between probe and surface cause a deflection of the cantilever, and this deflection sensed by a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Figure 1.5 shows the basic principles of an AFM. AFM also has nanoscale force and displacement resolution, which make it a perfect candidate for mechanical testing of nanomaterials. AFM can be operated in several modes for the purpose of doing mechanical properties characterization. Lieber et al. performed bending tests on cantilevered NT using lateral force mode of an AFM, as shown in Figure 1.6a. Wu et al. also utilized lateral force mode of an AFM to perform three-point bending tests on Au and Ag NWs. These NWs were clamped by metal deposition over a prefabricated micro trench, as shown in Figure 1.6b. Similar three-point bending test were done by Yu et al. using contact mode of an AFM instead of lateral force.
Another method based on AFM that can be used for mechanical testing is the contact resonance method. For this method, the resonance frequency of the AFM cantilever changes before and after contact with a material. The frequency shift is determined by the contact geometry and elastic properties of the material under study. Stan et al. used this method to study the size dependent elastic properties of ZnO NWs, as shown in Figure 1.6c. With proper AFM cantilever and force-displacement mode, AFM can also be used to perform nanoindentation experiments on nanomaterials.

**Figure 1.5** Schematic of conventional AFM’s scanning.\(^{[64]}\)
Figure 1.6. Schematic shows the AFM used to perform (a) the bending test\textsuperscript{[63]} (b) three-point bending test\textsuperscript{[49]} and (c) contact resonance test on different nanomaterials.\textsuperscript{[33]}

The advantage of using a nanoindenter or AFM to do mechanical testing at the nanoscale is quite obvious; both of them have high resolution and reliability in force and displacement measurement. However, neither method is able to get real time observation of the sample, which is a major drawback of these two techniques. One solution is to combine nanoindenter or AFM with SEM or TEM considering the real time imaging capability of SEM or TEM.
Madenci et al. developed a customized AFM system that can be put inside the SEM chamber, as one can see from Figure 1.7. This technique enables real time imaging capability of an AFM system. However, the AFM cantilever still blocks at least half of the view of the NW while applying bending load to the wire, as one can see from Figure 1.7c, so it is difficult to obtain real time observation of the whole NW using this configuration.

![Figure 1.7](image_url)

**Figure 1.7.** (a) Schematic showing a customized AFM (2) mounting on SEM stage (3) inside a SEM chamber (1), (b) Image of the customized AFM, top view, (c) SEM image showing a nickel NW after bending test. Inset shows the broken NW.[65]

Combining an indenter with SEM will allow large field of view, more accurate positioning of the indenter and continuous observation of surface deformation during an indentation test. The large field of view and accurate positioning capability provide the
possibility to conduct indentation test on nanoscale features. One can correlate the observed
deformation behavior with the load-displacement curve to get more information on how the
material has deformed and failed. Rabe et al. presented a nanoindentation and nanoscratch
testing setup for use inside a SEM in 2004, as shown in Figure 1.8a.\cite{66} This nanoindenter is
operated at an inclined angle with respect to the SEM column, which allows real time
imaging of indentation process while simultaneously recording load-displacement data. In
situ SEM or TEM nanoindenter now is commercially available (e.g. PicoIndenter from
Hysitron, as shown in Figure 1.8b). Gu et al.\cite{67} used an in situ SEM nanoindenter from
Nanomechanis, Inc. to do compression tests on Platinum nanopillars. By combining the
nanoindenter with a MEMS device, Lou et al studied the mechanical properties of various
NWs.\cite{68-70}

Figure 1.8. (a) Schematic of SEM compatible nanoindentation/nanoscratch device.\cite{66} (b) Image of a commercial nanoindenter, PI 85 SEM PicoIndenter, from Hysitron.
1.2.2 Resonance technique

Resonance is a simple and widely used method to measure the Young’s modulus of NWs. Amplitude and resonance frequency of NWs can be measured by microscopy imaging. According to a simple beam theory, one can calculate the Young’s modulus of a cantilevered 1D nanomaterials.

Based on the exciting mechanism, resonance method can be divided into thermal resonance and electromechanical resonance. In thermal resonance, the tested structure is excited by thermal vibration. The vibration amplitude is related to geometry, temperature and modulus. Treacy et al. extracted the elastic modulus of carbon NTs using this method.\cite{71} A more commonly used resonance method is electromechanical resonance. The tested sample is excited by a nearby oscillating electric field or by vibrating the supported substrate (e.g. piezoelectric substrate) using an oscillating electric signal, as shown in Figure 1.9.\cite{72} By changing the frequency of applied voltage, the resonance frequency of the tested structure can be indentified based on real time SEM imaging. The elastic modulus of carbon NTs,\cite{73} boron NWs,\cite{74} ZnO NWs,\cite{11} silicon carbide NWs,\cite{75} tungsten oxide NWs,\cite{76} and gallium nitride NWs\cite{77} has been studied using this method.

The advantage of the resonance technique is its simplicity. However, this method is applicable for elastic modulus measurement only. In addition, using simple supported beam theory to calculate Young’s modulus, the uncertainty in boundary conditions could lead to considerable errors in the Young’s modulus. A recent study systematically investigates the effect of clamping on the resonance frequency and thus the Young’s modulus of ZnO NWs.\cite{72} A general guideline was provided for experimental design on the critical clamp size,
which is useful in accurate measurement of the Young’s modulus of 1D nanostructure using the resonance method.

**Figure 1.9.** (a) A carbon NT response to nearby oscillating electric field with different frequencies.\(^{[73]}\) (b) A resonance testing setup use AC signal to vibrate piezoelectric sheet.\(^{[72]}\)

### 1.2.3 Manipulator and sensor based technique

To conduct mechanical testing of 1D nanomaterials, one faces the challenges of selecting a suitable individual nanostructure from the source substrate, clamping the nanostructure and transferring it to desired destination. This process requires a series of manipulating motions. While electron microscopy provides real time imaging capability with nanometer resolution for manipulating, a manipulator or nanomanipulator is used to perform the series of motions to complete the manipulating process. A nanomanipulator based on multi-axes piezo actuation can operate in both coarse micrometer resolution mode and fine
nanometer resolution mode, which gives the manipulator a large travel range in three axes directions and accurate positioning capability when needed. A nanomanipulator is also a powerful tool to prepare samples for MEMS device based in situ SEM or TEM mechanical testing. Various nanomanipulators have been developed to serve this purpose. Ugarte et al.\textsuperscript{[78]} developed a nanomanipulator system with two probe tips that can operate inside a SEM. The system consists of three two-axis tables and can operate in both coarse mode and fine mode, with a travel range of 15 mm and step resolution of 0.8 nm, respectively. An image of this system is shown in Figure 1.10a. Zhu et al.\textsuperscript{[79]} developed a mechanical testing system mounted in a SEM, as shown in Figure 1.10b. They performed uniaxial tensile testing using this system to study diameter dependence of the elastic modulus in ZnO NWs. More and more nanomanipulators are now commercially available. A nanomanipulator from Klocke Nanotechnik has been widely used by many research groups to explore nanomechanics area.\textsuperscript{[53, 80, 81]} Li et al.\textsuperscript{[82]} used several nanomanipulators from Kleindiek Nanotechnik to form a multi-probe platform inside SEM to perform a more complex mechanical testing system.

The nanomanipulator could serve as a loading mechanism during mechanical testing. Besides the nanomanipulator, a force sensor is needed to form a complete mechanical testing system. Force sensors can measure how much force is applied to the sample. With the geometry of the sample known from SEM image characterization, one can calculate the applied stress. AFM cantilever is the most commonly used force sensor. Cantilevers with various spring constants are available on market and ready for use in different applications.

Calibrating the stiffness of the cantilever is a very important step before using it as a force sensor. Similar cantilevers may have different stiffnesses because the thickness of the
A cantilever is difficult to control to get repeatable stiffness, especially for cantilevers with complex shape or various coating materials. A lot of methods have been developed to calibrate the stiffness of AFM cantilevers, for example, (1) to compare with a cantilever with known stiffness;\textsuperscript{83} (2) to calibrate against the energy of thermal vibration\textsuperscript{84} and (3) to combine measurements of resonance frequency with physical dimensions and materials properties to calculate the stiffness.\textsuperscript{85, 86} With the stiffness known, one can easily calculate the force applied to the sample during a test by measuring the deflection of the cantilever. A series of SEM images can be taken to record the deflection at each loading step.

\textbf{Figure 1.10.} (a) Image of a two probes nanomanipulator system.\textsuperscript{78} (b) Image of mechanical testing system consists with the indicated parts.\textsuperscript{79}
To avoid taking a series of images to measure the applied force, other types of force sensors have been developed. For example, an AFM cantilever with integrated measuring system has been developed to use as a force sensor, as shown in Figure 1.11a. This kind of cantilever utilizes the piezoresistivity of Si. For piezoresistive materials, the resistance varies as a function of applied stress. Thus, on-chip electronic readout can be integrated with the cantilever. Roukes et al. demonstrated a self-sensing cantilever with attonewton-scale force resolution. Gianola et al. developed an in situ nanomechanical testing setup. A transducer based on a three-plate capacitor system is used for force and displacement measurements, as shown in Figure 1.11b. The transducer can move with a displacement range ± 15 μm and generate a force about 10 mN.

Figure 1.11. (a) Schematic shows an array of piezoresistive cantilever. (b) Image of mechanical testing system consists with a nanomanipulator and a nanomechanical transducer.
With the nanomanipulator and force sensor available in SEM chamber, the testing setup is ready to perform mechanical testing on nanomaterials. One example using this setup is the testing of multiwalled carbon NTs, as shown in Figure 1.12a.[90] A stiffer AFM cantilever with very sharp tip was mounted on a 5-axis nanomanipulation system to pick up and mount individual NT, and a soft cantilever was used as a force sensor. A NT was clamped to the tip of cantilever by electron beam induced deposition method. The tensile experiments revealed a “sword-in-sheath” failure mechanism on 19 tested NTs. Similar double cantilever configuration was used to test the mechanical properties of boron NWs[74] and tungsten disulphide (WS₂) NTs.[91] The rigid cantilever can be replaced with a metallic probe, which has a large stiffness and a small diameter at the very end. The metallic probe is a better candidate to manipulate 1D nanostructures because it has relative simple geometry over an AFM cantilever. This configuration is shown in Figure 1.12b.[53] The mechanical properties of Si NWs,[53] ZnO NWs,[79, 92] Cu whiskers,[93] Au NWs,[94] Ag NWs,[95] and WS₂ NTs[91] have been measured using this testing setup. The AFM cantilevers can also be replaced with self-sensing cantilevers or other force sensors.[89] In some cases, the AFM cantilever can serve as both manipulator probe and sensor. For example, Haque et al.[96] used an AFM cantilever to bend ZnO NWs, as shown in Figure 1.12c. By measuring the deflection of the cantilever and NW, they were able to calculate the elastic modulus of the NW. Zhu et al.[97] also use an AFM cantilever to bend ZnO NWs with a large range of diameter (85-542 nm). They were able to quantitatively measure the fracture strain, strength, and flexibility of ZnO NWs. Ahmad et al.[98] characterized the mechanical properties of individual yeast cells.
by using an AFM cantilever to press the cells and measuring the compression force and indentation depth.

Figure 1.12. (a) A multiwalled carbon NT mounted between two opposing AFM cantilevers, inset shows the zoom-in view of the NT.\textsuperscript{[90]} (b) Image of a ZnO NW being stretched between a tungsten probe and AFM cantilever.\textsuperscript{[53]} (c) Superimposed images from the in situ bending experiment of a ZnO NW.\textsuperscript{[96]}
The manipulator and force sensor based technique provides plenty of room for manipulation. This can save time in picking up and mounting the samples. The size of tested sample might be limited by the electron beam induced carbon deposition. This clamping mechanism might not apply to sample with a size over 200 nm. For SEM equipped with metal deposition source, electron beam induced metal deposition can overcome this limitation. Another drawback of this technique is that for most testing setups both stress and strain measurements are deduced from microscopic images, which limit the possibility of simultaneously measuring stress and strain. The size of this testing setup also limits the possibility of putting it into TEM for in situ TEM testing to get more accurate measurements or investigate deformation mechanism. One solution is to develop a microelectromechanical system (MEMS) device suitable for mechanical testing.

1.2.4 MEMS based technique

MEMS device has the advantage of sensing the load without taking images and possesses a size of several tens or several hundreds micrometers. Besides, MEMS device can achieve load and displacement measurements with resolution of nano-Newton and nanometer or better. It appears to be the most advanced alternative for conducting mechanical testing on nanomaterials. The fabrication of MEMS device uses traditional microfabrication techniques, which can create various geometries for mechanical testing purposes. A MEMS device for mechanical testing usually includes three parts: actuator, sensor, and sample testing region. Based on the difference in actuation mechanism, these MEMS devices can be divided into two categories: external load actuated MEMS device and electronic actuated MEMS device.
The external load actuated MEMS devices do not have integrated actuation mechanism. They only provide mechanical connections to an external load. External load is usually applied by a piezo-actuator to pull or push the MEMS device to generate a desirable mechanical motion on the sample testing part. Haque and Saif\textsuperscript{[99]} introduced such a MEMS device to characterize mechanical properties of thin film, as shown in Figure 1.13a. The rectangular shaped test chip has one pin hole on each end. The test chip can be glued to a piezo-actuator (Figure 1.13b) or mounted on two pins on a TEM straining stage (Figure 1.13c). Force measurement of this device still needed to image the deflection of force sensor beam, which is indicated by relative distance between markers A, B and fixed beam (shown in inset of Figure 1.13a). MEMS devices with similar actuation mechanisms have also been developed later by Saif\textsuperscript{[100, 101]} and Haque.\textsuperscript{[36]} These devices have extended capability to test 1D nanostructure by changing the configuration of sample mounting area.

**Figure 1.13.** (a) A tensile MEMS device with co-fabricated thin film sample. Image showing the device glued to (b) a piezo-actuator and (c) mounted on two pins of a TEM straining stage.\textsuperscript{[99]}
Lou\textsuperscript{[68]} developed a MEMS device to convert compressive force from a nanoindenter to pure tensile loading. A SEM image of this device with a nanoindenter tip is shown in Figure 1.14. In this setup, force measurement is recorded by the nanoindenter. By utilizing the push-to-pull design, this device is able to perform mechanical testing on different 1D nanomaterials.

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{figure1_14.png}
\caption{SEM image of a push-to-pull device and the tip of a nanoindenter. Arrows show the moving direction of the tip and device. Inset shows a high magnification view of a NW bridging the gap on shuttle.\textsuperscript{[68]}}
\end{figure}

For electronic actuated MEMS devices, thermal actuation and electrostatic force actuation are the most common used actuation mechanisms. These devices provide electrical connection to outside electric signal (e.g. current or voltage). In a thermal actuator, mechanical motion is generated by joule heating. Under actuation voltage or current, the temperature increases on the device, this leads to thermal expansion of the components. By
carefully designing the structure of the actuator, one can get controllable displacement output. Zhu and Espinosa\cite{81} developed a thermally actuated MEMS device, as shown in Figure 1.15, which consists of a V-shaped thermal actuator and a capacitor load sensor. To minimize temperature increase near specimen testing area, the design of heat sink beams is necessary in the thermal actuator.\cite{102, 103} By measuring the capacitance change of a series of capacitors, they demonstrated a load resolution of 12 nN for their system. Other research groups also developed similar V-shaped thermal actuators for mechanical testing purposes.\cite{104, 105} Guan and Zhu\cite{106} recently developed a Z-shaped thermal actuator, which share many features in common with the V-shaped thermal actuator, as shown in Figure 1.16. However, a Z-shaped thermal actuator offers certain advantages such as smaller feature size and larger displacement. They also offer a large range of stiffness and output force that is between those of the V-shaped actuators and comb drive actuators, which are actuated by electrostatic force.

![Figure 1.15. SEM image of a MEMS device for mechanical testing. The device includes a V-shaped thermal actuator, a load sensor, and specimen testing region.\cite{81}](image)

\cite{81}
In an electrostatic force actuator, the mechanical motion is generated by the electrostatic force between a movable part and fixed part when there is an electrical potential difference between these two parts. While the thermal actuator provides displacement control in the experiment, the electrostatic force actuator provides force control. An example of this kind of actuator is the comb drive actuator, as shown in Figure 1.17. Comb drive actuator is able to generate mechanical motion without involving temperature, which is an
advantage over the thermal actuator.\textsuperscript{[108]} However, due to relatively small force generated by each pair of comb, a large number of combs are needed. This leads to a relative larger in the size for comb drive actuator than thermal actuator.

Capacitive load sensing can measure force without taking image and has high resolution in force measurement. Therefore, it has been widely used in both thermal actuated and electrostatic force actuated MEMS mechanical testing devices as sensing mechanism. Other sensing mechanisms involving image analysis have also been developed.

New development in MEMS device for mechanical testing of 1D nanomaterials is being directed to involve not just stress field but also multi-physical effects in one experiment. 1D nanomaterials have a very high surface to volume ratio, which magnify the surface effects. Many nanomaterials show totally different behaviors as compared to their bulk counterpart. Kang and Saif\textsuperscript{[109]} recently conducted a bending experiment on top-down fabricated Si NW using a MEMS device. The MEMS device is able to get controllable temperature. They reported clear plastic deformation when temperature increased to 293 °C for a 720 nm Si NW.

Table 1.1 is a comparative summary of the loading mode, capabilities, actuation and sensing mechanism, force and displacement resolution, and brief comments of several techniques for in situ SEM mechanical testing of 1D nanomaterials.
Table 1.1. Summary of the loading mode, capabilities, actuation and sensing mechanism, force and displacement resolution, and brief comments of several techniques for in situ SEM mechanical testing of 1D nanomaterials. $E$: elastic modulus, $\sigma$: stress, $\varepsilon$: strain, $\sigma_f$: failure strength, $\sigma_y$: yield strength and $\varepsilon_f$: failure strain, AFMC: AFM cantilever.

<table>
<thead>
<tr>
<th>Testing technique</th>
<th>Loading mode</th>
<th>Capabilities</th>
<th>Actuator</th>
<th>Sensor</th>
<th>Force and displacement resolution</th>
<th>Notes</th>
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<tr>
<td>Nanoindenter based and AFM based technique</td>
<td>Compression</td>
<td>$E, \sigma, \varepsilon, \sigma_f, \varepsilon_f$</td>
<td>Piezoactuator</td>
<td>Transducer</td>
<td>$\leq 3 \text{nN}$, $\leq 0.01 \text{nm}$</td>
<td>High resolution in force and displacement; Challenge in real time observation</td>
</tr>
<tr>
<td></td>
<td>Bending</td>
<td>$E, \sigma_y$</td>
<td>Piezoactuator</td>
<td>AFMC and Photodiode</td>
<td>Depends on the selection of actuator and AFMC</td>
<td></td>
</tr>
<tr>
<td>Resonance technique</td>
<td>Bending</td>
<td>$E$</td>
<td>Thermal, Electrostatic, Piezoelectric</td>
<td>N/A</td>
<td>N/A</td>
<td>Simplicity and high yield but limit to $E$</td>
</tr>
<tr>
<td>Manipulator and sensor based technique</td>
<td>Tension</td>
<td>$E, \sigma, \varepsilon, \sigma_f, \varepsilon_f$</td>
<td>Manipulator (piezoactuator)</td>
<td>AFMC/image</td>
<td>Depends on the selection of actuator and AFMC (e.g. 5 nN)</td>
<td>Easy manipulation; testing setup is large in size</td>
</tr>
<tr>
<td></td>
<td>Compression</td>
<td>$E, \sigma, \varepsilon, \sigma_f, \varepsilon_f$</td>
<td></td>
<td></td>
<td>$\leq 3 \text{nN}$, $\leq 0.02 \text{nm}$</td>
<td>Medium yield</td>
</tr>
<tr>
<td>MEMS based technique</td>
<td>Tension</td>
<td>$E, \sigma, \varepsilon, \sigma_f, \varepsilon_f$</td>
<td>Thermal actuator</td>
<td>Fabricated structure with known stiffness combine with image or capacitive sensor</td>
<td>3 nN, 58 nm, 12 nN</td>
<td>Small size (suitable for in situ TEM); possible for multi fields testing</td>
</tr>
<tr>
<td></td>
<td>Compression</td>
<td>$E, \sigma, \varepsilon, \sigma_f, \varepsilon_f$</td>
<td>Electrostatic force (e.g. comb drive) actuator</td>
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Chapter 2

Size Dependent Effect

2.1 Size Dependent Mechanical Behaviors of ZnO Nanowires

2.1.1 Background

As an important semiconducting and piezoelectric material with a large exciton binding energy and a wide band gap\textsuperscript{[1]}, ZnO NWs have found broad applications ranging from nanoelectromechanical systems (NEMS)\textsuperscript{[2]} to nanosensors\textsuperscript{[3, 4]} to nanogenerators.\textsuperscript{[5, 6]} Mechanical properties of ZnO NWs, including both elasticity and fracture, are of critical relevance to the design and reliability of these devices. In many devices such as nanogenerators,\textsuperscript{[5, 6]} ZnO NWs undergo different mechanical loadings such as tension, bending or buckling, therefore it is important to study the effect of loading mode on their mechanical properties.

Mechanical characterization of individual NWs is important but challenging. A number of methods have been developed for mechanical testing of ZnO NWs including resonance in scanning or transmission electron microscopes (SEM/TEM),\textsuperscript{[7, 8]} bending or contact resonance using atomic force microscopy (AFM),\textsuperscript{[9-11]} uniaxial tension in SEM or TEM,\textsuperscript{[12, 13]} and nanoindentation.\textsuperscript{[14]} In particular, in situ SEM/TEM tensile testing of NWs enabled by microelectromechanical systems (MEMS) has attracted a lot of attention recently.\textsuperscript{[12, 15, 16]} However, the experimental results showed both scatter and inconsistency.\textsuperscript{[17]} Some researchers observed that the Young’s modulus increased with the decreasing NW
diameter,\textsuperscript{[7, 9, 12]} while others reported essentially no size dependence.\textsuperscript{[8, 10]} On the other hand, computational studies including continuum mechanics and molecular dynamics (MD) exhibited similar disagreement. Various mechanisms such as bulk nonlinear elasticity,\textsuperscript{[18, 19]} surface bond saturation,\textsuperscript{[20]} surface reconstruction,\textsuperscript{[3, 7, 12]} and others\textsuperscript{[21]} have been proposed to explain the elasticity size effects in ZnO NWs, yet few experiments have conclusively supported these mechanisms.

In addition to the experimental errors, one possible reason for the observed discrepancy between experimental measurements on the Young’s modulus of ZnO NWs is because different loading modes (bending, resonance, tension) have been used. Surface effects are expected to be more pronounced under flexural loading (i.e., bending or resonance) than under tension as surfaces carry the most stress in the former.\textsuperscript{[22, 23]} Therefore, it is important to quantitatively conduct experiments under different loading modes while keeping the remaining experimental conditions constant. The objectives are twofold: 1) to explain the large discrepancy in experimental results in the literature, and 2) to elucidate the underlying mechanism(s) for the size effects, i.e., the relative importance of the surface and the core of NWs, especially when integrated with computational studies. So far only one study compared the Young’s moduli of ZnO NWs under tension and resonance and found considerable difference in the size effects, albeit the very different setups/conditions in two experimental methods.\textsuperscript{[24]}

A majority of the reported studies focused only on the elastic property (i.e., Young’s modulus) of ZnO NWs; few studies investigated their fracture under tension or bending.\textsuperscript{[10, 11, 25, 26]} No work has been reported on the postbuckling behavior of ZnO NWs despite its
relevance to NEMS, nanogenerators and other applications. Furthermore, failure of ZnO NWs under different loading modes has not been compared.

In this thesis, we report size effects on the elasticity and fracture of ZnO NWs under tension and bending. Bending was imposed in the buckling tests. Both types of tests were conducted in situ in SEM using the same setup (a nanomanipulator probe as actuator and an AFM cantilever as load sensor). Both tensile modulus (from tension) and bending modulus (from buckling) were found to increase as the NW diameter decreased from 80 to 20 nm. The bending modulus increased more rapidly than the tensile modulus. The fracture strain and fracture strength under tension increased as the NW diameter decreased. ZnO NWs were found to sustain very large bending deformation during postbuckling.

2.1.2 Experimental Section

The NWs used in this study were synthesized by the vapor-liquid-solid method on Si/SiO₂ substrates with Au colloids as the catalysts. A mixture of ZnO (Alfa Aesar, 99.999%) and graphite (Alfa Aesar, 99.9995%) powders in a quartz boat was used as the Zn source. This quartz boat was heated to 950 °C by a local heater, and the generated Zn vapor was carried by a flow of Ar to the growth zone, where O₂ was injected to enable the NW growth. The temperature of the growth zone was held at 820 °C during the growth under a constant pressure of 7.5 Torr. After the growth (the duration of which was 30 min), the reactor was first pumped to the base pressure and then was cooled down under a flow of Ar.

All the tension and buckling tests were performed inside an SEM (JEOL 6400F). A picture of the SEM was shown in Figure 2.1a. A nanomanipulator (Klocke Nanotechnik,
Germany) with 1 nm resolution and 1 cm travel range in three orthogonal directions was put into the chamber of SEM, as shown in Figure 2.1b. The manipulator was used to pick up protruding NWs from the Si wafer following the procedure outlined in Zhu and Espinosa\cite{16} and to carry out the tension and buckling experiments. For the tension test, an AFM chip (ORC8-10, Veeco) with two silicon nitride cantilevers on one side was mounted on a sample holder. A detailed description of the experimental process for tension test can be found elsewhere.\cite{28} The buckling tests were carried out similarly, but the cantilever used in the buckling tests was much softer (OBL-10, Veeco) than that used in the tension tests. Figure 2.2a and b show the SEM images the cantilever used in buckling test. After the NW was clamped between the nanomanipulator tip and the AFM cantilever, the NW was continuously pushed until it passed the critical force for buckling. The postbuckling shape of the NW can be clearly seen. Similarly, the force and compression data were directly obtained from the images.

**Figure 2.1.** (a) Image of JEOL 6400F showing the mounting position of manipulator. (b) Schematic showing the manipulator being mounted inside a SEM chamber.
Figure 2.2. Low magnification (a) and high magnification (b) SEM image of the cantilever for buckling test.

The cantilever stiffness was calibrated using the Sader method.[29] The measured value was 0.70±0.05 and 0.018±0.002 N/m for the cantilevers in the tension and buckling tests, respectively. The loads on the NW were calculated from the cantilever deflections, which were obtained in the SEM images with reference to a stationary feature. The stationary feature is a neighboring cantilever on the same chip and is out of focus in the SEM images; see the Supplementary Material for more details. For tension tests, the cantilever deflection was measured in images with lower magnification, where a resolution of half pixel translated to 9.6 nm. Therefore the force resolution was 6.72±0.48 nN. For NWs with diameters ranging from 20 to 80 nm, the stress resolution ranged from 21.4 to 1.3 MPa. The NW elongation was measured in images with higher magnification (the image possesses 2000×1600 pixels and a NW typically spans 1500~1800 pixels in length). Therefore the strain resolution was about 0.03%. For buckling tests, the cantilever deflection and the axial
displacement of the NW were measured from the same images, possessing a resolution of half
pixel translated to 3.9 nm. The force resolution was 0.07±0.01 nN.

2.1.3 Results and Discussion

Figure 2.3a shows a SEM image of the ZnO NW sample on a silicon substrate. Figure
2.3b displays the TEM image of a ZnO NW with diameter around 30 nm. It can be seen that
the NW is not only straight but also uniform in diameter along the growth direction. The
corresponding selected area electron diffraction (SAED) pattern in Figure 2.3c and high
resolution TEM image in Figure 2.3d indicate that the wires are single-crystalline, with a
growth direction along the [0001] axis.

During the tensile test, a series of SEM images were taken to measure the both force
and the elongation of the NWs. A few typical images from a NW with diameter of 20 nm are
shown in Fig. 2.4a-c. It can be seen that two ends of the NW are clamped on the
nanomanipulator tip (left) and the AFM cantilever (right), respectively. Figure 2.4a is the
image prior to loading. Figure 2.4b and Figure 2.4c show the NW under the tensile loads of
2.13 and 3.05 μN, respectively.

The NW was tested in a few loading and unloading cycles until fracture, as shown in
Figure 2.4d. Figure 2.4e shows the stress-strain response of this NW. The Young’s modulus
was measured to be approximately 169 GPa, which is higher than the bulk value of ZnO in the
[0001] direction (~140 GPa).\cite{12} It can also be seen that the loading and unloading processes
followed almost the same path showing a linear elastic behavior. No residual plastic
deformation was observed when the NW was totally unloaded. This observation is
corroborated with the enlarged image of the broken end shown in Fig. 2.4f. The broken end appears flat and no obvious diameter reduction or necking can be seen. No NW slippage was observed at both ends, indicating the carbon deposition clamp was strong enough for testing ZnO NWs with diameters up to 80 nm.\textsuperscript{[28]} Tension tests of all the NWs at different diameters were conducted following the same procedure with multiple loading/unloading cycles and all the NWs showed linear elastic behavior.

![Image](image1.png)

**Figure 2.3.** (a) Typical SEM image of the ZnO NWs with diameter of 50 nm. (b) TEM image of a single ZnO NW. (c) The corresponding SAED pattern of the ZnO NW. (d) High-resolution TEM image of the NW.
Figure 2.4. (a-c) A series of SEM images taken during the tensile test for a NW with diameter of 20 nm. Inset of (a): high resolution SEM image of the NW for strain measurements. (d) SEM image showing that fracture occurs on the NW when the load was applied to a certain value. (e) A typical stress-strain response of the specimens with diameter of 20 nm under repeated loading and unloading. The errors for the stress and strain are ±0.72GPa and ±0.004, respectively. (f) Enlarged SEM image of the broken end of the NW on the probe tip.

In situ SEM buckling tests of ZnO NWs were conducted in a similar fashion.\textsuperscript{[30]} In order to make a comparison with the tensile tests, NWs with similar diameters were intentionally sought and used for the buckling tests. Figure 2.5a is a SEM image of a ZnO NW with diameter of 46 nm. Both ends of the NW were clamped by EBID. The buckling
process accompanied by the shape change of the NW under an incrementally increasing compressive load is displayed in Figure 2.5b-e. Figure 2.5b shows the straight NW prior to the compressive loading. When the force reached the critical value, the NW buckled, as can be seen from Figure 2.5c. Figure 2.5d and 2.5e show progressive, symmetric postbuckling deformation of the NW. The applied force versus the axial displacement of the NW is plotted in Figure 2.5f. Initially, the force increased rapidly with the axial displacement. When the force reached the critical force ($P_{cr}$) for buckling, the load-displacement curve became nearly flat. $P_{cr}$ was determined to be 62 nN in this case.

According to the Euler’s formula, the buckling force $P_{cr}$ of an ideal elastic column is given by

$$P_{cr} = \frac{\pi^2 EI}{L_e^2} \quad 2.1$$

where $E$ is the Young’s modulus and $I$ is the moment of inertia of ZnO NW. Assuming the cross section of the NW is a circular shape (will be explained later), $I$ can be expressed as $I = \pi R^4/4$, where $R$ is the radius of the NW. Note that in buckling tests, the Young’s modulus is a bending modulus, as it is a measure of the structural resistance to bending deformation following the buckling instability. The effective length $L_e = 0.5L$ for the fixed-fixed boundary condition as in our experiments, where $L$ is the actual length of the column. According to this analysis, the Young’s modulus of the NW shown in Fig. 3 was calculated to be 151 GPa.

Figure 2.5g shows the large deformation of a typical ZnO NW after buckling. It can be seen that the NW was remarkably flexible and did not break even after a loop was formed.
During the postbuckling, the bending strain is $\varepsilon = R/\rho$, where $\rho$ is the radius of the loop. The maximum tensile strain ($\varepsilon$) occurs on the convex surface and the maximum compressive strain ($-\varepsilon$) on the concave surface. It was found that the NWs with diameter around 20 nm did not break under the strain of ~11%; those with a diameter larger than 80 nm did not break under the strain of around 5%. It is noted that the NWs may bend out of plane, in which case the actual radius of curvature should be smaller than what appeared in the image. Therefore, the bending strain in this paper represents a lower bond. In addition, we were not able to break the NWs with smaller diameters even when the manipulator tip touched the AFM cantilever because of the formation of loops as shown in Figure 2.5g. Clearly these strain values are much larger than the failure strain of bulk ZnO (~1%).\cite{13} The excellent resilience is advantageous to their potential applications such as nanogenerators\cite{5} and NEMS oscillators.\cite{2} It is surprising to note that the maximum strain under bending is larger than that under tension for ZnO NWs with the same diameters. This observation warrants further experimental and numerical investigations to probe the effect of loading mode on fracture in addition to elasticity of NWs.

To study the size effects on the mechanical properties of ZnO NWs, 7 NWs were tested under tension tests and 7 NWs under buckling tests. All the NWs ranged from 20 to 80 nm in diameter. Figure 2.6a shows the calculated Young’s modulus values for all of the tested NWs as a function of size. The errors are mainly from the measurement of NW diameters. It is evident that the Young’s modulus of ZnO NWs from both tension and buckling tests show the stiffening trend, i.e., it increases with the decreasing diameter.
Figure 2.5. (a) A SEM image showing the buckling test for a NW with diameter of 46 nm. (b-e) A series of enlarged SEM images of the NW under the application of a continuously increasing compressive load. (f) The corresponding plot of the applied force versus the axial displacement of the NW. (g) A SEM image showing the large deformation of a NW with diameter of 50 nm after buckling.

However, our data also show a loading-mode-dependent size effects. The disparity in the Young’s moduli under different loading modes (tension vs. buckling here) becomes larger as the NW diameter decreases. When the NW diameters are around 80 nm, the Young’s moduli from both tension and buckling are close to the bulk modulus. However,
when the diameters decrease to 20 nm, the modulus values obtained from the tension tests are around 170 GPa, while those from the buckling tests are more than 200 GPa. It is clear that the Young’s modulus obtained from the buckling tests exhibits stronger size effects in comparison to the tension tests.

Several mechanisms have been proposed to explain the size effects in the elastic behavior of ZnO nanostructures, i.e., increase in the Young’s modulus with decrease in the NW diameter. Kulkarni et al.\textsuperscript{[18]} and Cao et al.\textsuperscript{[19]} predicted that the nonlinear elastic response of the NW core (interior) plays the major role in determining the elastic modulus of NWs. In contrast, Zhang and Huang\textsuperscript{[20]} found that the surface bond saturation resulting from an increased electron density rather than bulk nonlinear elastic effects may be responsible for the size effects. Recently, Agrawal et al.\textsuperscript{[12]}, through a combined experiment/simulation study, showed that elastic stiffening in ZnO NWs was caused by a decrease in surface interatomic spacing due to surface reconstruction, which was in agreement with Chen et al.\textsuperscript{[7]}

The observed size effects in Figure 2.6a can be useful in assessing the relative importance of the surface and the core elasticity. For NWs under bending including buckling and resonance, the surfaces carry the largest stress and strain; by contrast, NWs subjected to uniaxial tension undertake uniform stress across the cross section. The Young’s modulus measured in both loading conditions is in fact the average between the surface and the core. If the bulk nonlinear elasticity dominates the stiffening size effects (i.e., the core modulus is larger than the bulk value), then the average modulus of ZnO NWs measured in tension tests is larger than that obtained from bending tests; if the surface contributes the most to the size
Figure 2.6. (a) Young’s modulus versus diameter of ZnO NWs from both tension and buckling tests. The fitting curves from the core-surface model (solid) and the core-shell model (dash) are also plotted. Inset shows the schematic of both models. (b) Fracture strain and (c) fracture strength of ZnO NWs from tension tests.
effects (i.e., the surface modulus is larger than the bulk value), then the average modulus measured in bending tests is larger. Our experimental results clearly confirmed the latter; that is, the surface elasticity plays the major role in the stiffening size effects in ZnO NWs.

To further quantify the surface and core elasticity, our results were fitted to two existing models: core-surface model (or Miller-Shenoy model)[22] and core-shell model,[7] see the inset of Figure 2.6a. Again we assume the NW cross section is circular. The core-surface model is a continuum mechanics approach that embodies the surface effect.[31-33] The model essentially assumes that a NW consists of a core with elastic modulus $E_c$ and a surface (zero thickness) with so-called surface elastic modulus $S$ (unit is $Pa \cdot m$). Under tension, the measured (or effective) Young’s modulus $E$ is given by

$$E = E_c + 4 \frac{S}{D}$$

where $D$ is the diameter of the circular cross section.

Under bending,

$$E = E_c + 8 \frac{S}{D}$$

In the core-shell model, the NW consists of a core with elastic modulus $E_c$ and a shell with elastic modulus $E_s$. Under tension,

$$E = E_c [1 + 4 \left( \frac{E_s}{E_c} - 1 \right) \left( \frac{r_s}{D} - \frac{r_s^2}{D^2} \right)]$$

where $D$ is the outer diameter of the circular cross section and $r_s$ is the shell thickness.

Under bending,
\[ E = E_c [1 + 8 \left( \frac{E_s}{E_c} - 1 \right) \left( \frac{r_c}{D} - 3 \frac{r_s^2}{D^2} + 4 \frac{r_s^3}{D^3} - 2 \frac{r_s^4}{D^4} \right)] \]

2.5

The tensile results are prone to fewer errors than the buckling results; therefore, both models were fitted to the tensile data following Equation 2.2 and 2.4, then the fitting parameters were plugged into Equation 2.3 and 2.5 to compare with the bending data. In the core-surface model, it was found that the core elastic modulus \( E_c = 115 \text{GPa} \) and the surface elastic modulus \( S = 267 \text{Pa} \cdot m \); in the core-shell model, \( E_c = 114.7 \text{GPa} \), the shell elastic modulus \( E_s = 244.4 \text{GPa} \) and the shell thickness \( r_s = 2.42 \text{nm} \). The fitting curves are plotted in Figure 2.6a in addition to the experimental data. Both models offered excellent fitting to the tensile data, but slightly overestimated the buckling data. Additionally, both models agreed very well between each other. It is noted, however, that the obtained core elastic modulus is lower than the bulk value (140 GPa), which appears contradicting. In fact, the Young’s modulus of the core is not necessarily equal to the bulk value as a result of the surface stress.\[^{[33]}\] Recent MD simulations showed that a core and a shell with different Young’s moduli exist in ZnO NWs; the Young’s moduli of the core and of the shell are lower and higher than the bulk value, respectively.\[^{[12]}\] The elastic modulus varies continuously from the core to the surface as a result of energy minimization.\[^{[12, 24]}\] Both models used in our work are first-order approximations (assuming step-like modulus distribution in the core and the shell) that, at the least, explain our experimental results reasonably well. Numerical simulations are warranted to further explain the effect of loading modes.
One important remark is on the cross sectional shape of the ZnO NWs used in the data analysis as well as in the fitting process. It is known that the [0001]-oriented ZnO NWs possess hexagonal cross sections. In the case of an edge facing the electron beam, treating the cross section as a circle overestimates the cross sectional area and moment of inertia; in the case of a vertex facing the electron beam, such a treatment underestimates these quantities. In experiments, the NW cross sections could orient randomly relative to the electron beam. Therefore statistically speaking, it is reasonable to use circular cross sections for ZnO NWs and other types of NWs with similar cross sections. This treatment does not introduce systematic errors, but it does introduce random errors that contribute to the total experimental errors.

Figure 2.6b and 2.6c show the fracture strain and fracture strength versus diameter of the NWs from the tension tests. Both fracture strain and fracture strength were found to increase with the decrease of the NW diameter. These values were much higher than that of bulk ZnO, which is typically smaller than 1% \cite{13} and 200 MPa.\cite{34} Similar size effects on the fracture strain have been reported by Desai and Haque.\cite{13} However, their fracture strain was more than 10% for the NWs with diameters less than 300 nm; in our experiments, the largest fracture strain is about 6.1% for the smallest NW with a diameter of 20 nm. Atomistic simulations predicted a phase transformation from wurtzite structure to body centered-tetragonal structure with four-atom rings (BCT-4) for ZnO nanorods.\cite{35} But such a phase transformation was not observed in our experiments, which can be seen from the repeated linear elastic behavior during the loading-unloading process. Perhaps due to the presence of defects, the maximum fracture strain in our experiments is less than the strain value of 7.5%
at which phase transformation was predicted to occur.\cite{35} Our experimental observation is consistent with recent in situ TEM tensile experiments by Agrawal et al.\cite{26} For the fracture strength, our values ranging from 4.10 to 10.32 GPa are comparable to those obtained from bending experiments by Wen et al.\cite{10} These authors also found a similar diameter dependence on the fracture strength of ZnO NWs. One possible reason for the size effects on the fracture strain and strength from tension is due to the bond-length contraction of surface atoms in ZnO NWs as a result of surface reconstruction.\cite{12, 13, 21} The bond-length contraction results in strengthening of the bond. Hence the binding energy of surface atoms tend to be higher than that of bulk atoms. With the increasing surface-to-volume ratio at the nanoscale, this mechanism could lead to higher fracture strain and strength values.\cite{13} Certainly another possible reason is the defects in the NWs. For NWs with a smaller size, the number of defects is reduced, causing the increase of the fracture strain and strength.

2.1.4 Conclusions

In summary, we present an experimental approach to evaluate the elastic and failure properties of ZnO NWs under different loading modes. In situ SEM tension and buckling tests on single ZnO NWs along the polar direction [0001] were conducted. Both tensile modulus (from tension) and bending modulus (from buckling) were found to increase as the NW diameter decreased from 80 to 20 nm. The bending modulus increased more rapidly than the tensile modulus, which demonstrates that the elasticity size effects in ZnO NWs are mainly due to surface stiffening. Both core-surface model and core-shell model were used to fit the experimental data very well. The tension experiments also showed that fracture strain
and strength of ZnO NWs increased as the NW diameter decreased. In particular, the buckling test was demonstrated to be an effective method for evaluating the elastic modulus of individual NWs under bending stress. The buckling experiments showed that the maximum strain under bending was larger than that under tension for ZnO NWs with the same diameters. The excellent resilience of ZnO NWs is advantageous for their applications in NEMS, nanosensors and nanogenerators.

2.2 Measuring True Young’s Modulus of a Cantilevered Nanowires

2.2.1 Background

1D nanostructures such as NWs and NTs are critical building blocks of nanotechnologies. They exhibit outstanding mechanical properties in addition to electrical, thermal and optical properties. As such, they have been demonstrated in a broad range of applications including nanosensors, nanoelectromechanical systems and nanoscale energy harvesting/storage. It has been reported that size dependent mechanical properties arise as the characteristic dimension approaches sub-100 nm. Therefore, it is important to accurately measure their mechanical properties, which is key to gaining fundamental understanding of surface effects on such properties.

Mechanical testing of 1D nanostructures is challenging in spite of recent advances. Notable experimental methods include vibration/resonance, bending, tension, ...
and nanoindentation.[46] In the resonance test, amplitude and resonance frequency of NWs can be measured using microscopy imaging. Following a simple beam theory, Young’s modulus of NWs can be calculated. The uncertainty in boundary conditions could lead to considerable errors in the Young’s modulus. In the bending method, AFM is used to deflect a single NW and measure the load and displacement simultaneously. However, the AFM tip might slip from the NW in the single-clamped case while the induced axial force might cause a nonlinear effect that is typically not considered in data reduction in the double-clamped case. The uniaxial tensile test is the most straightforward method for mechanical characterization of bulk materials. MEMS have recently emerged as a promising tool for in situ electron microscopy tensile testing of NWs.[13, 15, 16] However, the tensile testing of NWs generally requires specific nanomanipulation and testing procedures, which could be laborious.

Resonance is a simple and widely used method to measure Young’s modulus of NWs. According to a simple beam theory, the $n$th mode resonance frequency of a single-clamped (cantilevered) beam is

$$f_n = \frac{\beta_n^2}{2\pi L^2} \sqrt{\frac{EI}{\rho A}}$$

where $E$ is the Young’s modulus, $I$ is the moment of inertia, $L$ is the beam length, $A$ is the cross-sectional area and $\rho$ is the beam density. The $\beta_n$ term is the eigenvalue from the characteristic equation: $\cos \beta_n \sin \beta_n + 1 = 0$; $\beta_0 = 1.875$, $\beta_1 = 4.694$ and $\beta_2 = 7.855$ correspond to the first three resonance modes for any cantilevered beam.[11] When the resonance frequency is measured, the Young’s modulus can be calculated according to Equation 2.6.
However, Equation 2.6 assumes the “fixed” boundary condition that requires zero displacement and slope at the “fixed” end. For NW testing, two methods are often used to attach NWs to a substrate. The first method is to grow NWs on top of a substrate.[7] In this case, it is reasonable to assume a “fixed” boundary condition. But this method is limited to those NWs that can be directly grown on the substrate; plus such type of NW growth is not trivial. The second method involves picking up a single NW (e.g., using a nanomanipulator), attaching it to a substrate and clamping it. One way to clamp a NW is EBID of residual hydrocarbon in a SEM chamber or intentionally introduced precursor gas. This method is general and can be applied to any NWs. But the clamping materials are compliant, which leads to a concern over whether the boundary condition can be assumed “fixed”.

In this thesis, we systematically investigate the effect of clamping on the resonance frequency and thus the Young’s modulus of ZnO NWs. The reasons to study ZnO NWs are that they are one of the most important functional NWs[12] and their mechanical properties have been relatively well understood.[7, 12, 40] In situ mechanical resonance tests of ZnO NWs were performed inside a SEM, where the NWs were clamped on a tungsten probe by EBID of hydrocarbon (available in the SEM chamber). EBID was repeated several times to deposit more clamping material on the same location; after each deposition the resonance frequency was measured. The resonance frequency increased with the clamp size initially but then gradually approached a constant value. Finite element analysis was carried out to simulate the effect of the clamp size on the NW resonance frequency, which agreed well with the experimental results. Both experiments and simulations showed that with sufficient clamp
material, the resonance frequency converges to that under the “fixed” boundary condition
(i.e., the “fixed” boundary condition is met).

2.2.2 Experimental Section

The ZnO NWs were synthesized by the vapor–liquid–solid method on Si/SiO$_2$
substrates with Au colloids as the catalysts.$^{[27]}$ The mechanical resonance tests were
performed inside an SEM (JEOL 6400F). A nanomanipulator (Klocke Nanotechnik,
Germany) with 1 nm resolution and 1 cm travel range in three orthogonal directions was used
to pick up protruding NWs from the Si substrate following the procedure outlined by Zhu
and Espinosa.$^{[16]}$ After a ZnO NW was clamped to the second tungsten probe on the
nanomanipulator using EBID of carbonaceous materials in the SEM chamber, the NW was
pulled away from the Si substrate, moved toward the first tungsten probe (glued to the
piezoelectric sheet). Using EBID again, the NW was clamped on the tip of the first probe,
and then the other clamp was broken off. This depends on the strength difference of the two
clamps; the clamp on the second probe is intentionally weaker than that on the first probe.
This strength difference was achieved by controlling the deposition time. Note that the
second probe broke off from the short end of the NW (Figure 2.7a). Subsequently, the
piezoelectric sheet was excited into mechanical vibration by applying an AC voltage of 0.5
V, which drove mechanical resonance in the attached NW (through the first probe). For
mechanically induced resonance of NWs, the frequency of the applied AC signal is the NW’s
resonance frequency. The case of electrically induced resonance could be more
complicated.$^{[47]}$ Around the resonance frequency of each NW, SEM images of the vibrating
NW were taken at a number of frequencies, from which the vibration amplitude was measured as a function of the frequency (Figure 2.8a). Then the resonance frequency can be determined from the amplitude-frequency plot.

2.2.3 Results and Discussion

Figure 2.7a shows a schematic of the experimental setup. A piezoelectric sheet was used to provide mechanical vibration. The piezoelectric sheet was glued to the SEM sample holder on one side and a tungsten probe was glued to the other side. NWs were later clamped on the tungsten probe for vibration tests. The ZnO NWs used in this work were uniform in diameter along the growth direction. Figure 2.7b shows a stationary ZnO NW with one end clamped on the tip of the first tungsten probe as mentioned above. Figure 2.7c shows the vibrated NW under resonance. The NWs were only vibrated at the fundamental harmonic mode.

The procedure to test the effect of clamping on the resonance frequency of ZnO NWs was as follows. First, SEM images around the resonance frequency of the initially clamped NW were taken (the resonance frequency was determined later). EBID was then used to deposit more carbonaceous material at the same clamp location. SEM images around the new resonance frequency were taken again. The process of depositing more material at the same clamp location and taking SEM images around the new resonance frequency was repeated several times.
Figure 2.7. (a) Schematic of the experimental setup. (b) SEM image of a stationary ZnO NW with one end clamped on the tip of the tungsten probe. (c) SEM image of the ZnO NW under resonance at the fundamental harmonic mode.

Figure 2.8a shows the amplitude–frequency characteristics of a NW after each deposition. Overall, five deposition times were used for this NW. The deposition line widths were 19, 25, 39, 65 and 79 nm, respectively. It can be seen that the resonance frequency increased after each additional deposition, but approached a constant value after the line width of 65 nm (Figure 2.8b). The SEM image in the inset of Figure 2.8b shows a representative line pattern of hydrocarbon (deposited by EBID). The length of the deposition (clamp) line was measured to be ~440 nm, which was kept the same in spite of changing the width. The line width increased after each deposition. The line width, not the line thickness, was measured from SEM images. To systematically characterize the dimensions of the deposition lines, hydrocarbon was deposited on a polished tungsten foil (similar to the tungsten probe). On the tungsten foil, SEM and AFM (Park Systems, XE-70)
characterization can be conducted to measure the width and thickness of the same deposition line, respectively. The line thickness was found to increase with the line width; their relationship is shown in Figure 2.9.

**Figure 2.8.** (a) The amplitude–frequency characteristics of a NW after each deposition. The curves show the Lorentzian fits. (b) The resonance frequency of the NW as a function of the clamp width. The inset shows SEM image of the NW clamped by a line pattern (deposited by EBID).
Figure 2.9. (a) SEM image and (b) AFM image of a deposition line on polished tungsten substrate. (c) Line-scan profile of the AFM image in (b). (d) Thickness as a function of width for the deposition lines.

Finite element analysis (ABAQUS) was used to simulate the effect of deposition (clamp) on the resonance frequency. Figure 2.10 shows the configuration used in the simulation including the deposition line and the ZnO NW. A fixed boundary condition was applied to the bottom of the deposition line, and the NW was tied to the deposition line. 20-node quadratic brick elements (C3D20R) and 4-node linear tetrahedron elements (C3D4) were used for the NW and the deposition line, respectively. A numerical method, so-called linear perturbation step, available in ABAQUS, was used to extract the resonance frequencies. The dimensions of the deposition line used here were obtained from Figure 2.9d; the range of the line width was set to be from 10 to 83 nm while the corresponding thickness ranged from 28 to 117 nm. The cross section of the deposition line was a parabolic shape,
which was found to best fit the experimental results when compared to other shapes such as semicircle/rectangle and rectangle (see supporting information). The length of the deposition line was set to be 620 nm, the same as that in the experiments. The Young’s modulus of the deposited material was 40 GPa.\(^\text{[48]}\) The dimension of each NW was measured from experiments. The Young’s modulus of ZnO NWs has been found to depend on the NW diameter and loading mode (i.e., tension versus bending).\(^\text{[12, 24]}\) The Young’s moduli of NWs used in the simulation were taken from those under the same loading mode (i.e., resonance tests with NWs directly grown on a substrate).\(^\text{[7]}\)

![Figure 2.10](image.png)

**Figure 2.10.** 3-dimensional (3D) view of the configuration used in the simulation including the deposition line and the ZnO NW. The inset shows a magnified view of the middle part of the deposition line.

Three NWs were tested in our experiments and each NW underwent multiple depositions. The dimensions of these NWs are listed in Table 2.1. The length of each NW was measured from the middle of the deposition line to the vibrating end of the NW. The
Young’s moduli of the NWs corresponding to their diameters are also listed in the Table 2.1 (extrapolated from reference[7]). Using these values in the simulation, the resonance frequencies of these NWs with different clamp widths (and thus different thicknesses) were obtained. Both experimental and simulation results are summarized and plotted in Figure 4a, showing good agreement. The resonance frequency increased rapidly with the clamp width in the beginning and gradually approached a constant value.

**Table 2.1.** The dimensions of the NWs and the extrapolated Young’s moduli of the NWs corresponding to their diameters.

<table>
<thead>
<tr>
<th></th>
<th>NW1</th>
<th>NW2</th>
<th>NW3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>55</td>
<td>60</td>
<td>62</td>
</tr>
<tr>
<td>Length (µm)</td>
<td>7.14</td>
<td>7.04</td>
<td>6.73</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>173</td>
<td>168</td>
<td>167</td>
</tr>
</tbody>
</table>

However, the key question is not yet answered: is it acceptable to treat a clamped NW as the “fixed” boundary condition? To answer this question, we calculate the resonance frequencies with the Young’s moduli and our measured dimensions assuming the “fixed” boundary condition (*i.e.*, Equation 2.6), and compare them with the experimental and simulation results. ZnO NWs have hexagonal cross sections, so the resonance frequency at the fundamental harmonic mode can be written as

$$f_0 = \frac{\beta_0^2}{2\pi} \frac{D}{L^2} \sqrt\frac{5E}{96\rho}$$

where $D$ is the beam diameter (distance between two diametrically opposite vertices for a hexagon). The analytical results are also plotted in Figure 2.11a as dashed lines. Note that the
slight change in the resonance frequency is a result of the change in effective NW length (due to the increase in clamp width). The effective NW length (defined as the length from the closer edge of the deposition line to the free end of the NW) is used in the analytical calculation. Apparently, with the increase of clamp size, the discrepancy between the analytical calculation and experiment/simulation decreases. When the clamp width approaches 80 nm, the resonance frequencies from experiments and simulations are almost identical to that from the analytical calculation. Thus, it is reasonable to conclude that the “fixed” boundary condition is met when the clamp width reaches 80 nm or larger, for the ZnO NWs tested in this work (diameters between 55 and 62 nm).

Figure 2.11b plots the measured Young’s moduli of the three NWs as a function the clamp width, as calculated from the measured resonance frequencies using Equation 2.7. Note that the effective NW lengths are used in the calculation. For all the NWs, the Young’s moduli increase with the clamp size and approach the reported values.[7] This indicates that the errors in the Young’s modulus measurement from the resonance test can be minimized by increasing the deposition width. Two additional remarks are noted. First, when the clamp size is small, the resultant error in Young’s modulus can be as large as 13.4% (for instance, for NW1). The above analysis provides a rationale behind the low modulus values reported for ZnO nanobelts and NWs (also using the resonance test).[8, 49] Among other reasons, the low values might be caused by the imperfect boundary conditions, in which the nanostructures were barely attached to a gold ball or tungsten probe without deposition clamping. Second, the change in effective NW length causes a slight variation in the calculated resonance frequency (as shown in dashed lines in Figure 2.11a) and thus Young’s modulus. However,
the change in effective NW length is very small (40 nm versus a typical NW length of over 6 μm). According to Equation 2.7, the relative error is less than 2.6% for a measured resonance frequency, which might be negligible for most applications.

**Figure 2.11.** (a) Plots of the resonance frequencies of the three NWs versus clamp widths from the experiments, simulation and analytical calculation. In the analytical solution, since the effective NW length decreases with increasing clamp width, the resonance frequency increase slightly. (b) Young’s moduli of the three NWs as a function the clamp width, as calculated from the experimental resonance frequencies using the beam theory. The dash lines indicate the Young’s moduli of the NWs under “fixed” boundary condition.
To provide a design guideline for those who might use the EBID of hydrocarbon for clamping NWs, a parametric study was further pursued to illustrate the effects of clamp length, NW diameter and NW Young’s modulus. The clamp length does not play an important role as long as it exceeds about 4 times of the NW diameter. But the NW diameter and NW Young’s modulus play important roles, thus imposing stringent requirement on the clamp width to achieve the “fixed” boundary condition. Figure 2.12 shows the effect of the NW diameter on the resonance frequency (with a constant NW Young’s modulus of 168 GPa). For each NW diameter, the NW resonance frequency increases with the clamp width. The critical clamp width, above which the “fixed” boundary condition is reached, appears to be approximately equal to the NW diameter. Figure 2.13 shows the effect of the NW Young’s modulus on the resonance frequency (with a constant NW diameter of 60 nm). For each Young’s modulus, the resonance frequency increases with the clamp width. The critical clamp width appears to increase linearly with the resonance frequency under the “fixed” boundary condition (i.e., square root of the NW Young’s modulus according to Equation 2.6. Note that the critical width is defined as the width when the difference between the calculated (dashed line) and simulated (dots) resonance frequency of a NW is less than 1% in Figure 2.12. It is of additional note that the aspect ratio of NW (NW length over diameter) does not play an important role in determining critical clamp width as long as the ratio is larger than 40.

It becomes clear that the critical clamp width depends on the NW diameter and the NW Young’s modulus. Figure 2.14 plots the critical clamp width as a function of the NW
diameter and the NW Young’s modulus. A plane fitting was applied to the data, and a simple scaling law was extracted from Figure 2.14, viz.,

\[ w_{cr} = \alpha D \left( \frac{E}{E_{hc}} \right)^n \]  \hspace{1cm} (2.8)

where \( w_{cr} \) is the critical clamp width, \( D \) is the NW diameter, \( E \) is the NW Young’s modulus, \( E_{hc} \) is the hydrocarbon Young’s modulus (= 40 GPa\[^{[48]}\]), \( \alpha \) is a constant (= 0.786 in this work) and \( n \) equal to 0.2. The coefficient of determination (\( R^2 \)) using this fitting function is 0.97, indicating that the function fits the data very well.

![Figure 2.12. Resonance frequency as a function of clamp width for NWs with different diameters (from 15 nm to 120 nm). A constant NW Young’s modulus (168 GPa) is used here. The dash lines indicate the resonance frequencies under “fixed” boundary condition.](image)
Figure 2.13. Resonance frequency as a function of clamp width for NWs with different Young’s modulus (from 20 GPa to 600 GPa). A constant NW diameter (60 nm) is used here. The dash lines indicate the resonance frequencies under “fixed” boundary condition.

Figure 2.14. The critical clamp width as functions of diameter and Young’s modulus of NW. The fitting plane shows $w_{cr} = \alpha D (E / E_{nc})^n$, with $\alpha = 0.786$ and $n = 0.2$. 
2.3.4 Conclusions

We have systematically investigated the effect of clamping on the resonance frequency and hence the measured Young’s modulus of cantilevered NWs by a combined experiment and simulation approach. The resonance tests were performed in situ inside a SEM with ZnO NWs clamped on tungsten probes by EBID of hydrocarbon. EBID was repeated several times to deposit more hydrocarbons at the same location and the resonance frequencies were measured after each deposition until a stable resonance frequency was obtained. Finite element analysis was carried out to simulate the clamping effect, which agreed well with the experimental results. Initially the resonance frequency increased rapidly with the clamp size. When the clamp width reached a critical value, the resonance frequency approached that under the “fixed” boundary condition. Further numerical simulations were performed to investigate the effect of NW diameter and Young’s modulus on the clamp size (including width and length), which led to a simple scaling law that can be used as guidelines for future designs. Our work demonstrates that true Young’s modulus can be measured if the critical clamp size is reached. Also in calculating the Young’s modulus, it is acceptable to use the nominal NW length (from the center of the clamp to the vibrating end of the NW) instead of the effective NW length. Our work provides design guidelines on the critical clamp size, which is useful in accurate measurement of the Young’s modulus of 1D nanostructures using the resonance method.
2.3 Size Dependent Mechanical Behaviors of Ag Nanowires

2.3.1 Background

Bulk Ag exhibits the highest electrical and thermal conductivity among metals. As such, Ag NWs are expected to be outstanding conductors in nanoscale electronic devices.\textsuperscript{50, 51} Of particular note is that flexible electronics based on nanomaterials has received much recent attention.\textsuperscript{52, 53} Ag NWs hold promising potential as flexible conductors such as interconnects and electrodes.\textsuperscript{54} In addition, Ag NWs exhibit an interesting optical property known as surface plasmon resonance, which occurs as a result of the coherent oscillation of the conduction electrons upon interaction with electromagnetic fields.\textsuperscript{55} The plasmonic properties of Ag NWs have been used in a wealth of applications including biosensing\textsuperscript{56} and plasmonic waveguiding.\textsuperscript{57} Axial strain or bending deformation has been found to significantly affect the surface plasmon resonance of Ag NWs.\textsuperscript{57, 58} From an engineering perspective, mechanical properties of Ag NWs play an important role in the functionality and reliability of the above device applications.

Previous experimental studies on mechanical properties of Ag NWs have focused on elasticity using testing methods such as three-point bending\textsuperscript{59, 60} and nanoindentation.\textsuperscript{46, 61} In spite of large data scattering, a stiffening trend (\textit{i.e.}, increase in Young’s modulus with decrease in NW diameter) was generally observed. However, rare (and only indirect) experimental measurements on the plasticity and failure of Ag NWs were reported.\textsuperscript{59, 61} Tensile testing is a direct experimental method to obtain a full spectrum of mechanical properties (including elasticity, plasticity and failure). Indeed, such a full spectrum of mechanical properties under tensile loading has been investigated by atomistic
Ag NWs to be studied in this work possess a well-defined five-fold twinned microstructure. Ag NWs thus provide a model system for studying the combined effects of sample dimensions and internal interfaces on the mechanical properties of nanomaterials.

In this thesis, we report quantitative stress-strain measurements of individual five-fold twinned Ag NWs (30 to 130 nm in diameter) using in situ tensile tests inside a SEM for the first time. In addition to the stiffening size effect in the Young’s modulus, we found that the yield strength and ultimate tensile strength (UTS) both increased as the NW diameter decreased. The maximum yield strength and UTS in our tests were 2.64 GPa (close to the theoretical strength of Ag in the <110> orientation) and 4.84 GPa, respectively. The size effect in the yield strength is attributed to the increase in the Young’s modulus. Yield strain scales reasonably well with the NW surface area, which reveals that yielding of Ag NWs is due to dislocation nucleation from surface sources. Pronounced strain hardening was observed for most NWs in our study. The strain hardening, which has not previously been observed for NWs, is mainly attributed to the presence of internal twin boundaries.

2.3.2 Experimental Section

Five-fold twinned Ag NWs were synthesized by reducing AgNO₃ with ethylene glycol (EG) in the presence of poly(vinyl pyrrolidone) (PVP). Five-fold twinned Ag NWs were obtained by carefully controlling the synthesis conditions, including the temperature, the concentrations of AgNO₃ and PVP, as well as the presence of trace contaminants such as iron and chloride ions. A detailed description of the NW synthesis process can be found elsewhere.[50] The solution of Ag NWs was diluted with deionized water (5 times by volume)
and then purified by centrifugation at 3000 rpm for about 20 minutes to remove PVP and other unwanted materials such as Ag nanoparticles. This washing step was repeated multiple times to obtain the desired results. Purified Ag NWs were dropped on a TEM grid and a clean silicon wafer for TEM observation and in situ SEM testing, respectively.

The TEM observation was carried out in JEOL 4000EX. Figure 2.15a shows a low magnification transmission electron microscopy (TEM) image of Ag NWs with diameters ~80 nm. The Ag NWs are straight and uniform in width, which is critical for the calculation of strain and stress. Typically Ag NWs synthesized by this method have a multiple twinned, pentagonal structure with smooth, faceted surfaces. The microstructure of five-fold twinned NWs is well documented. The selected area electron diffraction (SAED) pattern (Figure 2.15b) confirm that the NWs are grown in the <110> direction and contain five-fold twins parallel to their longitudinal axis; the five twin boundaries are along {111} planes and the five surface facets are along {100} planes. The NWs are elastically strained and might contain stacking faults and dislocations, especially at the core area of the NWs, since the five subunits cannot make 360° (i.e., the angle between two {111} planes is 70.52° and five subunits can only make 352.6°). Some diffraction spots (as arrowed in Figure 2.15b) are elongated, which is evidence of the elastic strain.

The tensile tests were performed using a recently-developed, in situ SEM nanomechanical testing setup. Force was applied using a nanomanipulator (Klocke Nanotechnik, Germany) on one side of the freestanding specimen, and was measured on the other side using an AFM cantilever. The specimen was clamped on the nanomanipulator tip and the AFM cantilever using electron beam induced deposition (EBID) of carbonaceous
materials in the SEM (Figure 2.15c).[16, 28] The drop cast method used to prepare the NW samples ensures the NWs are perpendicular to the electron beam, thus no out-of-plane rotation is coupled to the tension and the strain measurement should be accurate. A small in-plane rotation might occur during the tension process as a result of the deflection of the AFM cantilever. We carefully selected AFM cantilevers with relatively large stiffness to ensure such an in-plane rotation is negligible.[28] The specimen was then loaded in tension until failure to investigate the full spectrum of mechanical properties including elastic, plastic and failure properties. A series of SEM images were taken during the tension tests. Both force and elongation were measured from the images and converted to stress and strain, respectively. Force was obtained by multiplying the force sensor’s (AFM cantilever’s) displacement by its calibrated stiffness. The resolution of the force sensor used in this study was 5.25 ± 0.38 nN. For NWs with diameters ranging from 34 to 130 nm, the stress resolution ranged from 5.78 to 0.37 MPa. Here the NW “diameter” is measured from the projected view in the SEM, which is the distance between two nonadjacent vertexes (as shown in the inset of Figure 1a) due to the pentagonal cross section. The real cross sectional area, \(5D^2/(8\sin72^\circ)\) (where \(D\) is the NW diameter), is used to calculate the stress. The NW elongation was measured by digital image correlation of the SEM images; additional SEM images with high magnification were taken at each loading step to increase the strain resolution (as shown in the inset of Figure 2.15c). As a NW typically spans 1500-1800 pixels in length and we can measure the NW elongation with the resolution of half a pixel, the strain resolution is about 0.03%. After each test, we carefully examined both clamps to ensure there was no slippage between the NW and the clamps, following a procedure we developed.[28]
Figure 2.15. (a) Low magnification TEM image of Ag NWs with a diameter ~80 nm. Inset of (a) shows a 3D schematic of five-fold twinned NW and the effective diameter $D$ used in this study. (b) SAED of an Ag NW. The indexed diffraction pattern corresponds to the overlapping of two zone axes, [001] (solid box) and [1 1 2] (dashed box). The direction of the electron beam is perpendicular to one of the {100} side facets as shown in panel (a). Elongated diffraction spots (as arrowed) are indicative of elastic strain in the NW. (c) SEM image showing the tensile test of a single Ag NW. Inset of (c) shows a high resolution SEM image of the NW for strain measurement. Two arrows indicate the clamps by EBID of carbonaceous materials.
2.2.1 Results and Discussion

Figure 2.16a shows a typical stress-strain behavior of Ag NWs. The first, second and third unloading occurred at a strain of 0.7%, 1.5% and 3.0%, respectively. It can be seen that the first loading and unloading curves followed nearly identical paths. No residual plastic deformation was observed when the NW was fully unloaded. By contrast, upon unloading at strains larger than 1.5%, the NW underwent plastic deformation with pronounced strain hardening, but the high magnification SEM images during the testing showed no sign of diameter reduction or necking prior to NW failure. After failure, a close examination of the NW fracture ends (Figure 2.16b) showed that there is no apparent diameter reduction (i.e., no large-scale yielding) along the NW except very close to the fracture surface. This observation is consistent with the stress-strain data where the plasticity is limited compared to bulk FCC metals. Both fractography and stress-strain data suggested that the dislocation induced shear is localized, which agrees with molecular dynamics (MD) simulations of five-fold twinned Ag NWs.\textsuperscript{[62]} Tension tests of all the NWs at different diameters were conducted following the same procedure with multiple loading/unloading cycles. A nearly constant strain rate (~0.1%/s) was maintained for all the tests. Note that our experiments were under load control, so the strain softening regime succeeding the UTS was not captured. Engineering stress and strain are plotted in this work.

To study the size effects on the mechanical properties of Ag NWs, a total of 13 NWs with diameters ranging from 34 to 130 nm were tested. The NW dimensions and measured properties are listed in Table 2.2. Figure 2.17a shows both the yield strength and the UTS as functions of the NW diameter. Since no apparent yielding was observed in our tests, the yield
strength was defined using the 0.2% offset method. The UTS was defined as the maximum stress that a NW can withstand in tensile test. In a typical stress-strain curve as shown in Figure 2.16a, the maximum stress value prior to the NW breakage was taken as the UTS for this NW. The yield strength was strongly size dependent, increasing from 0.71 GPa to 2.64 GPa as the diameter decreased from 130 nm down to 34 nm. The highest yield strength of Ag NWs was about 50 times higher than the bulk value (54 MPa) and was close to the theoretical tensile strength of Ag in the <110> direction, which was calculated to be 3.5 GPa following the Schmid factor analysis of the {111}/<112> slip system.\[66] The UTS was higher than the yield strength for most of the tested NWs, which indicates the Ag NWs underwent strain hardening. Only two out of the 13 NWs showed the same UTS as the yield strength. This is likely due to a small increase in stress between the two events, which was not captured in our experiments.

Figure 2.17b shows a log-log plot of the yield strength as a function of the NW diameter. This plot indicates that the Ag NWs in the diameter range tested obey the widely observed power-law size effect, with a power-law exponent of 0.66, well within the previously reported range.\[67] Plasticity of micro/nano-pillars has been extensively studied in recent years.\[67, 68] In general, strength increases as the pillar diameter decreases. For micropillars, plasticity occurs through the activation of single-arm sources (or truncated Frank-Read sources). A power-law size effect was generally observed with the power-law exponent between 0.5 and 1. For small nanopillars (e.g., diameter less than ~200 nm), plasticity occurs through dislocation nucleation from surface sources. A weaker size effect was predicted\[69] and recently confirmed experimentally.\[70] Thus, the power-law size effect
in yield strength (e.g., via the single-arm source mediated mechanisms) is somewhat contradictory to the fact that the NW diameters are well below 200 nm.

Figure 2.16. (a) Stress-strain of an Ag NW with diameter of 69 nm under tensile loading, where the Young’s modulus, yield strength and ultimate tensile strength (UTS) are 90, 0.72 and 2.10 GPa, respectively, and yield strain and strain at UTS are 0.92 and 4.14, respectively. (b) SEM image showing the fracture surfaces of the Ag NW.
Figure 2.17. (a) Yield strength and ultimate tensile strength (UTS), (b) Log-log plot of true yield strength as a function of NW diameter. The data show a power-law trend (shown by read line) with $n = -0.66$. 
Table 2.2. Dimensions and mechanical properties of 13 Ag NWs under tension

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Diameter (nm)</th>
<th>Length (μm)</th>
<th>Young’s modulus (GPa)</th>
<th>Yield strain (%)</th>
<th>Yield strength (GPa)</th>
<th>UTS (GPa)</th>
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<tr>
<td>1</td>
<td>34</td>
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<tr>
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<td>81</td>
<td>1.00</td>
<td>0.71</td>
<td>0.87</td>
</tr>
</tbody>
</table>

To further probe the mechanism for the size effect in the yield strength of Ag NWs, the yield strain is plotted as a function of the NW diameter, see Figure 2.18a. Yield strains show large scatter ranging from 0.92% to 1.64% with almost no correlation to the diameter. The yield strain is plotted as a function of the NW side surface area, see Figure 2.18b. This plot shows a general trend that yield strain increases with decreasing surface area but suggests that this size effect is quite weak, which is nevertheless in line with the mechanism of dislocation nucleation from free surfaces (surface sources\(^{[69]}\)). Note that the aspect ratio of NWs was not constant in this study. A Weibull-type weakest-link probabilistic model was applied to verify if the observed variation can be associated with the surface sources.\(^{[26]}\) Weibull statistics assume the probability of failure \(P_f\) for a specimen of surface area \(A\) under uniaxial tension as
\[ P_f = 1 - \exp\left(-\left(\frac{\varepsilon_f}{\varepsilon_{0A}}\right)^m A\right) \]  

where \( \varepsilon_f \) is the yield strain, and \( \varepsilon_{0A} \) is the characteristic strain relative to unit surface area, and \( m \) is the Weibull modulus. The Weibull statistics applied to this set of yield strain data with respect to the surface area are shown in Figure 2.18c.

The coefficient of correlation for NW side surface area is \( \sim 82\% \), in contrast to that for the NW volume (\( \sim 64\% \)). This indicates that yield strain, to some extent, is associated with the side surface area of the NWs. Better correlation could be achieved if the number of experiments was increased. Size effect on yield strain of NWs is likely caused by the statistical nature of surface dislocation sources, assuming the first dislocation is nucleated from the weakest-link source.\(^{[71]}\) Our results corroborate atomistic simulations of five-fold twinned NWs, where yielding occurs as partial dislocations nucleate from surfaces.\(^{[62, 72]}\)

While the weakest-link type of models are conventionally applied to brittle fracture, they could play an important role in the yielding at small scales, as applied to metal whiskers by Brenner\(^{[73]}\) and recently to nanopillars\(^{[74]}\) and NWs.\(^{[75]}\) The increased sensitivity to temperature and strain rate (related to the dislocation nucleation from surfaces) might account for the large data scatter in our yield strain as observed here.

The Young’s modulus is also plotted as a function of the NW diameter, as shown in Figure 2.19. The first unloading slope in a stress-strain curve was used to calculate the Young’s modulus in our study. A linear fitting was applied to the first unloading curve. Errors of the Young’s modulus measurement could come from the strain and stress measurements as well as the fitting (see error bars in Figure 2.19). The Young’s modulus of
bulk Ag in the <110> direction (84 GPa) is plotted as a dashed line for comparison. A stiffening trend was observed for NWs with diameters less than 80 nm; the Young’s modulus continuously increased with the decreasing diameter down to 34 nm. For Ag NWs with diameters over ~80 nm, their Young’s moduli appeared to be slightly lower than the bulk value. The Young’s modulus results from our in situ SEM tensile tests agree well with those from the AFM tests.

The observed size effect on elasticity of Ag NWs is generally a result of their large surface area to volume ratio, more specifically, surface elasticity and/or bulk nonlinear elasticity (due to surface stress). Though our results are in good agreement with other experimental results, we do note that there is a substantial gap between the experiments and the atomistic simulations in terms of the critical diameter where the elasticity size effect becomes marked. One significant reason for this is the difference in aspect ratio (length/diameter). The NW aspect ratio in atomistic simulations is much smaller than those in our experiments. As aforementioned, the aspect ratio was not intended to keep as constant in this study. Park et al. predicted that the aspect ratio plays an important role in the elasticity size effect in NWs; the small aspect ratio used in atomistic simulations could underestimate the size effect. Furthermore, the five-fold twin structure could play a critical role in the elasticity size effect. Recent atomistic simulations found that the intrinsic strain state leads to a much stronger size effect in elasticity for five-fold twinned NWs than twin-free NWs. It is of additional note that the embedded atom method (EAM) potential commonly used in MD simulations might underestimate the Young’s modulus to certain degree.
Yield (or fracture) strength is simply equal to Young’s modulus multiplied by yield (or fracture) strain. Brittle NWs such as Si and ZnO have been found to exhibit strong size effect in Young’s modulus.\cite{7, 12, 28, 40} It seems more fundamental to correlate fracture strain with (surface) defects instead of commonly used fracture strength, so as to eliminate the contribution of Young’s modulus.\cite{84} This argument is likely also applicable to ductile NWs such as the Ag NWs where yield strain can be correlated with side surface area.

In addition to the high yield strength and UTS, an intriguing mechanical behavior - strain hardening of NWs under tension - was observed for the first time. For micro/nano-pillars (with diameters ranging from sub-micrometer to tens of micrometers) under compression, strain hardening was observed and was mainly attributed to limited dislocation sources and not much to the interaction of slip systems as in the macroscopic scale.\cite{85-87} But recent experiments and simulations suggested that in single-crystalline nanopillars or NWs (with diameters typically less than ~200 nm), dislocations are relatively easily annihilated at free surfaces before they have the opportunity to interact (e.g., the gliding dislocations travel only very short distances before annihilating at a free surface), leading to no strain hardening.\cite{69, 88-90} Nevertheless, our results clearly show the strain hardening in five-fold twinned Ag NWs (Figure 2.16a). MD simulations of five-fold twinned NWs predicted that partial dislocations are nucleated from surfaces and glide towards the NW center following a \{111\}/<112> slip system.\cite{62, 72} The observed strain hardening in our case is likely due to the interaction between partial dislocations and twin boundaries\cite{91} in addition to the limited dislocation sources. Twin boundaries have been ascribed to the strain hardening observed in nanostructured materials\cite{92, 93} and NWs with orthogonally-oriented twins.\cite{94} A complete
analysis of the observed strain hardening in Ag NWs requires a combined experimental and modeling investigation, which is currently underway.

**Figure 2.18.** Yield strain as a function of (a) NW diameter and (b) NW side surface. (c) Plot of the Weibull statistics. Probabilities \((P_i)\) are calculated as \(P_i(\varepsilon_i) = \frac{i-1/2}{N}\), where \(N\) is the total number of specimens tested and the measured yield strains are ranked in ascending order.
2.2.1 Conclusions

The elasticity, plasticity and failure of five-fold twinned Ag NWs with diameters between 34 and 130 nm were measured by in situ SEM tensile testing. In addition to the stiffening size effect in Young’s modulus, we found that yield strength and ultimate tensile strength both increased as the NW diameter decreased. The maximum yield strength in our tests was found to be 2.64 GPa which is about 50 times the bulk value and close to the theoretical value of Ag in the <110> orientation. The size effect in yield strength was mainly attributed to the stiffening size effect in Young’s modulus, which is in turn a result of the surface effect and the unique five-fold twin microstructure. Yield strain scales reasonably well with the NW surface area, which is consistent with the mechanism of dislocation
nucleation from surface sources. Yield strain does not correlate well with the NW diameter; the aspect ratio (length/diameter) of the 13 NWs was not constant. The scaling of yield strain with NW surface area is quite weak when compared to the power-law relationship. Pronounced strain hardening was observed for most NWs in our study, which is hypothesized to result from the internal twin boundaries in addition to the limited dislocation sources. The present work provides valuable insight into the importance of the size and microstructure on the mechanical properties of NWs.

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Chapter 3

Temperature Dependent Effect

3.1 Brittle to Ductile Transition of Silicon at Different Length Scales

3.1.1. Introduction

Brittle-to-ductile transition (BDT) has been an important topic for many decades for a variety of materials, particularly ceramics. A crystalline material is described as brittle if a crack tip propagates along crystallographic planes in a cleavage manner. On the other hand, the crystal is considered to be ductile if the crack-tip extension is accompanied by plastic deformation features like dislocation motion or local amorphization. Understanding the nucleation and motion of defects such as dislocations, localized disordering and amorphization experimentally is critical for understanding of brittle-to-ductile transition.

Silicon is a ubiquitously important material in semiconductor industry. In the micrometer scale, single-crystal silicon (SCS) is commonly used material in MEMS devices. In the nanometer scale, Si NW is one of the key building blocks for nanoelectronic and nanoelectromechanical devices. Si NWs exhibit excellent mechanical, electrical, and optical properties in addition to interesting multifunctional properties such as piezoresistivity and thermoelectricity. Mechanical properties of Si thin-films and nanostructures are very important for the design and reliability of many MEMS/NEMS devices. In addition, because of the availability of large dislocation-free single crystals and its economic importance,
silicon has been extensively studied as a model material for understanding the BDT, both experimentally and numerically.

In this section, we summarize the BDT of Si at different size scales from bulk to thin films to nanostructures (wires and pillars), with a focus on the mechanisms of BDT, experimental methods, and recent progress in terms of experiments and simulations.

### 3.1.2. Brittle ductile transition of silicon at different size scales

The mechanical response of solids subject to extreme applied stress is controlled by atomistic mechanisms in the vicinity of stress concentrations such as crack tips. In a brittle material, the material responds by further extension and resulting growth of cracks, leading to a catastrophic failure through fragmentation. In a ductile material, the repeated shear of lattice planes through dislocations leads to macroscopic permanent change of the shape of the material without catastrophic failure. Whether a material is ductile or brittle depends on the competition of intrinsic material parameters (such as the energy required to create new surfaces, versus the energy required to initiate shearing of a lattice to form a dislocation).

Table 3.1 summarizes the methods used to investigate BDT of silicon at different size scales. In the experimental domain, one can divide the methods based on the loading mode, namely uniaxial tension or compression, and bending-based, where bending and buckling are employed.
Table 3.1. Summary of different experimental methods used to characterize the fracture behaviors of Si at different size scales

<table>
<thead>
<tr>
<th>Sample</th>
<th>Testing technique</th>
<th>Sample description</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
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<td>Bulk Si</td>
<td>Fracture: TDCB[1-5]</td>
<td>Pre-cracked, (111)</td>
<td>77 ~ 1273 K</td>
</tr>
<tr>
<td></td>
<td>Fracture: Four-point bending[6]</td>
<td>Pre-cracked, (111)</td>
<td>800 ~ 960 K</td>
</tr>
<tr>
<td>Si thin films</td>
<td>Tension[7-9]</td>
<td>50(L) ×40(W) ×4(T) μm[7,8]</td>
<td>RT ~ 800 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>227(L) ×4.3(W) ×4.8(T) μm[9]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;110&gt; align with loading direction</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>With[7] or without pre-crack[8,9]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AFM bending[10]</td>
<td>Top-down fabricated wire &lt;110&gt; in length direction</td>
<td>295 ~ 573 K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6(L) ×0.2–0.8(W) ×0.255(T) μm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compression[11]</td>
<td>Top-down fabricated pillar &lt;100&gt; align with loading direction</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 230–940 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AFM bending[12-14]</td>
<td>VLS synthesized &lt;111&gt; oriented</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 15~70 nm, [12]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100<del>700 nm,[13] 90</del>170 nm[14]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nanoindentation[12]</td>
<td>VLS synthesized &lt;111&gt; oriented</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 15~90 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wet chemically etched&lt;111&gt;, &lt;100&gt; oriented</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 200 &amp; 350 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100<del>700 nm,[13] 90</del>170 nm[14]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tension: in situ SEM[17]</td>
<td>VLS synthesized Major &lt;111&gt; oriented</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 15~60 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tension: in situ TEM[18-20]</td>
<td>Formed by contact and retraction, thermal evaporate to template, and VLS</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;100&gt;, &lt;18&gt; &lt;110&gt;,[10] and &lt;111&gt;,[20]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: <del>10 nm, 15</del>70 nm,[19]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8~42 nm[20]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;1-10&gt;,[21, 22] &lt;111&gt;,[20] and &lt;100&gt;[23]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: ~50 nm,[21, 22] ~40 nm[20,23]</td>
<td></td>
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</tbody>
</table>
Four-point bending or tapered-double-cantilever-beam (TDCB) tests are the most common techniques used in studying BDT in the bulk scale. When the size decreases, on-chip testing devices, AFM based testing techniques and in situ electron microscope testing setups have been developed to investigate mechanical behaviors of materials. These include AFM bending, in situ SEM, TEM tension, compression and bending test methods, as indicated in Table 3.1. Atomistic models, primarily MD and first-principles density functional theory (DFT) calculations have been used to predict the BDT of Si NWs.\textsuperscript{[24, 25]}

For bulk Si, the BDT is characterized experimentally by testing many specimens at a given loading rate and various uniform temperatures. The first to do this was St. John.\textsuperscript{[1]} A series of fracture experiments were carried out at various strain rates on pre-cracked silicon single crystal samples with the TDCB geometry and (111) crystal orientation between -196 °C and 1000 °C. He found that the BDT for silicon occurred within a narrow temperature range. The transition temperatures were rate dependent and changed from 700 °C to 940 °C when the cross-head loading speed increase from 0.0005 cm/min to 0.05 cm/min. He showed that the activation energy for the transition was close to that for thermally activated dislocation glide and proposed a crack-tip blunting mechanism for the sharp transition, which assumed that dislocation nucleation occurs relatively easily at the crack tip, and that the rate of blunting is controlled by the rate at which dislocations can move away from the crack tip.

Samuels and Roberts\textsuperscript{[6, 26]} and Brede and Haasen\textsuperscript{[2]} confirmed the dependence of the transition on dislocation mobility by testing doped silicon with four-point bending and TDCB method, respectively.
Michot and George\textsuperscript{[3-5, 27, 28]} conducted a large number of experiments to investigate many other aspects of the transition, such as other cleavage planes, activated slip systems, and heterogeneous source configurations (sample surfaces and cleavage ledges being the most prominent sources). These authors suggested that dislocation shielding was more important than crack blunting as the dominant mechanism for the BDT. The general consensus is that dislocation mobility does control the BDT and the activation energy for the BDT equals the activation energy for dislocation glide. However, with the dislocation mobility controlled mechanism alone is not sufficient to explain the sharp transition observed in experiments, because dislocation mobility increases gradually with temperature. Michot et al.\textsuperscript{[5]} argued that a large number of dislocations need to be generated at transition temperature in order to achieve such a sharp transition. They showed that cross slip of dislocation near the crack tip was a plausible mechanism for dislocation multiplication. And, the activation of multiple slip systems is one of the key factors in determining the sharpness of the BDT.

For Si thin films and nanostructures, one needs to utilize or develop other techniques to conduct BDT characterization. Nakao et al.\textsuperscript{[7, 8]} developed an on-chip tensile testing technique to investigate the effect of temperature on the mechanical properties of micro-sized SCS thin film. The silicon thin film sample was integrated to a loading system with $<$110$>$ direction align with loading axis and a dimension of $50 \times 40 \times 4 \ \mu m$ (length($L$)$\times$width($W$)$\times$thickness($T$)). In their first report,\textsuperscript{[7]} they observed that the stress strain relationship of the specimens was linear below 300 °C and nonlinear at 400 °C and 500 °C. An SEM observation revealed dislocation and cross slip lines near fracture surface of samples failed at 400 °C and 500 °C. A change in the fracture mode of a micrometer-sized
SCS film was observed at a temperature slightly higher than room temperature (RT) in their second report.\(^8\) This time, silicon films with a notch on one side were tested under tensile stress at temperatures ranging from RT to 500 °C. The fracture toughness remained constant at temperatures ranging from RT to 60 °C and drastically increased between 60 and 70 °C. The change in fracture toughness indicates a change in fracture mode from brittle to ductile. Uniaxial tensile tests were recently carried out on the Si sample at room temperature to 403 °C in SEM using a silicon carbide tensile testing stage by Kang and Saif.\(^9\) The Young’s modulus of tested Si samples was found to decrease with increase of temperature. However, the fracture information was not available in their report.

This very low transition temperature seems to agree with the finding by Namazu et al.\(^{10}\) They tested the top-down fabricated Si wires with thickness of 255 nm and width of 200 to 800 nm used AFM bending. The \(<110>\) oriented wires were found to fracture in a brittle manner at room temperature, but deform plastically above 373 K. Slip lines comprised of edge dislocations responsible for the plastic flow was observed by AFM and SEM. At a similar length scale (from 230 to 940 nm), Ostlund et al.\(^{11}\) conducted uniaxial compression test on focused ion beam (FIB) fabricated \(<100>\) nanopillars at room temperature. They observed room temperature BDT on silicon nanopillars with diameters less than 400 nm.

It is astounding how much the transition temperature changes as the nanometer scale is approached (for bulk silicon, the BDT temperature range from 500 to 900 °C). There is general agreement that dislocation shielding is important in many of these cases and that the activation energy for dislocation nucleation and motion are necessary features. In the context of relatively dislocation free crystals of small size, dislocation nucleation at a stress
concentration will produce a slip band with a back stress from emitted dislocations. This shields existing nanocrack or potential crack sites from achieving sufficiently large local stresses to cause fracture.

A sufficiently high stress to exceed the Peierls barrier for dislocation nucleation and/or motion is critical to the achievement of plastic deformation in brittle solids. In the studies mentioned above, these high tensile stresses can be achieved either in thin film (5~10 GPa)\textsuperscript{7, 8} or nanopillars (4~6 GPa)\textsuperscript{11} under compression at room temperature. These stresses are sufficient to nucleate a dislocation either homogeneously from inside the body or heterogeneously from a surface defect. These nucleated dislocations serve several purposes.\textsuperscript{29} First, they represent an energy dissipation mechanism; and second, from any singular site, they provide dislocation shielding to prevent premature fracture. For appropriate crystallographic orientations, intersecting slip bands can form a crack which then nucleates.\textsuperscript{30} So for special orientations, the dislocations could participate in both crack nucleation and arrest. Another key to lowering the BDT temperature is the rapid dislocation motion. If a dislocation is emitted from a potential stress concentration site and does not move away from the site rapidly, then a second and third dislocation will have difficulty emitting. This limits the amount of shielding possible. It also restricts the magnitude of plastic energy dissipation. The key aspect is to allow dislocations to move rapidly and sufficiently far to allow a number of dislocations to provide shielding. This can happen if the developed stresses are sufficient to decrease the activation energy of dislocation motion in addition to nucleate dislocation. Researchers\textsuperscript{31, 32} showed that the stress-dependent activation energy model they proposed projected large drops in the stress-modified activation...
energy for dislocation motion at very high stresses. Gerberrich et al.\cite{29} predicted that the BDT temperature shifted by a factor of three in absolute temperature was possible by reducing size through a thermal activation analysis.

With strong evidence showing the dramatic decrease in BDT temperature when the size of SCS reduces to several hundreds nanometers, one would expect significant plastic deformation for bottom-up synthesized one dimensional silicon NWs. These NWs usually have diameter less than 100 nm. Many studies have been conducted to elucidate the deformation and fracture mechanism of Si NWs using various methods, such as bending using AFM,\cite{12-14} MEMS tensile testing device,\cite{15, 16} nanoindentation,\cite{12} in situ SEM,\cite{17} TEM\cite{18-23} tensile or bending testing and molecular dynamic simulation.\cite{20, 24} However, controversial results have been reported in term of brittle or ductile for Si NWs at room temperature. For example, Si NWs have been reported to be brittle and possessed a sole elastic deformation before catastrophic fracture,\cite{12-17} while Han et al.,\cite{19, 21, 22} Zhu et al.,\cite{23} and Kizuka et al.\cite{18} demonstrated that Si NWs could sustain substantial plastic deformation.

Plastic deformation so far has only been observed for Si NWs tested in situ inside the TEM, as we can see from the deformation mechanism summary on Si NWs above (Table 3.1). For example, Han et al.\cite{19} used in situ TEM to study the tensile deformation of Si NWs with diameter range from 15 nm to 70 nm, and found severe plastic deformation (necking) prior to failure at room temperature. The authors observed an increase in ductility (plasticity) with decreasing size of NW. Unfortunately, quantitative stress-strain measurements were not available in this study. However, using in situ SEM tensile testing, Zhu et al.\cite{17} found linear elastic behavior followed by brittle fracture for Si NWs with similar diameter ranging from
15 to 60 nm also at room temperature. The linear elastic behavior was confirmed by the repeated loading-unloading and fractography of the fracture surfaces. Zhu’s results are consistent with MD simulations by Kang and Cai,\textsuperscript{[25]} who observed that only NWs with diameters smaller than 5 nm fail in a ductile manner at room temperature, while the transition diameter increases with an increase in temperature.\textsuperscript{[24]} The discrepancy between Han’s and Zhu’s results is possibly due to electron beam-induced heating that could be present in Han’s experiments. Another possible reason responsible for the large plastic deformation as recently studied by Dai et al.\textsuperscript{[23]} is the amorphization of silicon under high energy electron beam. Tang et al.\textsuperscript{[20]} recently studied the deformation of Si NWs under both tensile and bending loading conditions and revealed that the deformation mechanism was loading mode dependent. Under uniaxial tension, the Si NWs fractured in a brittle manner by nucleation and propagation of a single crack and cleavage along the (111) planes for $<\bar{1}11>$ oriented wires. Under bending, the Si NWs demonstrated considerable plasticity.

3.1.3. Conclusions and outlook

Figure 3.1 summarizes the available BDT temperature from literatures discussed in this section\textsuperscript{[1-3, 6-8, 10, 11, 18-23]} and shows the BDT temperature as a function of size. Sample size is defined as the smallest dimension of the sample.
BDT of Si is an interesting phenomenon. Due to its high Peierls force, Si is typically a brittle material at low homologous temperature with very limited dislocation mobility. As temperature increases, Si undergoes a BDT associated with plastic flow. For bulk Si, BDT is mainly controlled by dislocation mobility. The transition typically starts around 500 °C, although the transition temperature can range from 500 to 900 °C, depending on strain rate and impurity concentration.\textsuperscript{33, 34} Dislocations in Si are generally dissociated into two partial dislocations that are separated by a stacking fault.\textsuperscript{33} If the feature size of the specimens is smaller than the dissociation distance of the partials, a single partial is responsible for the
plastic deformation. The deformation rate is then limited by the mobility of this partial dislocation. For larger specimens, the rate is limited by the mobility of the slower trailing partial.\textsuperscript{[11]} Dislocations in Si can be formed by shear between either the narrowly-spaced planes (glide set dislocations) or the widely-spaced planes (shuffle set dislocations). The glide set dislocations are favored at higher temperatures, while the shuffle set has been proposed to be the dominant mechanism at low temperatures.\textsuperscript{[35, 36]}

Two different models have been proposed for BDT of bulk SCS: one based on dislocation nucleation and the other based on dislocation mobility. The general consensus is that dislocation mobility does control the BDT of bulk and the activation of multiple slip systems is one of the key factors in determining the sharpness of the BDT.

To date, several experiments have reported evidence of BDT for small-scale Si at room temperature. Such as indentation/compression of Si nanoparticles or nanopillars.\textsuperscript{[11, 37]} In this case, hydrostatic stress involved in these experiments could promote BDT. Several others are in situ TEM tensile or bending tests of Si NWs. However, it is likely that high-energy (200 keV) electron beam could heat the NWs and/or enhance the dislocation mobility and/or cause amorphization of silicon. High energy electron beam is a possible factor because reported in situ TEM testing results are controversial with those in situ SEM or AFM bending results.

MD simulations on thin Si NWs (diameter from 2 to 7 nm) by Kang and Cai\textsuperscript{[24]} showed that the dislocations nucleate from the surface and are along the shuffle-set planes. The authors concluded that the BDT responsible for Si NWs is nucleation controlled rather than mobility controlled as for bulk Si. In the small size system without pre-existing cracks,
both dislocation and crack need to be nucleated preferably from surface. And the high stress to nucleate dislocation or crack also sufficient to ensure them move across the entire cross section, even at very low temperature.

Clearly experimental efforts are needed to confirm the existence of BDT for Si NWs and if existent, quantify the effects of size and temperature. A testing stage with controllable temperature is essential and needed to develop for this purpose. Modeling efforts are also needed to quantify the energy barrier of a dislocation and a crack and find out the reason why dislocation is preferred at the size becomes extremely small.

NW length and surface coated materials are the possible additional factors that would affect the deformation mechanism of nanoscale materials and thus noteworthy. Wu et al.\textsuperscript{[38]} showed that the length plays an essential role in determining NW tensile failure modes and fracture surface morphologies. A failure mode transition occurs with increasing NW length. Short NWs fail via dislocation plasticity along multiple slip planes and ductile necking, while long NWs fail by an unstable localized shear along a single slip plane without appreciable necking. Li et al.\textsuperscript{[39]} showed that amorphous carbon coatings can shield opening cracks on silicon carbide NWs, making them damage-tolerant. Increasing the coating thickness leads to a brittle-to-ductile transition for the NWs.
3.2 Temperature Control in Thermal Microactuators

3.2.1 Background

In the field of MEMS, electrothermal actuators (ETAs) have emerged as structurally simple, compact, stable, and high-force actuation apparatuses.\textsuperscript{[40-43]} ETAs have been exploited in a variety of configurations to achieve desired in-plane motion, such as U-shape (pseudobimorph),\textsuperscript{[40]} V-shape (bent-beam)\textsuperscript{[41, 42]} and Z-shape.\textsuperscript{[43]} They are used in a broad range of applications, including on-chip nanoscale material testing systems,\textsuperscript{[16, 44-48]} micromotors,\textsuperscript{[49, 50]} microtweezers\textsuperscript{[51]} and bistable mechanisms.\textsuperscript{[52]} The operating principle of most MEMS ETAs is based on Joule heating and the resulting thermal expansion of beams. The ETAs are heated to a high temperature (e.g., hundreds of degree Celsius), which might limit their applications and thus invokes the need to control the actuator temperature, especially at the end where end effector is attached. Due to constraints in microfabrication of ETAs, solutions to dissipate the heat are limited. One solution was to leave cuts in the ETAs and fill with dielectric spacers,\textsuperscript{[42]} which inevitably caused additional fabrication steps.

Of particular interest is the mechanical testing of nanostructures using ETAs. Understanding mechanical behavior of nanostructures such as nanowires and nanotubes is important not only for their applications as nanomechanical devices, but also for gaining insight into fundamental mechanisms of deformation and failure at the nanoscale. MEMS offer unprecedented opportunities for quantitative \textit{in-situ} electron microscopy testing of nanostructures.\textsuperscript{[53, 54]} ETAs provide stable, displacement-controlled loading and become widely adopted for nanomechanical testing. However, the mechanical behavior can be affected by temperature (e.g., for silicon\textsuperscript{[7, 17, 55]}). To circumvent the heating problem, Zhu et
al.\textsuperscript{[48]} introduced so-called heat sink beams as a simple but effective method. Though predicted by modeling, the effect of such a design has not been verified by any experiments. In fact, the modeling treated only the vacuum condition, which made it not possible to compare with experiments as temperature measurement of MEMS devices is typically conducted in air. Generally speaking, while a large amount of modeling work has been devoted to ETAs, heat dissipation to air is either neglected\textsuperscript{[56]} or considered in specific cases (e.g., heat conduction through air to substrate),\textsuperscript{[57]} with very few exceptions.\textsuperscript{[58, 59]}

In this thesis, we report experimental measurement and multiphysics modeling of the temperature profile of a V-shaped ETA (Figure 3.2). The temperature measurement was based on Raman scattering in air. Fully 3D multiphysics (coupled electrical-thermal-mechanical) simulation treated both the air and vacuum conditions; the air and vacuum conditions are of relevance to the Raman measurement and the \textit{in-situ} electron microscopy testing of nanostructures, respectively. For the same ETA, the Raman measurement and multiphysics modeling were carried out with and without the heat sink beams; the heat sink beams were carved out by focused ion beam (FIB). Our results demonstrated that the heat sink beams play a critical role in reducing the temperature in the ETA. Additional analyses and simulations were conducted to provide design guidelines on how to achieve both low temperature and large actuator displacement for nanomechanical testing. Our results should be easily applicable to temperature control of MEMS thermal actuators for other applications.
3.2.2 Experimental Section

The ETAs were fabricated at MEMSCAP (Durham, NC) using the Silicon-on-Insulator Multi-User MEMS Processes (SOI-MUMPs). The structure layer is n-type (phosphorus-doped) single crystalline silicon. Dimensions of an ETA are summarized in Table 3.2. The temperature measurements were conducted using a HORIBA LabRAM HR Raman microscope in air. The excitation source is a 633 nm laser. The laser power on the sample is kept below 0.003 mW to avoid laser-induced local heating. The focused laser spot is approximately 1 μm in diameter. The Raman signal is collected in backscatter through the microscope objective, relayed to a grating spectrograph and detected using a deep-depletion, thermoelectrically cooled CCD camera. Each measurement takes approximately 60 seconds.

Figure 3.2. SEM image of a nanomechanical testing stage including a V-shaped ETA (on the right), a load sensor (on the left) and a gap in between where nanostructures are mounted.
Table 3.2. Dimension of the SOI V-shaped ETA

<table>
<thead>
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<th>Dimension</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Inclined beam length</td>
<td>$l$</td>
<td>296</td>
<td>µm</td>
</tr>
<tr>
<td>Inclined beam width</td>
<td>$b$</td>
<td>8</td>
<td>µm</td>
</tr>
<tr>
<td>Gap between actuator and sensor</td>
<td>$d$</td>
<td>2</td>
<td>µm</td>
</tr>
<tr>
<td>Inclination angle</td>
<td>$\theta$</td>
<td>10</td>
<td>degree</td>
</tr>
<tr>
<td>Heat sink beam length</td>
<td>$l_{sb}$</td>
<td>50</td>
<td>µm</td>
</tr>
<tr>
<td>Heat sink beam width</td>
<td>$b_{sb}$</td>
<td>5</td>
<td>µm</td>
</tr>
<tr>
<td>Shuttle Length</td>
<td>$l_s$</td>
<td>627</td>
<td>µm</td>
</tr>
<tr>
<td>Shuttle width</td>
<td>$b_s$</td>
<td>60</td>
<td>µm</td>
</tr>
<tr>
<td>Thickness</td>
<td>$t$</td>
<td>10</td>
<td>µm</td>
</tr>
<tr>
<td>Gap to substrate</td>
<td>$g$</td>
<td>400</td>
<td>µm</td>
</tr>
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</table>

Figure 3.3 shows the Stokes-shifted Raman spectra of a representative position (620 µm from the specimen edge) on the ETA at four different temperatures (room temperature and temperatures under actuation voltages of 2, 3 and 4 volts). Several features were observed with increasing temperature: 1) the position of the Raman peaks is shifted toward lower phonon energies, 2) the Raman lines broaden, and 3) the intensity of the anti-Stokes signature relative to the Stokes-shifted line increases. Kearney et al.\([60]\) found the peak position of the Stokes-shifted Raman spectrum to be a robust indicator of temperature compared to the other two signals, therefore, the Stokes shift was recorded and analyzed in our experiments. The Raman spectra were fit to a Voight lineshape function to determine the Stokes peak location. It can been seen that with increasing actuation voltage, the Stokes peak blue-shifted.
To calibrate the Raman (Stokes) shift as a function of the temperature, a MEMS chip was placed on top of a hot plate. A large area of the single crystalline silicon substrate was chosen, where both the Raman scattering and the infrared thermometer based temperature measurements were conducted. The Raman spectrum was fit to a Voight function to determine the Stokes peak location and linewidth. Figure 3.4 shows the calibration curve of the Raman shift versus temperature.

To quantify the effect of the heat sink beams, the Raman spectra were obtained on the same ETA with and without heat sink beams. Following the calibration experiment, the change in the peak position can be converted to the temperature rise in the ETA, viz.,
where \( \Omega_0 \) and \( \Omega \) are the measured peak positions at the laboratory temperature of 296 K and at the operating temperature, respectively.

\[
\Delta T = \frac{\Omega - \Omega_0}{-0.0242 \text{ cm}^{-1}} \quad (3.1)
\]

**Figure 3.4.** Calibration curve of the Raman shift versus temperature.

Nonlinear multiphysics finite element analysis (FEA) was carried out using ANSYS 13.0 to study temperature distribution of the ETA. The ETA behaviors were simulated both in vacuum and in air. For the vacuum condition, the only heat dissipation mechanism is the heat conduction through the device itself to the anchors (substrate). For the air condition, an additional heat dissipation mechanism is the thermal conduction through the air to the silicon substrate and neighboring devices. Also, the thermal convection from the ETA to the air is considered, but not the thermal radiation.
The simulation is a coupled-field analysis involving electric, thermal and mechanical fields. The input is the actuation voltage across the anchor sites and the output includes the actuator temperature and displacement fields. The thermal boundary conditions are zero temperature change at the anchors for the vacuum condition, but zero temperature change at the anchors, the surrounding substrate and the neighboring device (e.g., the load sensor to the left of the actuator in Figure 3.2) for the air condition. The mechanical boundary conditions are fixed displacements at the anchor sites. Element type SOLID 98 was used for the ETA and SOLID 70 (heat transfer element) was used for the air. The laboratory temperature during the RAMAN experiments (296 K) is set as the reference temperature in the simulations. The material parameters used in the simulations are listed in Table 3.3.

### Table 3.3. Material parameters used in the simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Young’s modulus[^43]</td>
<td>$E$</td>
<td>160</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson ratio[^43]</td>
<td>$\nu$</td>
<td>0.28</td>
<td>–</td>
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<tr>
<td>Thermal conductivity of Si[^61]</td>
<td>$K_S(T)$</td>
<td>210658×$T^{-1.274}$</td>
<td>W/(mK)</td>
</tr>
<tr>
<td>Thermal conductivity of air[^62]</td>
<td>$K_{air}$</td>
<td>0.026</td>
<td>W/(mK)</td>
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<tr>
<td>Free convection coefficient of air[^63]</td>
<td>$C_{air}$</td>
<td>20</td>
<td>W/(m²K)</td>
</tr>
<tr>
<td>Thermal expansion coefficient[^64]</td>
<td>$\alpha(T)$</td>
<td>$-4\times10^{-12}T^2 + 8\times10^{-9}T+4\times10^{-7}$</td>
<td>K⁻¹</td>
</tr>
<tr>
<td>Resistivity[^43]</td>
<td>$\rho(T)$</td>
<td>$5.1\times10^{-5}[1+3\times10^{-3}(T-273)]$</td>
<td>Ωm</td>
</tr>
</tbody>
</table>

### 3.2.3 Results and Discussion

Figures 3.5a and b show the temperature distributions of an ETA without and with heat sink beams in vacuum, respectively. Without the heat sink beams, the only heat dissipation path is to the two anchors of the ETA through the inclined beams. As a result, the
highest temperature is in the shuttle, which is nearly constant from the left to the right end of the shuttle. With the addition of the heat sink beams to the specimen end, more heat dissipation paths are provided (i.e., through the heat sink beams to the anchors). Hence the temperature of the shuttle at the specimen end is significantly reduced. Note that the temperature is constant from the specimen edge to the nearest pair of heat sink beams since no heat dissipation occurs in that segment of the shuttle. In addition, the highest temperature in the ETA is lower than that without the heat sink beams.

Figures 3.5c and d show the temperature distributions of the ETA without and with heat sink beams in air, respectively. Without the heat sink beams, the temperature distribution is similar to that in vacuum, except that the temperature at the specimen end is considerably lower. The temperature continuously decreases along the shuttle from the opposite end (605 K) to the specimen end (573 K). This is mainly due to the heat conduction to the load sensor on the left side through the air gap. Note that heat dissipation through convection to the air is negligible (causing ~1 K difference in the ETA temperature). This heat dissipation is quite significant (i.e., causing ~40 K difference at the specimen edge) and cannot be captured in previous thermal models\textsuperscript{13}. With the heat sink beams, the temperature distribution is nearly identical to that in vacuum. Since the temperature at the specimen end is already very low (just slightly above room temperature) even in vacuum, the heat conduction through the air gap is insignificant.
Figure 3.5. Temperature distributions of an ETA under 4 volt actuation voltage. (a) Without heat sink beam in vacuum, (b) with 6 pairs of heat sink beams in vacuum, (c) without heat sink beam in air and (d) with 6 pairs of heat sink beams in air. For all simulations, the thermal beams and heat sink beams are connected to the anchors, which are indicated in Figure 1. The temperature at the specimen end is (a) 612.7 K, (b) 315.6 K, (c) 572.5 K and (d) 315.2 K, respectively.

Figure 3.6 shows the measured temperature profiles along the shuttle (starting from the edge of the sample end) under two different actuation voltages, which agree very well with the simulation results for the air condition. With the heat sink beams, the temperature changes markedly along the shuttle length. In contrast, without the heat sink beams, the temperature only changes a little along the shuttle length. This confirms the critical role that
the heat sink beams play in reducing the temperature at the specimen end. There is a notable discrepancy in temperature (~15 K) between the experiments and simulations, especially for the case without heat sink beams at 4 volt actuation voltage. In this case, the temperature is quite high. This discrepancy might come from both experiments and simulations. Experimentally, alignment drift of the optical system, the accuracy in determining position of Raman peak, and the slope of calibration curve fit might cause errors in the temperature measurement\textsuperscript{15}. Numerically, material parameters, especially temperature dependent parameters, might not be accurate. In our case, it is likely that the numerical error is more relevant since the discrepancy is more noticeable at high temperature.

**Figure 3.6.** Raman measurement and FEA of the temperature profile along the shuttle (starting from the specimen edge) under two different actuation voltages. Solid lines represent the FEA results and dots represent Raman measurements. The dashed vertical line shows the position of the nearest pair of heat sink beams (from the specimen edge).
For many applications such as the nanomechanical testing, ETAs often need to have both a low temperature increase and reasonably large travel range at the specimen edge. To gain insights for proper design of ETAs, additional FEA were employed to assess the effects of several parameters (number of thermal beams $m$, number of heat sink beams $n$, inclination angle $\theta$ and length of heat sink beams $l_{sb}$). The simulations were performed in vacuum as it is relevant for in-situ electron microscopy nanomechanical testing. Note that no specimen was attached to the ETA in these simulations. Analytical approximation showing the ETA displacement as a function of these parameters was provided elsewhere.  

Several guidelines can be drawn as follows (cf. Figure 3.7): 1) the more the inclined thermal beams (assuming other parameters remain unchanged), the larger the displacement at a given temperature rise at the specimen edge. In this case, the temperature in the ETA remains nearly constant for a given applied voltage, while the driving force due to thermal expansion and thus the displacement both increase. 2) The more the heat sink beams, the larger the displacement at a given temperature rise at the specimen edge. This seems in contrary to the first point. Though more heat sink beams increase the overall stiffness, they lead to drastically reduced temperature at the specimen edge. 3) As long as the length of the inclined beams does not change, the temperature in the ETA is independent of the inclination angle ($\theta$). Without the heat sink beams, the ETA displacement increases with the decreasing $\theta$ until $\sim 5^\circ$, conservatively speaking (when $\theta < 5^\circ$, the ETA might buckle), because the reduction in stiffness outweighs the reduction in driving force. But with the addition of the heat sink beams, the reduction in stiffness is not that gainful any more. As shown in Figure 5, inclination angles of $5^\circ$ and $10^\circ$ yielded about the same results. 4) It is advisable to have
relatively short heat sink beams. Though shorter heat sink beams lead to larger stiffness of the overall device, they dissipate more heat and thus reduce the temperature at the specimen edge. Overall, 10 or 20 pairs of thermal beams, 9 pairs of heat sink beams, 5° or 10° inclination angle, and 50 μm heat sink beams were found to offer the best performance (cf. Figure 3.7).

![Figure 3.7](image)

**Figure 3.7.** Temperature increase at specimen edge as a function of actuator displacement for different number of thermal beams $m$, different number of heat sink beams $n$, different inclination angle $\theta$, and different length of heat sink beams $l_{sb}$. In the legend, the four values represent $m$, $n$, $\theta$, and $l_{sb}$, respectively.

The tradeoff of adding the heat sink beams is, however, the decreasing efficiency in loading (or actuating) the specimen. A considerable fraction of the heat (power) is dissipated through the heat sinks, which lowers the ETA temperature for a given voltage. In addition,
part of the load applied by the ETA is distributed to the heat sink beams. To address this concern, we performed FEA with specimens of different diameters attached to the ETA under two cases: with (9 pairs 50 μm long) and without heat sink beams. We used silicon specimens (2 μm long, circular cross section and Young’s modulus of 160 GPa) as an example and assumed no heat loss through the specimens. For an ETA with twenty 5° inclined thermal beams, Figure 3.8 shows the ETA displacement (at the specimen edge) as a function of the specimen diameter. As one can see, the addition of heat sink beams dramatically decreases the ETA displacement. But the temperature increase at specimen edge also dramatically decreases from 823 to 21 °C (not shown, similar to Figure 3.6). Even for the largest diameter of 2 μm, the ETA still moves 0.35 μm with the presence of the heat sink beams, corresponding to a strain of 17.5% on the specimen. Therefore, the reduced loading efficiency is not an issue for nanoscale specimens (e.g., nanowires commonly with diameters less than 100 nm) or microscale specimens with relatively short length. For long microscale specimens (e.g, >> 2 μm), such reduced loading efficiency should be taken into account. FEA should be carried out to optimize the device performance (in terms of loading efficiency and temperature control) in more details.

3.2.4 Conclusions

In summary, we report experimental measurement and multiphysics modeling of the temperature profiles of a V-shaped ETA in the cases of with and without the heat sink beams. The Raman measurement of temperature agreed very well with the modeling results in air. Heat conduction through air to neighboring devices is considerable, while heat convection to
the air is negligible. Our work unambiguously demonstrated that the heat sink beams play a critical role in reducing the temperature at the specimen end in the ETA. To reach reasonably large actuator displacement while maintaining low temperature, several design guidelines are provided including more inclined thermal beams, more heat sink beams, small inclination angle, and relatively short heat sink beams. These design guidelines will be valuable to design ETAs for in-situ nanomechanical testing. It should be cautioned that while mitigating the undesired heating problem, heat sink beams also reduce the loading efficiency of the ETAs. The combined experiment-modeling methodology presented here can be applied to MEMS thermal actuators for other applications in both air and vacuum.

![Figure 3.8](image.png)

**Figure 3.8.** Displacement results of the ETA (20-9-5°-50) actuated at 6 V and being attached to a Si NW ($E_{NW} = 160$ GPa, $L_{NW} = 2 \mu$m) with different diameters. The ETA is either with (9 pairs 50 μm) or without heat sink beam.
3.3 Temperature Dependent Mechanical Behaviors of Silicon Nanowires

3.3.1 Background

As mentioned previously, controversial results have been reported in terms of brittle or ductile behavior of Si NWs at room temperature. In order to understand the BDT behavior of Si NWs of different sizes under different temperatures, it is necessary to carry out in situ mechanical testing of these samples. High quality single crystal Si NW samples synthesized via various methods provide the possibility of conducting mechanical testing at this scale. However, several challenges still remain, including manipulation and positioning of samples, high-resolution load and displacement measurements and acquiring a testing setup that allows in situ heating of NW with controllable temperature.

In this section, we first present the design of a MEMS device that can be used to conduct in situ tensile testing of Si NWs at different temperatures. In order to decouple actuation mechanism and heating mechanism, a comb drive actuator is chosen. Identical structure is designed for the sensor to get identical temperature on both ends of the NW and thus achieve uniform temperature distribution along the NW sample. Multiphysics finite element analysis (coupled electrical-thermal-mechanical) is used to optimize the structural design and minimize undesired thermal loading/unloading. A Si NW with diameter of 50 nm is later tested on the device under different temperatures. Stress strain curves at different temperatures reveal that plastic deformation occurs at temperature of 55 °C.
3.3.2 Experimental Section

Si NWs were synthesized by chemical vapor deposition (CVD) using gold nanoclusters as catalysts and silane (SiH₄) as a vapor-phase reactant following the method developed by Wu et al.⁶⁵ NWs synthesized by this method with diameters larger than 20 nm grow primarily along <111> direction, whereas the NWs with smaller diameters could have three growth directions: <110>, <112> and <111>.⁶⁵, ⁶⁶ Figure 3.9a shows a SEM image of Si NWs on substrate. Figure 3.9b shows a TEM image of a Si NW. It can be seen that the NW is not only straight but also uniform in width along the growth direction.

![SEM and TEM images of Si NWs](image)

**Figure 3.9** (a) SEM image of Si NW grown from 50 nm diameter Au nanoparticle on Si substrate. (b) Low magnification TEM image showing the surface morphology of a Si NW with diameter of 20 nm.
A MEMS device for in situ thermo-mechanical testing is shown in Figure 3.10. The device was fabricated using silicon on insulator (SOI) multi users MEMS processes (MUMPs) by MEMSCAP Inc. (Durham, NC). The thickness of the device is 10 μm. To decouple actuation mechanism and heating mechanism, a comb drive actuator was chosen, as shown on the right of Figure 3.10. A voltage between moveable combs and fixed combs will generate electrostatic force, so the movable combs move toward the fixed ones. During actuation, no heat will be generated on device. Actuation force generated can be calculated as

\[ F = \varepsilon a V^2 N / d \]  

where \( V \) is the applied voltage, \( N \) is the total number of total pair of combs, \( \varepsilon \) is the permittivity, \( d \) is the distance between fixed and movable combs, and \( a \) is the figure depth. In this design, there are total 964 combs with \( d = 2 \) μm and \( a = 10 \) μm. Thus a force of 107 μN is generated while 50 V actuation voltage is applied to the device. This force, combined with a proper stiffness (90 N/m in our case), ensures that the device is capable of stretching Si NW with diameter up to 80 nm until fracture. The parameter design was based on the mechanical properties of Si NWs measured by tension test at room temperature.[17]

To increase temperature on the sample, heating coils are electrically connected to a power supply, so the device is resistively heated. An identical structure is designed for the sensor on the left to get identical temperatures on both ends of the NW and thus achieve uniform temperature distribution along the NW sample. Temperature distribution on device and sample was analyzed by multiphysics finite element analysis, which was done using ANSYS 13.0. SOLID 98 elements coupled electrical, thermal and mechanical were used in the analysis. The input is the heating voltage across the anchor sites and the output includes
the actuator temperature and displacement fields. The thermal boundary conditions are room temperature at the anchors. Parameters used in simulation were listed in Table 3.3.

Figure 3.10. SEM image showing the fabricated MEMS comb drive tensile testing devices. Actuator is on the right and sensor on the left. Actuator and sensor has identical geometry for symmetry temperature profile consideration. There is a gap of 2 μm between actuator and sensor. Four heating coils are used to heat up the sample on sample mounting area.

A nanomanipulator (Klocke Nanotechnik, Germany) with 1 nm resolution and 1 cm travel range in three orthogonal directions was used to pick up protruding NWs from a Si
wafer and move to the sample mounting area on the device. A NW was clamped using electron beam induced carbon deposition on both ends and bridged the 2 um gap between the actuator and the load sensor, as shown in Figure 3.11. In situ SEM tensile testing was then performed at different temperatures to characterize stress strain behaviors of the NW. Force applied on the NW was obtained by measuring the displacement of sensor. Strain was calculated based on measuring the length change between two feature points, A and B, as shown in Figure 3.11.

![Figure 3.11](image.png)

**Figure 3.11** SEM image showing a Si NW with diameter of 50 nm mounting across the gap of actuator and sensor.

### 3.3.3 Results and Discussion

Figure 3.12 shows the temperature contour of the actuator when temperature on the sample testing area increases to 373 K, which corresponds to a heating voltage of 4.4 V. The highest temperature occurs on heating coil with a value of 420 K. Simulation was performed on the actuator only because the sensor has the same geometry as the actuator. Symmetry in
geometry and loading conditions ensures identical temperature distribution on sample mounting area. This leads to uniform temperature distribution along the NW. Uniform temperature distribution is important to study BDT behavior of Si NWs because local heating of samples may cause local plastic deformation. The accuracy of the temperature simulation results were verified by Raman temperature measurement as presented in previous section. Figure 3.13 shows the displacement contour of the actuator after being heated under the same heating voltage as in Figure 3.12. The displacement nonuniformity was caused by thermal expansion of the shuttle and the straight supported beams. Displacement of the device at specimen edge in the testing direction is 74 nm.

**Figure 3.12** Temperature distribution of actuator when temperature on sample testing area increases to 373 K.
Figure 3.13. Displacement contour of actuator as caused by applying heating voltage of 4.4V.

Figure 3.14. Actuator displacement as a function of actuation voltage before mounting any NW sample on the device.
Figure 3.14 shows the actuator displacement as a function of actuation voltage before mounting any NW sample on the device. By comparing the displacement difference before and after mounting a NW sample, one can calculate the force applied on the sample and then convert it to stress. Figure 3.15 shows the stress-strain behaviors of a Si NW with diameter of 50 nm under two different temperatures: room temperature (panel a) and 55 °C (panel b). At room temperature, the NW was loaded to 2.37% strain and then unloaded. It can also be seen that the loading and unloading processes followed almost the same path showing a linear elastic behavior. No residual plastic deformation was observed. Young’s modulus was obtained by least-square linear fitting of the curve. At room temperature, \( E = 175 \text{ GPa} \), which agrees well with the value obtained from uniaxial tensile tests.\(^{[17]}\) When the Si NW was loaded at 55 °C and unloaded from 4.27% strain, clear plastic deformation was observed from the unloading curve, as shown in Figure 3.15b. Young’s modulus at this temperature is around 129 GPa, which is smaller than that obtained at room temperature. A Young’s modulus decrease with increasing temperature was also observed for other small scale Si samples. Kang and Saif reported decreasing Young’s modulus with increasing temperature for a micro scale SCS sample under uniaxial tensile testing condition.\(^{[9]}\) Similar temperature dependence for Young’s modulus was also reported for millimeter-scale resonance test and micrometer-scale bending to stretch test.\(^{[7, 10, 67]}\) Our work is consistent with these findings. One possible reason is the interatomic bond distance of Si increasing due to thermal vibration, and Young’s modulus is associated with bonding force between atoms, which is changing with interatomic distance.
Figure 3.15. Stress strain curve of Si NW under (a) room temperature and (b) 55 °C. Dash line shows the linear fitting to (a) loading and unloading data with slope E= 175 GPa, and (b) loading data with slope E= 128.6 GPa.

Our in situ thermal-mechanical testing on the Si NW indicates that BDT temperature for SCS at this size is around 55 °C, which is about 30 °C higher than room temperature. On the other hand, Si NW shows pure elastic behavior at room temperature, this is consistent with the report of Zhu et al. [17] for in situ SEM testing of Si NWs with size less than 100 nm. They reported that for Si NW with diameters as small as 15 nm still showed linear elastic behavior at room temperature. Based on Kang and Cai’s [25] MD study of mechanical properties of Si NW, plastic deformation can only be observed on NW with a diameter less than 4 nm. Our unaxial tensile testing with elevated temperature confirms that temperature is an important factor to observe plastic deformation on Si NWs. Surface effects become dominant for NW due to very large surface-to-volume ratio, and dislocation nucleated from surface likely requires less energy than that nucleated in the bulk. As mentioned previously,
critical to the achievement of plastic deformation in brittle solids is a sufficiently high stress to exceed the Peierls barrier for dislocation nucleation and/or motion. As we can see from the stress strain curve, the stress in the Si NW tested was as high as 5 GPa. High stress state on NW would lower the dislocation nucleation energy and thus facilitate dislocation nucleation even at relative low temperature.

3.3.4 Conclusions

In summary, we designed a MEMS device that can be used to conduct in situ tensile testing of Si NWs at different temperatures. In order to decouple actuation mechanism and heating mechanism, the comb drive actuator was chosen instead of thermal actuator. Identical structure was designed for the sensor to get identical temperature on both ends of the NW and thus to achieve uniform temperature distribution along the NW sample. Mutiphysics finite element analysis (coupled electrical-thermal-mechanical) was used to optimize structure design and minimize undesired thermal loading/unloading. A Si NW with diameter of 50 nm is later tested on the device under different temperatures. Stress strain curves at different temperatures reveal that plastic deformation occurs at temperature of 55°C.
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[16]. M. S. Steighner; Snedeker, L. P.; Boyce, B. L.; Gall, K.; Miller, D. C.; Muhlstein, C. L., Dependence on diameter and growth direction of apparent strain to failure of Si nanowires, *Journal of Applied Physics* 2011, 109, 033503.


Chapter 4

Interfacial Mechanics of One Dimensional Nanomaterials

4.1 Friction and Shear Strength at the Nanowire-Substrate Interfaces

4.1.1. Background

In nanodevices, NWs are typically integrated to larger structures. The NW-substrate interfaces, therefore, play a critical role in both mechanical reliability and electrical performance of these nanodevices. Such interfaces include two configurations, NW length or NW tip, in contact with the substrate, and both configurations have a wide range of applications. For example, the tip-substrate contacts are present in nanogenerators, nanostructured solar cells, AFM with carbon nanotube (CNT) tips, CNT tapes and many other nanodevices. Indeed, as recently outlined by Wang, one critical future direction for nanogenerator research is study of the NW-metal interface to build a robust, low wearing structure for improving the device lifetime.

Experimental work on NW interfacial mechanics has been limited so far due to experimental challenges at the nanoscale and the fact that many existing tribology tools such as AFM, surface force apparatus (SFA), quartz microbalance and microfabricated devices cannot be readily applied. Static friction force between NWs (including CNTs)
and substrates was estimated from the highly deformed shapes of NWs.\cite{11} Recently CNTs were found to slip on silicon oxide surface at 8 nN,\cite{12} and ZnO NWs to slip on silicon surface at a few \(\mu\)N.\cite{13} However, the above studies on friction are only limited to the configuration of NW length in contact with a substrate. To the best of our knowledge, no experiments have been reported to investigate the configuration of an individual NW tip in contact with a substrate.

In this thesis, we report the first experimental study on the friction between NW tips (ends) and a substrate. Silver and ZnO NWs with a gold-coated substrate were studied as model systems in view that silver and ZnO NWs have very different tip shapes. Silver NW is an important class of metallic NWs because of its potential use as interconnects in view that bulk silver exhibits very high electrical and thermal conductivity.\cite{14} ZnO is one of the most important semiconductor NWs with a broad range of applications including nanogenerators, biosensors, nanolasers and nanoelectromechanical systems (NEMS).\cite{15} The friction measurements reported in this paper were enabled by an innovative experimental method based on column buckling theory. The experiments were conducted \textit{in-situ} inside a scanning electron microscope (SEM) using a nanomanipulator as the actuator and an AFM cantilever as the force sensor.

\subsection*{4.1.2. Experimental section}

The Ag NWs were synthesized using a seed-assisted, solution-phase method with a five-fold twinned structure.\cite{16} Figure 4.1a is a TEM image showing the NW tip. Figure 4.1b and 4.1c are high-resolution TEM images showing a layer of silver oxide with varying
thickness on the NW surface. The ZnO NWs were synthesized using the vapor-liquid-solid (VLS) method with a wurtzite structure and growth direction of [0001].\textsuperscript{17} Figure 4.1d is a SEM image showing the tip of a ZnO NW, which appears to be flat.

![Figure 4.1](image1.png)

**Figure 4.1.** (a-c) TEM images of a silver NW. (b) and (c) show an oxide layer on the surface of the silver NW. (d) SEM image of a ZnO NW.

*In situ* SEM buckling tests of NWs were conducted as shown in Figure 4.2. A nanomanipulator (Klocke Nanotechnik, Germany) that possesses 1 nm resolution in three orthogonal directions was used to pick up individual NWs.\textsuperscript{18,19} A NW was clamped onto the tungsten tip on the nanomanipulator using electron beam induced deposition (EBID) of carbon. Then the NW was approached to make contact with an AFM cantilever (OBL-10, Veeco). Carbon deposition was not employed at the NW-cantilever interface. Compressive force was applied to the NW by the nanomanipulator movement, which led to buckling of the
NW. In this case, the boundary condition was fixed-pinned. Continued loading further changed the postbuckling shape of the NW until sliding occurred at the NW-cantilever interface.

**Figure 4.2.** Buckling process of an individual NW. (a) is before buckling and (b) is after buckling and just prior to sliding on the right end.

After buckling of the NW, there exist two forces at the NW-substrate interface, a compressive (normal) force and a frictional (lateral) force. The compressive force on the NW can be easily measured from the deflection of the AFM cantilever; however it is not trivial to measure the friction force. Below we describe a method to measure friction force based on the buckling theory. A free-body diagram of a buckled member under fixed-pinned boundary condition is shown in Figure 4.3a, with the left end fixed and the right end pinned. A small lateral deflection gives rise to a moment $M$ at the fixed end and shear force (friction force) $F$ at each end of the member. From the moment balance, it can be easily obtained that $F = M / L$, where $L$ is the length of the member. The governing equation at a section with a distance $x$ from the right end is given by
\[ y'' + k^2 y = \frac{M}{EI} \frac{x}{L} \quad 4.1 \]

where \( k^2 = \frac{P}{EI} \), \( E \) is the Young’s modulus and \( I \) is the moment of inertia. The solution to Equation 4.1 is

\[ y = A \sin kx + B \cos kx + \frac{M}{P} \frac{x}{L} \quad 4.2 \]

Taking into account the fixed-pinned boundary condition, we obtain

\[ y = \frac{M}{P} \left[ \frac{x}{L} + 1.02 \sin(4.49 \frac{x}{L}) \right] \quad 4.3 \]

Equation 4.3 describes the shape of the member in the postbuckling stage. Details on the equation derivation can be found elsewhere.\[20\] Equation 4.3 provides the theoretical basis of our method to measure the friction force. By fitting the observed shape of the NW just prior to sliding to Equation 4.3 using the nonlinear least squares method, \( M \) can be determined since \( P \) is measured from the deflection of the AFM cantilever. Then \( F \) can be obtained using \( F = \frac{M}{L} \). Figure 4.3b shows the fitting of a deformed NW to Equation 4.3. Clearly the agreement is very good.

**4.1.3. Results and discussion**

Following the method described above, three silver NWs and three ZnO NWs were tested for friction measurements. The Amonton–Coulomb friction law is written as \( F = \mu P \), where \( \mu \) is the so-called coefficient of friction. The normal force, friction force and coefficient of friction for all six NWs are listed in Table 4.1. Note that these NWs did not break in the buckling experiments so that each NW was tested multiple times with very good
repeatability. However, the Amonton–Coulomb law was obtained from empirical observations with many counterexamples; for instance, geckos are able to move on walls and ceilings when $P \leq 0$. A more fundamental friction law that links friction and adhesion was proposed by Bowden and Tabor,

$$F = \tau A \quad \text{(4.4)}$$

where $\tau$ is the interfacial shear strength and $A$ is the true contact area. This law has been supported by numerous SFA and AFM experiments. The two theories were reconciled by considering the multiple asperities among the contacting surfaces; as a result, the true contact area is typically proportional to the normal force.

![Free-body diagram of a buckled column with fixed-pinned boundary condition](image1)

![Nonlinear least squares fitting of Eq. (3) to digitized shape of a NW prior to sliding](image2)

**Figure 4.3.** (a) Free-body diagram of a buckled column with fixed-pinned boundary condition. (b) Nonlinear least squares fitting of Eq. (3) to digitized shape of a NW prior to sliding.
The NW-substrate contact is treated as the single-asperity contact because the NW diameters are smaller than the wavelength of the substrate topography. In order to evaluate interfacial shear strength using Equation 4.4, the true contact area must be determined. In our experiments as well as AFM experiments, the true contact area is calculated using continuum mechanics models. The well-known Hertzian model does not take into account attractive adhesion forces between the contacting surfaces. Other widely-accepted models that take adhesion force into account are due to Johnson, Kendall, and Roberts (JKR),\(^{[23]}\) Derjaguin, Mutter, Toporov (DMT)\(^{[24]}\) and Maugis,\(^{[25]}\) respectively.

**Table 4.1.** Normal force, friction force and coefficient of friction in each experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silver 1</th>
<th>Silver 2</th>
<th>Silver 3</th>
<th>ZnO 1</th>
<th>ZnO 2</th>
<th>ZnO 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal force (P) (nN)</td>
<td>263</td>
<td>277</td>
<td>465</td>
<td>186</td>
<td>203</td>
<td>215</td>
</tr>
<tr>
<td>Friction force (F) (nN)</td>
<td>32.5</td>
<td>31.7</td>
<td>40.0</td>
<td>18.6</td>
<td>30.8</td>
<td>21.1</td>
</tr>
<tr>
<td>Coefficient of friction (\mu)</td>
<td>0.12</td>
<td>0.11</td>
<td>0.09</td>
<td>0.10</td>
<td>0.15</td>
<td>0.10</td>
</tr>
</tbody>
</table>

For simplicity, the continuum models typically assume the contact between a sphere and a flat surface. It is known that the JKR and DMT theories are two extremes of a spectrum of elastic solutions determined by the Tabor parameter,\(^{[26]}\) which is given by

\[
\mu = \left( \frac{16R\gamma^2}{9K^2z_0^3} \right)^{1/3}
\]

4.5
where $R$ is the radius of the sphere, $K$ is the reduced modulus of two materials

$$K = 4/3[(1-v_1^2)/E_1 + (1-v_2^2)/E_2]^{-1}$$

with $E_1$ and $E_2$ the respective Young’s moduli, and $v_1$ and $v_2$ the respective Poisson’s ratios, $z_0$ is the interatomic equilibrium distance (= 0.2 nm), $\gamma$ is the interfacial energy per unit area (work of adhesion). Each NW tip was fitted with a sphere. When $\mu > 5$, the JKR model is valid; when $\mu < 0.1$, the DMT model should be applied; in the intermediate range, the Maugis model becomes appropriate. In all our experiments $2.05 < \mu < 2.39$ (see Table 4.2), so the Maugis model should be used. However, the Maugis model does not have an explicit expression for contact radius. For the Tabor parameter in this range, the JKR model was found to approximate the Maugis solution very closely,[27] therefore the JKR model was used in our calculation due to its simplicity.

Following the Hertz and JKR models, the contact radius $a$ as a function of the externally applied load $P$ is given by

$$a = \left[\frac{PR}{K}\right]^{1/3} \quad 4.6a$$

$$a = \left[\frac{R}{K}\left(P + 3\gamma\pi R + \sqrt{6\gamma\pi RP + (3\gamma\pi R)^2}\right)^{1/3}\right] \quad 4.6b$$

respectively, where $\gamma = \gamma_1 + \gamma_2 - \gamma_{12} \approx 2\sqrt{\gamma_1\gamma_2}$ with $\gamma_1$ and $\gamma_2$ the respective surface energy and $\gamma_{12}$ the interface energy. $\gamma_1 = 1.37 \text{J/m}^2$ for gold, $\gamma_2 = 0.8 \text{J/m}^2$ for silver oxide[28] and $\gamma_2 = 1.74 \text{J/m}^2$ for ZnO with {0001} surface.[29] Therefore, $\gamma = 2.09 \text{J/m}^2$ and $\gamma = 3.09 \text{J/m}^2$ for the contacts between gold and silver oxide and between gold and ZnO, respectively. In addition, $E_{\text{gold}} = 78 \text{GPa}$, $E_{\text{silver}} = 84 \text{GPa}$, $E_{\text{ZnO}} = 140 \text{GPa}$, $\nu_{\text{gold}} = 0.44$, $\nu_{\text{silver}} = 0.35$, and $\nu_{\text{ZnO}} = 0.26$. 

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\[ \nu_{\text{silver}} = 0.37, \ \nu_{\text{ZnO}} = 0.30. \] The contact radius, contact pressure and interfacial shear strength calculated using the two models are listed in Table 4.2. It can be seen that the interfacial shear strengths between silver NW and gold substrate and between ZnO NW and gold substrate are 134-139 MPa and 78.9-95.3 MPa, respectively. These values are in good agreement with those obtained from AFM and mesoscale friction tester in similar environment (vacuum or dry).\(^{[31]}\)

**Table 4.2.** Contact pressure and interfacial shear strength using the Hertz and JKR models.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silver 1</th>
<th>Silver 2</th>
<th>Silver 3</th>
<th>ZnO 1</th>
<th>ZnO 2</th>
<th>ZnO 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tip radius (R) (nm)</td>
<td>27</td>
<td>27</td>
<td>29</td>
<td>25</td>
<td>40</td>
<td>25</td>
</tr>
<tr>
<td>Tabor’s parameter</td>
<td>2.28</td>
<td>2.28</td>
<td>2.33</td>
<td>2.05</td>
<td>2.39</td>
<td>2.05</td>
</tr>
</tbody>
</table>

**Hertz model**

<table>
<thead>
<tr>
<th>Contact radius (a) (nm)</th>
<th>4.79</th>
<th>4.87</th>
<th>5.93</th>
<th>3.90</th>
<th>4.69</th>
<th>4.09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact pressure (GPa)</td>
<td>3.65</td>
<td>3.72</td>
<td>4.21</td>
<td>3.90</td>
<td>2.94</td>
<td>4.09</td>
</tr>
<tr>
<td>Shear stress (\tau) (MPa)</td>
<td>451</td>
<td>425</td>
<td>362</td>
<td>390</td>
<td>445</td>
<td>402</td>
</tr>
</tbody>
</table>

**JKR model**

<table>
<thead>
<tr>
<th>Contact radius (a) (nm)</th>
<th>8.64</th>
<th>8.68</th>
<th>9.58</th>
<th>8.32</th>
<th>11.1</th>
<th>8.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact pressure (GPa)</td>
<td>1.21</td>
<td>1.17</td>
<td>1.61</td>
<td>0.86</td>
<td>0.52</td>
<td>0.97</td>
</tr>
<tr>
<td>Shear stress (\tau) (MPa)</td>
<td>139</td>
<td>134</td>
<td>139</td>
<td>85.6</td>
<td>78.9</td>
<td>95.3</td>
</tr>
</tbody>
</table>
Several issues related to the experiments and analyses are discussed. First of all, our measurements showed that no metallic bonding formed between silver NWs and the gold substrate as the strength of metallic bonding is typically on the order of GPa. This is due to the presence of a thin layer of silver oxide, as shown in the high-resolution TEM images (Figure 4.1). Second, it is not appropriate to treat the ZnO NWs as the molecular junctions where the contact areas remain constant (in our case the NW cross sections), otherwise the interfacial shear strength would be too small. This is reasonable because it is very likely that the NW is not perfectly perpendicular to the substrate. The edge of the NW tip is in contact with the substrate, and the contact area can then be approximately fitted with a sphere. Third, previous experiments showed that electron beam increases adhesion force between semiconductors and metals. For contacts between ZnO NW tips and a gold substrate, we found a similar trend. The adhesion force increased from 30 nN to about 240 nN when contact time increased to 10 minutes; but the adhesion force did not show any noticeable change when the contact time was short (e.g., less than 10 seconds). Last, although our experimental method is innovative, giving rise to the first measurement of the friction data between NW tips and a substrate, we are aware that it cannot measure the friction as a function of the progressively-applied normal force. MEMS devices with normal and lateral force measurement capability are under development to address this issue.

Our results on interfacial friction and shear strength could have direct implication on the AFM three-point bending tests that are widely used in extracting mechanical properties of one-dimensional nanostructures including CNTs and NWs. Often the adhesion between the NWs and the substrate is assumed to be strong enough to provide a fixed–fixed boundary
condition for the three-point bending tests. The assumption is valid for NWs with small diameters; for those with large diameters, it could lead to large data scattering as typically observed in experiments. Our results could be incorporated into data reduction in the three-point bending experiments to quantify the influence of adhesion and friction on the measured mechanical properties. Other methods that could also be used to eliminate the ambiguity caused by the NW–substrate friction in the three-point bending tests include EBID of platinum or carbon to reinforce the clamps.\cite{39}

4.1.4. Conclusions

In summary, a new experimental method to measure the friction between a NW tip and a substrate has been developed. Silver and ZnO NWs were tested with a gold coated surface as the substrate. The coefficients of friction between silver NW and gold substrate and between ZnO NW and gold substrate were found to range from 0.09 to 0.12 and from 0.10 to 0.15, respectively. The adhesion between NWs and the substrate substantially modified the true contact area, which in turn affected the interfacial shear strength significantly. According to the calculated Tabor parameter, the JKR model was selected to approximately calculate the contact area and the interfacial shear strength. The interfacial shear strengths between silver NW and gold substrate and between ZnO NW and gold substrate ranged from 134 to 139 MPa and from 78.9 to 95.3 MPa, respectively. These values are in good agreement with previous results obtained in similar environments (vacuum or dry).\cite{31}
4.2 Static Friction between Silicon Nanowires and Elastomeric Substrates

4.2.1 Background

1D nanomaterials have been used in a broad range of flexible/stretchable technologies ranging from photovoltaics and electronics to sensors and energy harvesting/storage. In these flexible technologies, nanomaterials are typically bonded onto polymeric or plastic substrates. In addition to the competent electronic performance of these nanomaterials, their flexibility and interface interactions with the substrate also play important roles. Si NWs are one of the key building blocks for nanoscale electronic, photonic and electromechanical devices. For stretchable electronics, buckling induced coiled or wavy shape of Si NWs on elastomeric substrates offers an effective approach to increase the stretchability of the devices. In this case, the static friction (in the horizontal direction in contrast to the commonly used adhesion that is in the vertical direction) plays the key role in holding the NWs in their deformed shapes. In addition, scalable assembly of NWs is an enabling step for fabricating integrated, functional devices. The static friction between NWs and substrates is also critical in the NW assembly process. Si NWs have been found to possess excellent mechanical properties including flexibility/stretchability. However, the surface interaction between Si NWs and elastomeric substrates is largely unknown.

AFM based single-asperity measurements have seen significant progress in nanoscale interface mechanics. However, mechanics studies on the interfaces between 1D nanomaterials and substrates are limited. For adhesion measurement, AFM or
nanomanipulators were used to conduct peeling tests of nanostructures from a substrate or from each other\textsuperscript{[53, 54]} for kinetic friction measurement, AFM or microfabricated devices were used to slide nanostructures on a substrate and record the friction force\textsuperscript{[113, 55]} for static friction measurement, AFM or nanomanipulators were employed to manipulate/deform nanostructures either parallel or normal to a substrate\textsuperscript{[8, 11, 19, 56-58]}

In this thesis, we report direct measurements of the static friction force and interfacial shear strength between Si NWs and poly(dimethylsiloxane) (PDMS) for the first time. A micromanipulator was used to manipulate and deform the NWs under a high-magnification optical microscope. The static friction force was measured based on “the most-bent state” of the NWs\textsuperscript{[56]} The static friction and shear strength were found to increase rapidly and then decrease with the increasing ultraviolet/ozone (UVO) treatment of PDMS. Water contact angle on PDMS was independently measured as a function of the UVO treatment time which suggested that the UVO-induced hydrophobic-to-hydrophilic conversion of PDMS surface was responsible for the increase in static friction, while the hydrophobic recovery effect contributed to the decrease. PDMS possesses a unique combination of material properties including high stretchability over a wide temperature range, low toxicity, high electrical resistance and long-term endurance, which makes it an important substrate material for flexible technologies\textsuperscript{[40, 59]} The experimental method presented in this paper can be easily extended to other types of substrates (e.g., plastics).
4.2.2 Experimental section

Si NWs were synthesized on Si substrates by chemical vapor deposition (CVD) using gold nanoclusters as catalysts and SiH₄ as a vapor-phase reactant, following the method reported previously. PDMS substrates with a thickness of 2 mm were prepared using ‘Sylgard 184’ (Dow Corning) by mixing the ‘base’ and the ‘curing agent’ with a ratio of 10:1. The mixture was first placed in a vacuum oven to remove air bubbles, and then cured at 65 °C for 12 hours. Rectangular slabs of suitable sizes were cut from the cured piece.

NW manipulation was performed in ambient conditions on a probe station. A tungsten probe was mounted to the micromanipulator, which can move in three directions. Every NW was bent beyond the most-bent state and then relaxed to the most bent state after retracting the manipulator probe (Figure 4.5). The competition between lateral friction force and elastic restoring force brings the NW back to an equilibrium state. Most NWs used in this study ranged from ~4 to ~8 μm in length.

The PDMS slabs were radiated under the UV lamp (low-pressure mercury lamp, 30 µW/cm² for 254 nm and 16 µW/cm² for 185 nm at the distance of 20 cm from the lamp, BHK) with the assistance of UV-generated ozone. UVO treatment is a photosensitized oxidation process in which the molecules of the treated material are excited and/or dissociated by the absorption of short-wavelength UV radiation. The UV light induced ozone converts the unmodified hydrophobic surface of PDMS dominated by -Si(CH₃)₂O- groups, to a highly polar and reactive surface terminated with silanol groups (−SiOH). In addition, the UVO treatment generates a silica-like layer (SiOₓ containing a small amount of carbon) on the surface of PDMS.⁶¹⁻⁶³
The water contact angle was measured using the sessile drop method. The experiments were performed using a simple custom-made setup that includes a CCD camera, a horizontal stand, a light source, a syringe and syringe holder. PDMS samples were placed on the horizontal stand. The syringe was fixed vertically about 4 mm on top of the PDMS surface using the syringe holder. Contact angle was measured by applying a single drop of deionized (DI) water to the PDMS surface. Each data point reported in this paper represents an average of five measurements on different areas of the same sample and has an error less than ±2.5°.

4.2.3 Results and discussion

A contact printing method was used to dry transfer the Si NWs\textsuperscript{[44, 48]} to the PDMS substrates. Subsequently, the friction measurements were carried out in a probe station (Micromanipulator 6200) under ambient conditions (with temperature of the laboratory ~23°C and the relative humidity ~50%). A tungsten probe was manually controlled to manipulate and deform NWs; the resolution of probe movement in all three orthogonal directions is 0.5 μm. The entire process was monitored under an optical microscope (1000× magnification). AFM (XE70, Park Systems) was used to take high-resolution images of the NWs before and after the manipulation. Figure 4.4 shows a typical NW manipulation process: (a) - (d) are optical images; (e) and (f) are AFM images corresponding to (a) and (d), respectively. The arrows indicate where the probe pushed the NW. The NW was progressively bent until a critical state was reached, which is “the most-bent state”. The shape of the NW results from competition between the elastic restoring force of the NW and the static friction at the
NW/substrate interface.\textsuperscript{[11,56]} At the critical state, the elastic restoring force is in equilibrium with the lateral static friction force along the NW. In order to ensure our NWs reached “the most-bent state”, we always bent them beyond this state (certainly without breaking them), as shown in Figure 4.5a. Upon retraction of the manipulator tip, the elastic restoring force was large enough to bring the NWs back to equilibrium, as shown in Figure 4.5b. The resolution of our micromanipulator (0.5 μm in this work) was not as fine as AFM but sufficient for our purpose, because we always pushed a NW beyond “the most-bent state” and let the NW itself relax back. The advantage, however, was the real-time observation and easy control of the manipulation process.

Figure 4.4. Optical and AFM images showing the manipulation process of a NW. (a) ~ (d) are optical images; (e) and (f) are AFM images corresponding to (a) and (d), respectively.

In the following section, we analyze the static friction force from “the most-bent state”.\textsuperscript{[57]} This method assumes that bending deformation contributes predominantly to the
strain energy, while the contributions due to axial stretching and transverse shear are negligible. In addition, this method assumes the NW slopes and curvatures are smooth (i.e., no fracture or kinking), which is true for all the NWs in our experiments (as shown in Figure 4.6a). This is because Si NWs possess a large fracture strain as found in our previous work.¹⁹

![Image](152x422 to 312x582)

**Figure 4.5.** Two consecutive optical images from the last step of a manipulation process showing a Si NW (a) beyond “the most-bent state” and (b) at “the most-bent state” after retracting the manipulator probe. The competition between lateral friction force and elastic restoring force brings the NW back to an equilibrium state.

In this method, the image of a bent NW was digitized using DataThief software⁶⁴ to obtain the Cartesian coordinates \((x, y)\) of each centerline point along the NW. The curvature along the length of the NW is given by

\[
\frac{d\theta}{ds}(s) = \frac{1}{\rho(s)} = \sqrt{\left[\frac{d^2x}{ds^2}(s)\right]^2 + \left[\frac{d^2y}{ds^2}(s)\right]^2}
\]

(1)

where \(\theta(s)\) is the angle between \(ds\) and \(dx\) as indicated in Figure 4.6(a). With the curvature along the NW known, the strain energy distribution per unit length, as shown in Figure 4.6b, is calculated.
Figure 4.6. (a) AFM image of a NW at “the most-bent state”, where the data points were digitized using Datathief. The geometric relationship was shown in the inset. (b) and (c) are strain energy and lateral friction force distribution along the NW shown in (a), respectively.
\[ U_s(s) = \frac{EI}{2} \left[ \frac{d\theta}{ds}(s) \right]^2 \]  

where \( E \) is the elastic modulus and \( I \) is the moment of inertia of the NW \( (I = \frac{5\sqrt{3}}{144} D^4, \ D \) is the diameter of the NW). Considering the size effect on the elastic modulus of Si NWs, the size-dependent modulus is used in our analysis.\textsuperscript{[19]} Note that Si NWs in this work are oriented in the [111] direction and possess hexagonal cross sections.\textsuperscript{[19, 60]} \( D \) is the height of the NW (distance between two parallel edges of the hexagon) as measured by AFM. The lateral friction force per unit length, as shown in Figure 4.6c, is related to the third derivative of \( \theta(s) \), viz.,

\[ f(s) = -EI \frac{d^3\theta}{ds^3}(s) \]  

The static friction force per unit length \( (F) \) is the maximum lateral friction force along the length of the NW at “the most-bent state”. The interfacial shear strength \( (\tau) \) is the static friction force per unit length divided by the contact width. A key step in this analysis method is the numerical differentiation (derivative) as involved in all three equations. The data is smoothed using a five-point moving average method before the numerical differentiation;\textsuperscript{[65]} the first derivative data is also smoothed using the five-point moving average method before the second derivative; this process is repeated until the third derivative of \( \theta(s) \) is obtained.

Figure 4.7a shows the static friction force per unit length between Si NWs and PDMS as a function of UVO treatment time. For each treatment time, three to five NWs were tested. All the NW diameters \( (D) \) ranged from 35 to 55 nm. For treatment time less than 20 minutes, the friction force increased modestly from 0.006 to 0.06 N/m. When the treatment time
increased from 20 to 45 minutes, a rapid increase in friction force was observed. The friction
force decreased for longer treatment time (beyond 60 minutes). In addition, no dependence
on the NW orientation on the substrate was found in all our experiments.

Figure 4.7. (a) Static friction force and (b) interfacial shear strength between Si NWs and
PDMS substrate at different UVO treatment times.
To calculate shear strength between Si NWs and PDMS, one needs to determine the true contact area between them, which is nontrivial.\textsuperscript{[10]} Since the NWs are long and compliant, they are expected to have intimate contact with the substrate,\textsuperscript{[13]} especially considering the roughness of the PDMS substrate before or after the UVO treatment is very small (as shown in Figure 4.8). In addition, our measurement is local in nature; the static friction (i.e., maximum lateral friction as measured following Eq. 3) is expected to occur at a specific location. Therefore, we assume the contact area is the flat side surface of the NW.

The Si NWs in our work are oriented in the <111> axial direction with hexagonal cross sections\textsuperscript{7, 29}. The shear strength $\tau$ was obtained by setting the contact width $w = D/\sqrt{3}$ (for hexagonal cross sections). The maximum shear strength was \textit{ca.} 10.57 MPa at 60 minutes of UVO treatment, as shown in Figure 4.7b.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_8.png}
\caption{(a) A typical AFM image (in non-contact mode) showing the surface topography of PDMS. (b) Surface roughness ($R_q$) of PDMS as a function of the UVO treatment time.}
\end{figure}
PDMS is a silicon-based rubber material with highly hydrophobic surfaces. Various techniques have been utilized to modify the surface properties of PDMS.\(^{[66, 67]}\) As part of the oxygen plasma treatment family, UVO treatment converts the \(\text{–OSi} (\text{CH}_3)_2\text{–}\) groups on PDMS surface into \(\text{–O}_n\text{Si(OH)}_{4-n}\text{ terminated groups}\)\(^{[59]}\) and forms a thin and brittle silica-like layer on the surface. The increase of silanol groups (Si–OH) is at the expense of methyl groups (–CH\(_3\)); X-ray photoelectron spectroscopy (XPS) study of atomic composition of PDMS surface revealed that the carbon content decreased, the oxygen content increased, while the silicon content remained almost unchanged with increasing exposure time.\(^{[68-70]}\) As silanol groups are polar in nature, UVO treated PDMS surface becomes highly hydrophilic and can react with various inorganic surfaces such as glass, silicon, silicon oxide and quartz to form strong siloxane (Si–O–Si) bonds through condensation reactions.\(^{[59]}\) UVO treatment is very similar to the oxygen plasma treatment in the surface modification of PDMS, except that UVO treatment is a much milder process. UVO treatment of PDMS has been widely used in sealing microfluidic channels,\(^{[59]}\) increasing adhesion force for soft lithography\(^{[71]}\) and fabricating stretchable electronic devices.\(^{[72]}\)

Without UVO treatment, the interaction between Si NWs and PDMS was based on van der Waals force. The shear strength value measured in our experiments (0.30 MPa) is much smaller than those obtained with AFM measurements.\(^{[10, 31]}\) On the other hand, in several experiments with pushing nanoparticles or NWs on substrates, values as small as 0.05 – 1 MPa were indeed reported.\(^{[55, 73, 74]}\) Moreover, our results are in close agreement with the static friction measurements between InAs NWs and silicon oxide or silicon nitride substrates.\(^{[11, 56]}\) With the UVO treatment, the interaction was based on chemical bonding
(siloxane bond). The concentrations of the surface methyl groups and siloxane bonds
decreased and increased, respectively, in an exponential fashion with the UVO treatment
time.\cite{61} This agreed very well with the rapid increase in the shear strength for UVO
treatment up to 30 minutes as observed in our case.

The effect of UVO treatment on PDMS was independently investigated by water
contact angle measurements. The change of water contact angle is directly related to the
concentration of surface hydrophilic functional groups.\cite{75} Figure 4.9a shows water contact
angle as a function of the UVO treatment time. For a given treatment time, the contact angle
was measured three times, zero (immediately), two and four hours after the treatment,
respectively. Two and four hours were chosen here since the manipulation process of NWs
(for friction measurement) typically took two to four hours. The water contact angle
decreased with the increase of UVO treatment time. A decrease of the contact angle is
indicative of the increase of the hydrophilic groups on the surface\cite{62, 68, 76} and thus the
increase of chances to form chemical bonds with Si NWs. The contact angle measurement
was consistent with our friction force measurement. Figure 4.9b plots shear strength as a
function of water contact angle (average value of the two- and four-hour post-treatments).
This confirmed that the increase of hydrophilic groups on a PDMS surface was responsible
for the increase in static friction force and shear strength. The bond strength and water
contact angle between plasma treated PDMS and glass showed similar relationship at
relatively short treatment time.\cite{77} We note that relatively large scatter in the shear strength
exists for the water contact angle between 60 and 70°. For this range of water contact angle,
the UVO treatment time was quite long (45, 60, 75, and 90 min), and the hydrophobic
recovery effect (to be discussed) was pronounced. The water contact angle was highly dependent on the post-treatment time especially for the long UVO treatment time (see Figure 4.9a). The NW manipulation process typically took 2-4 h. It is likely that the large scatter is due to the uncertainty in the post-treatment time when the NW manipulation was conducted.

Figure 4.9. (a) (Left) water contact angle as a function of UVO treatment time and (right) images showing water contact angles at different treatment times (immediately after UVO treatment). (b) Shear strength as a function of water contact angle. The water contact angle is the average value of those two and four hours after UVO treatment. The increase of shear strength is in line with the decrease of water contact angle.
It is interesting to note that the friction force and shear strength decreased for UVO treatment over 60 minutes. A similar behavior was observed previously in the bond strength between plasma treated PDMS and glass;\cite{77, 78} it was attributed to the formation of cracks on the PDMS surface and the increase in surface roughness when overexposed. We characterized UVO treated PDMS surface with AFM and scanning electron microscopy (SEM); however, no crack was found for a treatment time up to 120 minutes, as shown in supporting materials Figure 4.10. Non-contact AFM imaging of UVO treated PDMS revealed that surface roughness ($R_q$) actually decreased for short treatment time and remained nearly constant for longer treatment time, as shown in supporting materials Figure 4.8. For each treatment time, the roughness data was obtained from at least three different locations on the surface. Our results ruled out the contributions of cracks and increasing surface roughness to the observed decrease of friction force.

![Figure 4.10](image)

**Figure 4.10.** SEM images showing the surface of PDMS used in the friction measurements (a) without UVO treatment and (b) with UVO treatment for 120 minutes. No cracks were observed in all the PDMS surfaces after UVO treatment.
Surface hydrophobic recovery is likely the major mechanism for the decrease in friction force at longer treatment time. Free low-mass-molar chains, which are formed by chain scission reactions during the UVO treatment or intrinsically present as residues from the polymerization in PDMS preparation, could migrate to the surface after the treatment. Excessive silanol bonds on the surface lead to surface chain scission reactions and reduce the number of silanol bonds. As a result, the density of the siloxane bonds with Si NWs decreases and so does the static friction. Such an effect becomes more pronounced with the increasing post-treatment time. Surface hydrophobic recovery has been observed by the water contact angle measurement and XPS study. Our water contact angle measurements also revealed such a recovery effect, see Figure 4.9a. The recovery effect was dependent on the post-treatment time in addition to the treatment time. The recovery effect was stronger for longer treatment time; for the same treatment time, the recovery effect increased with the increasing post-treatment time. For UVO treatment longer than 60 minutes, the recovery effect was so pronounced that the contact angle even started increasing after two hours of post-treatment. The water contact angle measurements strongly suggested that surface hydrophobic recovery was responsible for the observed decrease of friction force.

4.2.4 Conclusions

We have reported direct measurements of static friction force and interfacial shear strength between Si NWs and PDMS substrate. UVO treatment was found to convert the unmodified hydrophobic surface of PDMS to a highly polar and reactive surface, which formed strong siloxane bonds with Si NWs. As a result, the static friction force increased to
the maximum value of ~0.236 N/m at ~60 minutes of UVO treatment, corresponding to the shear strength of 10.57 MPa. The effect of hydrophobic recovery of the treated PDMS surface contributed to the decrease in friction force at longer treatment times. The static friction between NWs and PDMS plays a critical role to hold the NWs in deformed shapes, which is important for a variety of applications ranging from NW assembly to NW-based flexible electronics and sensors to nanocomposites (e.g., supercapacitors). Our measurements will contribute to rational interface design and control for such applications. Furthermore, quantifying the effect of UVO treatment on PDMS provides valuable guidelines for selectively tuning the interactions at NW/PDMS interfaces, which might provide a simple route for patterned printing of NWs on PDMS. The methodology presented in this study can be used to investigate static friction between other types of 1D nanomaterials (e.g., carbon nanotubes) and substrates (e.g., plastics).
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Chapter 5

Conclusions and Future Work

5.1 Conclusions

In this thesis, we focus on the mechanical properties of three important 1D nanomaterials: ZnO NWs, Ag NWs and Si NWs. From experimental point of view, we improved existing nanomaterial mechanical testing techniques, and developed a new testing device for in situ SEM mechanical testing under controllable temperatures. We studied the size and temperature effects on the mechanical properties of these three nanomaterials. We also presented the interfacial mechanics study of these NWs. Following are the conclusions made through this work:

(1) Elastic and failure properties of ZnO NWs under different loading modes were measured.

In situ SEM tension and buckling tests on single ZnO NWs were conducted. Both tensile modulus (from tension) and bending modulus (from buckling) were found to increase as the NW diameter decreased from 80 to 20 nm. The bending modulus increased more rapidly than the tensile modulus, which demonstrates that the elasticity size effects in ZnO NWs are mainly due to surface stiffening. Both the core-surface model and core-shell model were used to fit the experimental data very well. The tension experiments also showed that fracture strain and strength of ZnO NWs increased as the NW diameter decreased. In particular the buckling test was demonstrated to be an effective method for evaluating elastic modulus of individual NWs under bending stress. The buckling
experiments showed that the maximum strain under bending was larger than that under tension for ZnO NWs with the same diameters.

(2) We have systematically investigated the effect of clamping on the resonance frequency and hence the measured Young’s modulus of cantilevered NWs by a combined experiment and simulation approach. The resonance tests were performed in situ inside a SEM with ZnO NWs clamped on tungsten probes by EBID of hydrocarbon. Initially the resonance frequency increased rapidly with the clamp size. When the clamp width reached a critical value, the resonance frequency approached that under the “fixed” boundary condition. Further numerical simulations were performed to investigate the effect of NW diameter and Young’s modulus on the clamp size (including width and length), which led to a simple scaling law that can be used as guidelines for future designs.

(3) The elasticity, plasticity and failure of five-fold twinned Ag NWs with diameters between 34 and 130 nm were measured by in situ SEM tensile testing. In addition to the stiffening size effect in Young’s modulus, we found that yield strength and ultimate tensile strength both increased as the NW diameter decreased. The maximum yield strength in our tests was found to be 2.64 GPa, which is about 50 times the bulk value and close to the theoretical value of Ag in the <110> orientation. The size effect in yield strength was mainly attributed to the stiffening size effect in Young’s modulus, which, in turn, is a result of the surface effect and the unique five-fold twin microstructure. Yield strain scales reasonably well with the NW surface area, which is consistent with the mechanism of dislocation nucleation from surface sources. Pronounced strain hardening was
observed for most NWs in our study, which is hypothesized to result from the internal twin boundaries in addition to the limited dislocation sources. The present work provides valuable insight into the importance of the size and microstructure on the mechanical properties of NWs.

(4) Experimental measurement and multiphysics modeling of the temperature profiles of a V-shaped ETA in the cases of with and without the heat sink beams were conducted. The Raman measurement of temperature agreed very well with the modeling results in air. Heat conduction through air to neighboring devices is considerable, while heat convection to the air is negligible. Our work unambiguously demonstrated that the heat sink beams play a critical role in reducing the temperature at the specimen end in the ETA. To reach a reasonably large actuator displacement while maintaining low temperature, several design guidelines are provided including more inclined thermal beams, more heat sink beams, small inclination angle, and relatively short heat sink beams. These design guidelines will be valuable to design ETAs for in situ nanomechanical testing. It should be cautioned that while mitigating the undesired heating problem, heat sink beams also reduce the loading efficiency of the ETAs. The combined experiment-modeling methodology presented here can be applied to MEMS thermal actuators for other applications in both air and vacuum.

(5) A MEMS device was designed to conduct in situ tensile testing of Si NWs at different temperatures. A Comb drive actuator is chosen for the device in order to decouple actuation mechanism and heating mechanism. Mutiphysics finite element analysis (coupled electrical-thermal-mechanical) is used to optimize structure design and
minimize undesired thermal loading/unloading. A Si NW with diameter of 50 nm is tested on the device under different temperatures. Stress strain curves at different temperatures reveal that plastic deformation occurs at temperature of 55°C.

(6) A new experimental method to measure the friction between a NW tip and a substrate has been developed. Ag and ZnO NWs were tested with a gold coated surface as the substrate. The coefficients of friction between silver NW and gold substrate and between ZnO NW and gold substrate were found to range from 0.09 to 0.12 and from 0.10 to 0.15, respectively. The adhesion between NWs and the substrate substantially modified the true contact area, which in turn affected the interfacial shear strength significantly. According to the calculated Tabor parameter, the JKR model was selected to approximately calculate the contact area and the interfacial shear strength. The interfacial shear strengths between silver NW and gold substrate and between ZnO NW and gold substrate ranged from 134 to 139 MPa and from 78.9 to 95.3 MPa, respectively. These values are in good agreement with previous results obtained in similar environment (vacuum or dry).

(7) We reported direct measurements of static friction force and interfacial shear strength between Si NWs and PDMS substrate. UVO treatment was found to convert the unmodified hydrophobic surface of PDMS to a highly polar and reactive surface, which formed strong siloxane bonds with Si NWs. As a result, the static friction force increased to the maximum value of ~0.236 N/m at ~60 minutes of UVO treatment, corresponding to the shear strength of 10.57 MPa. The effect of hydrophobic recovery of the treated PDMS surface contributed to the decrease in friction force at longer treatment time. The static friction between NWs and PDMS plays a critical role to hold the NWs in deformed
shapes, which is important for a variety of applications ranging from NW assembly to NW-based flexible electronics and sensors to nanocomposites. Our measurements will contribute to rational interface design and control for such applications. Furthermore, quantifying the effect of UVO treatment on PDMS provides valuable guidelines for selectively tuning the interactions at NW/PDMS interfaces, which might provide a simple route for patterned printing of NWs on PDMS.

5.2 Future Work

For mechanical properties characterization of 1D nanomaterials, one aspect worthy of further investigation is to conduct mechanical testing on NW with diameter less than 20 nm or even smaller size (e.g. sub 10 nm). It would be of interest to see how surface effects affect the mechanical properties of NW in this size range. Theoretical prediction and MD simulation have found very interesting behaviors in this size range, like increasing sensitivity to strain rate and temperature\(^1\) and phase transformation\(^2, 3\) due to surface stress. With samples of even smaller size, in situ TEM mechanical testing technique is essential for this purpose.

Our resonance technique provides a simple and reliable method to evaluate elastic modulus of 1D nanomaterials. This method can be extended to measure Young’s modulus of a broad range of NWs.

For BDT study of Si NWs, further effort is required in the design process to eliminate undesired thermal displacement. Si NWs with different diameter could be tested to find out the critical size of a Si NW that shows BDT in room temperature.
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