MILLS, STEVEN CHRISTOPHER. Ultra-low Power Room Temperature Metal Oxide Gas Sensors: A Study in Sensitivity, Selectivity and Reliability. (Under the direction of Veena Misra.)

The goal of this research is to evaluate Atomic Layer Deposited (ALD) tin dioxide SnO$_2$ for application as a portable, ultra-low power, room temperature operation gas sensor for detection of pollutant gases in an individual's immediate environment. In particular, detection of ozone (O$_3$), which can vary significantly in concentration both spatially and temporally. The aim is to develop technology that will empower individuals with the knowledge needed to manage their wellness with regard to respiratory conditions like asthma in a world with ever increasing sources of pollution.

The first part of this work is focused on the characterization of ALD SnO$_2$ films by deposition and annealing temperatures. It was found that an oxygen deficient film with an Sn:O ratio of around 1:1.8 - 1:1.9 was obtained at a rate of 1 Å/cycle. The film was amorphous deposited at 200°C and below. Deposition at 250°C or annealing at 400-800°C resulted in rutile crystalline phase.

The second part of this work focused on room temperature response to ozone and sensor recovery using UV light. Thin films of 6 nm were found to have the highest sensitivity and the derivative of the resistance change was correlated with ozone concentration. UV light with a wavelength of 385 nm desorbed the ozone and reset the sensor with average power consumption as low as 150 µW.

The final part of the work evaluates sensor reliability by investigating humidity effects, cross sensitivity to NO$_2$ and CO, and evaluating stability over time. Humidity was found to have a reducing on the surface in air and nitrogen but enhance the oxidation when coupled with ozone exposure. Changes in the humidity caused the strength of the ozone oxidation response to change significantly over 10-20 minutes and continue to drift more slowly for an hour or longer. Several other rapid oxidation responses associated with humidity increase were discovered as well. These were attributed to interactions with protons from dissociated water on the surface. The sensor was found to be insensitive to CO and NO$_2$ at atmospheric concentrations. Finally, strategies for improving sensor stability in humid environments were outlined.
Ultra-low Power Room Temperature Metal Oxide Gas Sensors: A Study in Sensitivity, Selectivity and Reliability

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

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BIOGRAPHY

Steven Mills was born in Fredericksburg Virginia in 1979. In 2000, his college studies at Virginia Commonwealth University were cut short by a car accident. Upon recovery he entered the workforce for six years before joining North Carolina State University where he received Bachelor of Science, Masters of Science, and Doctor of Philosophy in Electrical Engineering. His Masters work involved investigating the breakdown characteristics of Atomic Layer Deposited SiO$_2$ and improvement of the oxide through annealing conditions. His dissertation research focused on the application of atomic layer deposited metal oxides for design of low power environmental gas sensors. Both his Masters and Doctoral research was conducted under the direction of Dr. Veena Misra.
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CHAPTER

1

INTRODUCTION

1.1 Background and Motivation

Human health is strongly influenced by the environment and there are many conditions, such as asthma and cardiovascular diseases, that are directly impacted by the quality of the air [1]. While the air quality varies significantly based on location and environmental factors, tools to evaluate the air quality are not yet ubiquitous. The National Ambient Air Quality Standards (NAAQS) were established by the United States Environmental Protection Agency (EPA) to protect human health under the authority of the Clean Air Act, passed by the US Congress in 1970 and amended in 1977 and 1990 [2]. The NAAQS identify six criteria air pollutants that cause health problems and standards for acceptable concentrations in outdoor air. The six criteria pollutants are ground-level ozone ($O_3$)}.
...particulate matter (PM), sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), carbon monoxide (CO) and lead. [2, 3].

The EPA periodically conducts comprehensive reviews of accumulated public health and environmental data, including at-risk populations such as children and the elderly, to maintain an adequate margin of safety when specifying acceptable pollutant levels. The strengths and limitations of available data, the severity of the health effects, the size of at-risk populations, and whether minimum thresholds below which health effects do not occur have been identified are all considered when determining revisions to the safety margins for each pollutant. Note that this safety margin does not mean that there is no risk, only that the risk is reduced sufficiently as to protect human health on a large scale. In fact, there is currently no evidence that a minimum threshold exists for the six criteria pollutants where exposure causes no impact on human health [3].

The scope of this work includes design, fabrication and testing of sensors for monitoring exposure to ground-level ozone. Ozone is formed when pollutants such as nitrogen oxides and VOCs are emitted by industrial facilities, power plants, chemical solvents, and combustion engines and react with ultraviolet (UV) radiation from sunlight [4]. Unlike the stratospheric ozone layer which protects the earth from harmful wavelengths of solar radiation, ground-level ozone poses a risk to human health. It has been shown to negatively impact respiratory health resulting in inflammation of the lining of the lung, reduced lung function, chronic cough, wheeze, chest pain, burning in the chest, shortness of breath, and chest colds with phlegm [5, 6]. Ground-level ozone exposure can limit the ability to perform exercise [4], increase susceptibility to viral infections [7] and is linked to exacerbation of emphysema, chronic pulmonary obstructive disease, bronchitis, and asthma. With regards to asthma, the risk for an asthma attack remains high for many hours or even multiple days after initial exposure. Given knowledge about personal exposure levels throughout the day, individuals will be empowered to avoid activities that may trigger an attack [1, 8, 9].

In addition to the negative quality of life impact for the individual, this places additional stress and demands on the economy and health care system through increased medication use, missed
work, emergency room visits, hospital admissions, and even premature death [4]. Long term exposure to ozone may even result in an otherwise healthy individual developing asthma and permanent damage to lung tissue, especially in the at-risk populations of the elderly, children who play outdoors frequently, and people with genetic predisposition to respiratory problems [10, 11, 12].

In the United States alone, asthma affects 1 in 12 people, costs over $50 Billion every year, kills about 9 people every day, and is getting worse with nearly 15% growth in the number of people with asthma over the last decade. These statistics highlight the need for long term, continuous, real-time, and portable monitoring of personal exposure levels [13, 14, 15].

Ground-level ozone and its precursors vary in concentration both temporally and spatially, forming complex dynamic micro-environments. Concentrations are higher in industrial zoned and high traffic areas, especially during rush hour. Meteorological conditions also impact concentrations as higher UV radiation on hot sunny days catalyzes the chemical reactions that form ozone [16]. The EPA's NAAQS for $O_3$ average concentration over an eight hour period is 70 parts per billion (ppb), although concentrations of only 50 ppb can cause problems for sensitive and at-risk populations [4]. To frame this with context, consider that ozone concentrations in parts of Los Angeles, despite slowly decreasing over the last couple decades, still routinely exceed 100 ppb as shown in Fig. 1.1.

1.2 Sensor Technology Overview

Many gas sensor technologies exist, each with their own strengths and limitations. A good sensor has high sensitivity to detect concentrations required for the application, selectivity to reduce false positives, reversibility to enable multiple measurements, long lifetime, stability, and scalable fabrication methods for mass production with a low unit cost. In order to achieve long term, continuous, real-time, and portable monitoring of ambient ozone levels, the sensor must also have very low power consumption so that a dead battery halfway through the day won't result in a dead person that evening.
Existing sensor technologies include conducting polymers, optical, electrochemical, piezoelectric, and metal oxides. Conducting polymers suffer from short lifetime and lack reversibility. Optical and electrochemical sensors lack the sensitivity required for ppb concentration measurements, and piezoelectrics introduce large variability in sensor coatings and respond strongly to temperature and humidity. Metal oxides sensors are limited by their high operating temperature, which consumes large amounts of power, and poor specificity. However, they do have the requisite high sensitivity and small size for the application. After careful consideration of the limitations of sensor technologies and strategies to overcome their respective challenges, metal oxides were chosen to explore for this work. Table 1.1 summarizes the advantages and disadvantages of each sensor type.
<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<tbody>
<tr>
<td>Polymer based</td>
<td>Room temperature operation</td>
<td>Lifetime/reliability/reversibility issues</td>
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<td></td>
<td>Low power</td>
<td>Drift/calibration problems</td>
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<td></td>
<td>High sensitivity</td>
<td>Broad selectivity</td>
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<td></td>
<td>Fast response</td>
<td>High humidity sensitivity</td>
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<td>Small size</td>
<td>Degrade under UV and ozone exposure</td>
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<td>Optical</td>
<td>Very fast response time</td>
<td>Large size</td>
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<td></td>
<td>Room temperature operation</td>
<td>Short lifetime</td>
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<td></td>
<td>Good selectivity</td>
<td>Complex driving circuit and high cost</td>
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<td></td>
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<td>Expensive</td>
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<td>Electrochemical</td>
<td>Low power</td>
<td>Difficult to achieve ppb sensitivity</td>
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<td></td>
<td>Linear output</td>
<td>Slower response</td>
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<td></td>
<td>Good repeatability</td>
<td>Poor lifetime/stability</td>
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<tr>
<td>Piezoelectric</td>
<td>High sensitivity</td>
<td>Temperature and humidity dependence</td>
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<td></td>
<td>Fast response time</td>
<td>Variability in sensor coating</td>
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<td></td>
<td></td>
<td>Difficult to replace sensors</td>
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<tr>
<td>Metal Oxide</td>
<td>High sensitivity</td>
<td>High temperature (power) operation</td>
</tr>
<tr>
<td></td>
<td>Fast response/recovery times</td>
<td>Broad selectivity</td>
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<tr>
<td></td>
<td>Low cost manufacturing</td>
<td>Humidity sensitivity</td>
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<td></td>
<td>Small size</td>
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<td></td>
<td>Long term stability/lifetime</td>
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1.3 Metal Oxide Sensing Mechanism

1.3.1 Oxygen Vacancies

Transition metal oxides (e.g. \(SnO_2\), \(TiO_2\), \(ZnO\), \(WO_3\), etc.) for sensing applications have attracted much interest in literature due to their small size, long lifetime and reliable, reversible gas sensing response. The metal oxides display sensitivity to oxidizing and reducing gases due to the metal cations exhibiting dual valency, or dual oxidation states [20]. This is compensated for by many point defects in the crystal lattice in the form of oxygen vacancies which modulate the metal oxide conductivity and serve as adsorption sites for gas molecules. Ionosorption, a form of adsorption, occurs when a gas molecule occupies an oxygen vacancy and charge transfer occurs between the metal oxide and the gas. The charge transfer serves to bind the gas molecule to the surface and changes the conductivity of the metal oxide. Oxygen vacancy concentration and occupation on the surface strongly influences conductivity, giving rise to semiconductor behavior and enabling the transducer function of conductometric metal oxide sensors.

1.3.1.1 Dual Valency

The cause of dual valency can be explained through valence theory. Group IV of the periodic table typically show a +4 oxidation state. The outer electron configuration of Group IV elements is \(d^{10}\) \(s^2\) \(p^2\) indicating only two unpaired electrons are available for chemical bonding. However, Hund's rule states that each orbital in a sublevel is singly occupied with like spin electrons before any orbital is doubly occupied. This means that the s and p orbitals want to be half filled with electrons of the same spin before the s orbital gains a second electron. Carbon, for example, will form four \(sp^3\) hybridized orbitals at equivalent energy levels, and all four electrons may be used in chemical bonds resulting in a +4 oxidation state [20].

Moving down the Group IV column of the periodic table, there is an increasing trend for the \(s^2\)
electrons not to be involved in bonding due to the "inert pair effect" [21]. With heavy atoms there is an effect known as relativistic contraction that draws electrons closer to the nucleus [22]. This effects the s orbital much more than the p orbital, which increases the energy difference between the two and makes promotion to hybridized \(sp^3\) levels more difficult. If the \(s^2\) electrons are inert, then only the \(p^2\) electrons participate in bonding and a +2 oxidation state occurs. This effect becomes noticeable moving down the periodic table with tin demonstrating +2 and +4 oxidation states and is even more powerful with lead where the +2 oxidation state is actually more likely [20].

Tin dioxide (SnO\(_2\)), for example, is a post-transition metal oxide that exhibits this behavior. The dual valency results in non-stoichiometric, oxygen deficient films composed of Sn(II) cations with a +2 oxidation state and Sn(IV) cations with a +4 oxidation state. With few electrons available for chemical bonds with the Sn(II) ions, oxygen vacancies form in the atomic structure making SnO\(_2\) sensitive to gas adsorption.

### 1.3.1.2 Semiconductor Behavior of Metal Oxides

A semiconductor is characterized by a conductivity between that of an insulator, such as glass, and a conductor, such as copper. A pure stoichiometric metal oxide crystal would actually be an insulator, but oxygen vacancies in the crystal act as donor sites that can easily donate conduction electrons to the metal oxide. A brief summary of semiconductor physics follows to aid in understanding the gas sensing mechanisms.

The conductivity of a semiconductor increases with temperature, in contrast to conductors where conductivity decreases with temperature. This is due to quantized (discrete) energy states for electrons and the structure of the energy bands in a semiconductor. Electrons are fermions, and are governed by the Pauli exclusion principle which states that no two fermions can exist in identical quantum energy states.

The energy band structure includes the valence band \((E_V)\) and the conduction band \((E_C)\). In insulators and semiconductors, the valence and conduction bands are separated by an energy
gap commonly referred to as the band gap \( (E_g) \). Electrons in the valence band typically do not contribute to conduction because they are core electrons and tightly bound to atomic nuclei, while the conduction band electrons are free to move about the material. The valence and conduction bands have a large density of energy states that electrons may occupy, but the band gap has no intrinsic available energy states. However, oxygen vacancies create shallow (near the conduction band) donor energy levels \( (E_D) \) in the band gap which provide electrons that are easily excited to the conduction band by energy from thermal optical or other sources [23].

The Fermi level \( (E_F) \) is another important concept in band structure. This is the maximum energy level that would be filled by electrons if there were no energy input to excite them to higher levels. It can also be described as the energy level with a 50% probability of containing an electron when the system is in thermodynamic equilibrium, or the average energy level of the electrons. The Fermi level often falls within the band gap for semiconductors. The closer the Fermi level is to the conduction band, the more electrons occupy conduction band energy levels contributing to the conductivity. This is characteristic of an n-type semiconductor.

When the Fermi level is close to the valence band, the conduction band is mostly empty which would imply very low conductivity. However, deep acceptor states \( (E_A) \) may be formed within the band gap through material dopants and defects which are close enough for electrons to be easily excited from the valence band to the acceptor state. The absence of an electron in the valence band is referred to as a hole and can be thought of as a positively charged mobile carrier contributing to conductivity. This is the conduction mechanism of p-type semiconductors.

The carrier concentration for non-degenerated semiconductors is given by Maxwell-Boltzmann statistics as shown in Eq. 1.1 for electrons and Eq. 1.2 for holes. In these equations, \( n, p, N_C, \) and \( N_p \) are the number of conducting electrons, holes, and the effective density of states in the conduction band and the valence band, respectively. \( k_B \) is the Boltzmann constant and \( T \) is the temperature.
\[ n = N_C e^{\frac{E_F - E_V}{k_B T}} \]  
\[ p = N_V e^{\frac{E_C - E_F}{k_B T}} \]  

1.3.2 Transduction through Ionosorption

A typical atmosphere at sea level is 19.5% oxygen (O\(_2\)) and 80.5% nitrogen. All oxidizing or reducing gas molecules, including O\(_2\), will have an adsorption rate and desorption rate dependent on the concentration of gas molecules, the energy required for reaction and the available energy in the system. However, only ionosorbed species will affect the carrier concentration and result in a response.

When oxidizing molecules, such as O\(_2\), O\(_3\) or NO\(_x\), ionosorb at oxygen vacancy sites on the surface of a metal oxide, acceptor states are formed deep in the band gap and electrons in the metal oxide are trapped by the gas molecule. A net negative surface charge is formed and the conduction and valence bands bend upward near the surface. The bending of the energy bands changes the distance between the Fermi level and the conduction/valence bands at the surface which influences the carrier concentration. The resulting modulation of the charge carrier concentration and conductivity is the transducer function for detection of gas species. The charge transfer as an oxygen molecule physically adsorbs, \((ad)\), and then ionosorbs, \((ion)\) is detailed in Eq. 1.3 and Eq. 1.4. The dissociation into atomic oxygen and subsequent double ionization in Eq. 1.5 and Eq. 1.6 requires temperatures above 160°C [24]
\[ O_2(gas) \leftrightarrow O_2(ad) \] (1.3)

\[ O_2(ad) + e^- \leftrightarrow O_{2(i\text{on})}^- \] (1.4)

\[ O_{2(i\text{on})}^- + e^- \leftrightarrow 2O_{(i\text{on})}^- \] (1.5)

\[ O_{(i\text{on})}^- + e^- \leftrightarrow O_{(i\text{on})}^{2-} \] (1.6)

For n-type semiconductors where electrons are the conducting charge carrier, upward bending of the bands moves the conduction band near the surface away from the Fermi level. This forms a potential barrier and an electron depleted layer of width \( x_0 \) resulting in reduced conductivity. If the electron can be excited back to the energy levels of the gas molecule, the gas may desorb and the band bending decreases. The carrier concentration and conductivity then increase as the sensor recovers \([25]\). Reducing gases like CO can react with surface oxygen species resulting in electron donation and decreasing the band bending.

For p-type gas sensors, the conducting charge carrier is a hole and the Fermi level is just above the valence band. Similar to n-type metal oxides, oxygen species trap negative surface charge and bend the energy bands upward. However, for a p-type semiconductor the valence band bending results in a hole accumulation layer at the surface rather than an electron depleted layer. This means that the surface of a p-type metal oxide is more conductive while the bulk is more resistive, in contrast to n-type metal oxides. Reducing gases interact these ionosorbed oxygen species rather than directly with the surface. The reducing gas is oxidized by the surface oxygen species resulting in electron donation to the metal oxide. The electron then combines with a hole, reducing the number of positive charge carriers and the conductivity \([26]\). This behavior is illustrated in Fig. 1.2 for n and p-type metal oxides.

The change in carrier concentration at a distance \( x \) from the surface may be described as in Eq. 1.7 and Eq. 1.8 where \( V(x) \) is the magnitude of the band bending from the flat band conditions.
Figure 1.2 Result of negative surface charge on n-type and p-type semiconductors: (a) n-type surface electron depletion region, (b) p-type hole accumulation region, (c) n-type band bending, (d) p-type band bending, (e) n-type electron concentration and (f) p-type hole concentration
in the bulk and \( n_b \) and \( p_b \) are the bulk electron and hole concentrations as calculated from Eq. 1.1 and Eq. 1.2, respectively. Evaluation of the equations at the surface yields expressions for surface concentration of electrons, \( n_S \), and holes, \( p_S \). \( V_S \) is the surface potential, or the magnitude of the band bending at the surface.

\[
n(x) = n_b e^{\frac{qV(x)}{kT}} \quad \rightarrow \quad n_S = n_b e^{\frac{qV_S}{kT}} \tag{1.7}
\]

\[
p(x) = p_b e^{\frac{qV(x)}{kT}} \quad \rightarrow \quad p_S = p_b e^{\frac{qV_S}{kT}} \tag{1.8}
\]

Eq. 1.7 and Eq. 1.8 can be further extrapolated to relate the change in band bending and carrier concentration to the change in surface conductance. The conductance of a semiconductor, \( \sigma \), is given by Eq. 1.9, where \( \mu_n \) and \( \mu_p \) are the mobilities for electrons and holes, respectively. In an n-type semiconductor, the hole quantity is negligible and vice-versa for p-type. The conductivity, \( G \), is a function of the conductance and geometry as shown in Eq. 1.10, where \( A \) is the semiconductor cross-sectional area normal to the current flow and \( l \) is the length in the direction of the current flow.

\[
\sigma = q(n\mu_n + p\mu_p) \tag{1.9}
\]

\[
G = \sigma \frac{A}{l} \tag{1.10}
\]

Carrier mobilities are also a function of carrier concentration as scattering effects increase with the number of carriers. However, the change in mobility is much smaller than the change in carrier concentration, so a first order approximation may assume the mobilities to be constant. In this case, the change in surface conductivity (Eq. 1.11) is equal to the change in carrier concentration (Eq. 1.12) as shown in Eq. 1.13. Substituting Eq. 1.7 yields Eq. 1.14 which reduces to Eq. 1.15. Finally,
in Eq. 1.16 the relationship between the change in surface conductance is related to the change in band bending [27].

\[
\Delta G = \frac{G}{G_0} \quad (1.11)
\]

\[
\Delta n = \frac{n}{n_0} \quad (1.12)
\]

\[
\frac{G}{G_0} = \frac{n}{n_0} \quad (1.13)
\]

\[
\frac{G}{G_0} = \frac{n_b e^{qV}}{n_b e^{qV_0}} \quad (1.14)
\]

\[
\frac{G}{G_0} = e^{\frac{q(V-V_0)}{kT}} \quad (1.15)
\]

\[
\frac{G}{G_0} = e^{\frac{q\Delta V}{kT}} \quad (1.16)
\]

### 1.3.2.1 Thermally Activated Sensing and Recovery

The chemical reactions required for ionosorption and the corresponding conduction change do not occur spontaneously. Sufficient energy input to the system is required to enable the reactions at a rapid rate. Commercial metal oxide gas sensors use heating elements to provide thermal energy. They are typically four terminal devices with two terminals across the sensing element and two additional terminals for contact to a heating element which is suspended on a micro-hotplate or membrane to reduce the thermal mass and the power required to heat it [28]. The temperatures for sensing and recovery reactions typically range from 200 to 500°C. Oxygen species on the surface, including molecular O$_2^-$ and atomic ions O$^-$ and O$_2^-$ play an important role in the sensing process. Generally below 150 °C, molecular oxygen dominates while at higher temperatures atomic oxygen dominates. The distribution of oxygen species by temperature can be seen in Fig. 1.3 [28].

Temperatures above 150 °C allows for increasing mobility of atoms at the surface, which is
constantly in flux as oxygen atoms in the crystal move around and the oxidation state of the metal ions changes. This coupled with the more reactive atomic oxygen species results in fast chemical reactions and a corresponding fast resistance change when the ambient around the metal oxide changes [25]. As the operating temperature decreases, adsorption rates and especially desorption rates decrease as fewer electrons are excited to the conduction band to react with gas species. 150 °C is below the practical operating temperature for today’s commercial metal oxide sensors. A survey of sensors available from companies like SGX SensorTech and Hanwei Electronics reveals operating temperatures ranging from 220 °C for the MiCS-2710 NO₂ sensor to 430 °C for the MiCS-2610 O₃ sensor resulting in power consumption up to 80 mW, a far cry from the power levels required for reliable and portable monitoring.

1.3.2.2 Photo Activated Sensing and Recovery

Energy input to the system is not limited to thermal sources. Ultraviolet (UV) light has been suggested in literature as an alternative source [29, 30, 31, 32, 33, 34, 35, 36, 37, 38]. For example, Camagni et al. [31, 32] used continuous illumination from a Xenon UV sources to enable detection of carbon
monoxide (CO) and nitrogen dioxide NO$_2$ with room temperature SnO$_2$ films. The photo-excitation of charge carriers enhances the adsorption rate by providing more carriers for reaction and decreasing the potential barrier to charge transfer at the surface [30, 32, 39], which can range from 0.5 to 1 eV [27, 40, 41, 42]. Saura et al. [43] suggested the application of UV for exciton generation to increase charge carriers and decrease the surface and grain barrier heights to facilitate reactions with gas species. [44, 45]. An additional perk of UV illumination is the oxidation of hydrogen, resulting in self cleaning and dehydroxylation of the surface [46].

Desorption of gas species using UV has also been demonstrated. UV assisted desorption of NO$_2$ was described by [32] where the desorption rate depends on radiative intensity and Mills et al. demonstrated ozone sensor recovery using 385 nm UV light [47].

There are two mechanisms proposed for desorption: (i) direct excitation of binding electrons to the conduction band and (ii) recombination with a photo-generated hole in the valence band. [48]. These reactions are described in Eq. 1.17 where the subscript (ad) indicates an adsorbed surface species and ($h\nu$) indicates a photo-excited carrier [29, 48, 49, 50]. Increasing UV energy beyond the band gap is not helpful because a larger fraction of conduction electrons are lost due to inelastic scattering [30].

\[
\begin{align*}
O_2(ad) - p_{(h\nu)} & \leftrightarrow O_2(gas) \\
O_2(gas) + e_{(h\nu)} & \leftrightarrow O_2(ad) \\
O_3 + e_{(h\nu)} & \rightarrow O^- + O_2(gas) \\
2O^- + p_{(h\nu)} & \rightarrow O_2(gas) + 2e^-
\end{align*}
\]

(1.17)

Of course photo induced electrons are simultaneously interacting with gas phase molecules, increasing the adsorption rate as well. UV accelerates both reactions, but which one dominates depends on the occupancy of adsorption sites on the surface. Under constant illumination, the
equilibrium positions are shifted toward consuming more electrons [33, 52, 53, 54] until the adsorption and desorption rates reach equilibrium. In this case the constant illumination results in a surface that is heavily reduced resulting in a very high adsorption rate but also requires higher power levels. A short-term, intermittent UV illumination to partially recover the sensor results in a lower adsorption rate but the average power consumption may be drastically reduced.

1.3.3 Ionosorption of Ozone

The previous sections described the general mechanisms behind gas sensing with metal oxides in the context of oxygen, but the reactions with ozone are less certain. Debate continues on whether an ozone molecule ionosorbs associatively as in Eq. 4.1 or dissociatively as in Eq. 4.2 [28].

\[
\begin{align*}
O_3 (\text{gas}) & \rightarrow O_3 (\text{ad}) + e^- \rightarrow O_3^- (i\text{on}) \\
O_3 (\text{gas}) & \rightarrow O_3 (\text{ad}) + e^- \rightarrow O_2 (\text{gas}) + O^- (i\text{on})
\end{align*}
\] (1.18) (1.19)

Ozone is highly reactive and readily donates an oxygen atom to free radical species, indicating that decomposition followed by ionosorption of the negatively charged oxygen atom is more likely. However, ozone is also a resonant structure which results in a dipole that is positively charged on the center oxygen atom and negatively charged on one of the terminating atoms as shown in Fig. 4.3. This dipole would facilitate molecular ionosorption as the negatively charged oxygen atom would be attracted to the positively charged oxygen vacancy.
1.3.4 Thickness Effect

Ensuring sufficient sensitivity to low concentrations is essential for ambient environmental monitoring. In addition to adding energy to speed up the chemical reactions and obtain a measurable response in a timely manner, the sensitive layer geometry can also be exploited. It is known that the sensitivity and response time of a metal oxide is related to the Debye length, which influences the depth of the surface electron depleted region [55, 25, 56]. More specifically, as the crystallite size in the metal oxide film approaches twice the Debye length, the resistance change due to charge transfer is amplified dramatically, as illustrated in Fig. 1.5.

For an n-type metal oxide, when the crystal is large compared to the Debye length (Fig. 1.5a), resistance change at the surface is negligible compared to the bulk of the material and potential barriers between grains control the conductivity. As the crystal size gets closer to the Debye length (Fig. 1.5b), narrow necks within grains begin restricting current flow and conduction depends not only on the potential barriers but also the cross sectional area of the narrow necks. Additional ionosorbing molecules modulate the conductive cross sectional areas to cause large changes in conductivity, so the structure becomes more sensitive. Finally as the crystal shrinks to less than twice the Debye length (Fig. 1.5c), the entire structure become depleted of carriers and the potential barriers between the grains flatten. Now the conductivity is dominated by the crystal conductivity. In this mode, small amounts of charge from surface reactions cause very large changes in conductivity and the film is highly sensitive to ionosorbed gas molecules.

The Debye length, $L_D$, and the width of the space charge region, $x_0$, are given by Eq. 6.10 and Eq. 1.21, respectively [57]. Combining these equations yields an expression for the space charge width in terms of the Debye length in Eq. 1.22. Here, $\varepsilon$ is the material permittivity, $k_B$ is the Boltzmann constant, $T$ is the temperature, $q$ is the elementary charge, $N_d$ is the donor density and $V_S$ is the surface potential.
Figure 1.5 Illustration of effect of crystallite size \( t \) on sensitivity of metal oxide gas sensors for (a) crystallite size much larger than Debye length. (b) crystallite size greater than or equal to twice the Debye length and (c) crystallite size less than twice the Debye length, adapted from [25].
\[ L_D = \sqrt{\frac{\epsilon k_B T}{q^2 N_d}} \]  
\[ x_0 = \sqrt{\frac{3\epsilon V_S}{q N_D}} \]  
\[ x_0 = 2L_D \sqrt{\frac{q V_S}{2k_B T}} \]

Eq. 1.22 shows that the space charge depth is proportional to the Debye length, decreases with temperature and increases with the surface potential. An increase of the surface potential corresponds with a decrease in the number of conduction electrons while an increase in temperature yields more thermally excited conduction electrons, so \( x_0 \) is inversely correlated to the number of free electrons in the crystal.

### 1.4 Tin Dioxide

The reader has likely noticed that tin dioxide, \( \text{SnO}_2 \) has been mentioned several times already in this text. This is no coincidence as \( \text{SnO}_2 \) will be the material of choice for gas sensor development in this work.

Tin dioxide is an n-type, direct band gap semiconductor that combines high electrical conductivity with optical transparency, making it suitable for a wide range of applications. It has widespread use as a transparent conductor, oxidation catalyst and solid state gas sensors. Many oxides exhibit sensitivity toward gas species but \( \text{SnO}_2 \) was the first metal oxide considered for chemical sensing and is still the most frequently used [58].

The high conductivity and n-type semiconductor behavior are due to the large 3.6 eV direct band gap and the very low formation energy for point defects in the form of oxygen vacancies and tin interstitials. A pure stoichiometric \( \text{SnO}_2 \) crystal would be an insulator, but the low defect
formation energy results in sub-stoichiometric films with oxygen vacancies contributing electrons to the conduction band [27].

Additionally, the energy bands have additional features that contribute to conductivity. Previous discussions of the energy bands have described the behavior moving through spatial dimensions. However, a Fourier transform of the spatial dimension allows examination of the energy bands in k-space, also called reciprocal space or momentum space. The Brillouin zone is a primitive cell in k-space where more details of the energy bands can be seen, including multiple energy levels within bands and energy level curvature with respect to the momentum of a particle traveling through the crystal structure.

The conduction band in SnO$_2$ is a single band of s-type character that is strongly dispersed with the minimum at the $\Gamma$ point in the Brillouin zone. This strongly dispersed band, common to transparent conducting oxides, results high conductivity due to a low effective mass of electrons, heavy holes, a uniform spatial distribution of electron charge density, and low scattering. The curvature of the conduction band also leads to the Burstein-Möss effect. As the carrier concentration increases and the semiconductor becomes degenerate, filling of the conduction band results in an increased energy needed to promote additional electrons from the valence band and an associated increase in the optical band gap [27]. Finally, a large internal gap in the conduction band prohibits inter-conduction band adsorption of photons in the visible (and into the UV) range. The band diagram for SnO$_2$ in the Brillouin zone can be seen in Fig. 1.6.

1.5 Goals and Challenges of the Following Work

The following work is focused on developing an ozone sensor that meets the design constraints for long term, continuous, portable monitoring for personal exposure. More specifically, detection of ozone concentrations in the range of 60-150 ppb over a large range of ambient conditions including temperature, humidity and the presence of other common interfering gases such as NO$_2$ and CO.
Figure 1.6 Diagram of SnO$_2$ band structure. Reprinted figure with permission from [59], ©1995 by the American Physical Society.
Reasonably fast response and recovery times of several minutes or less are desirable and an average power budget on the order of 100 $\mu$W is paramount.

1.6 Document Preview

This chapter (Chapter 1) has been an introduction to gas sensing in general and to the basic mechanisms of conductometric sensing using metal oxides. Literature relevant to the remaining work has been presented to provide background on the concepts investigated.

Chapter 2 describes the fabrication and characterization techniques that are used throughout this work.

Chapter 3 covers characterization of the sensing material using the various physical and electrical characterization techniques covered in Chapter 2.

Chapter 4 documents experimental work done to evaluate the response and recovery aspects of the sensor. In particular the effect of thickness and impurities on the sensing response, the effect of UV illumination on sensor recovery and introduces the effect of humidity.

Chapter 5 is relegated to discussing the effect of humidity in detail. The nature of dissociation of water and its the impact on the surface and sensing properties will be evaluated in zero air, ozone and inert environments.

Chapter 6 evaluates the stability of the sensor over longer exposure periods and investigates drift in the baseline resistance and response. Cross sensitivity to other oxidizing and reducing gases is also examined.

Chapter 7 discusses integrating the sensor into a testbed system associated system level engineering considerations. Data will be presented and discussed from further testing with that system in the EPA ozone chamber which more accurately mimics the end use case testing conditions.

Chapter 8 is a summary of the document with conclusions determined from the data collected and projected paths for future work.
CHAPTER
2

FABRICATION AND CHARACTERIZATION PROCEDURES

This chapter describes the fabrication processes involved in designing gas sensors and then continues to discuss the physical methods used to characterize the sensing material. Finally, the electrical characterization, gas exposure testing procedures, and data acquisition methods are described.

2.1 Sensor Fabrication Process

One key advantage to choosing conductometric metal oxide sensors is their inherent simplicity with regards to device fabrication. The most basic metal oxide sensor requires only the metal oxide
sensitive material and two electrodes for making contact and measuring the resistance. Practically, commercial metal oxide sensors to date also require a thermal energy source which introduces two additional electrodes and necessitates some thermal isolation of the structure via micro hotplates or membranes as shown in Fig. 2.1, adapted from literature [60, 61]. This requirement involves Micro ElectroMechanical Systems (MEMS) fabrication techniques which complicates the process and adds additional cost.

2.1.1 Electrical Isolation

The gas sensor fabrication begins with electrical isolation in the form of a field oxide. P-type or N-type silicon wafers were cleaned in a JTB-100 solution to remove any surface contaminates [62]. A 3000Å isolation oxide was then grown by wet oxidation for 30 minutes at 1000°C in an O₂ / H₂ / HCl / N₂ environment [63].
2.1.2 Atomic Layer Deposition

After oxidation, the metal oxide sensing material was deposited in a Cambridge Nanotech Savannah 100 model Atomic Layer Deposition (ALD) reactor. The tetrakis(dimethylamino)tin (TDMASn) precursor and ozone (O$_3$) reactants were used to deposit tin dioxide (SnO$_2$) at temperatures from 150°C to 250°C.

ALD is the core of the sensor technology developed in this work. In an ALD process, illustrated in Fig. 2.2, a metal-organic precursor is heated (if required) to increase its vapor pressure and ensure it is volatile. The precursor is then introduced to the reactor chamber where it saturates the surface of the substrate, depositing a monolayer of molecules before being purged. ALD precursors are volatile due to the ligands attached to the metal atom and designed to react chemically with oxidized or OH terminated surfaces where some ligands will detach as the metal atom bonds to the surface. After the chamber is purged of the metal-organic precursor, an oxidizer is introduced. This results in another chemical reaction that cleaves the remaining ligands from the metal atoms and leaves behind a monolayer of oxygen atoms, preparing the surface to accept the next cycle of the metal precursor.

In this way, ALD is a self saturating process where all adsorption sites are filled before the precursor or oxidizer is purged from the chamber. This results in conformal coverage over interior surfaces that are difficult to coat with other methods and very uniform, conformal film growth. Due to the self saturating nature of the process, ALD film thickness is controllable to monolayer precision by changing the number of deposition cycles and has been demonstrated on features with aspect ratios as high as 200:1 [64]. Due to these outstanding film deposition characteristics, ALD has become ubiquitous in the microelectronics industry and these properties make ALD an ideal candidate for deposition of sensing films where large specific surface area and accurate film thickness control are paramount.
Figure 2.2 Illustration of Atomic Layer Deposition (ALD) process.
2.1.3 Crystallization Anneal

After deposition of metal oxide, the films were annealed in air at temperatures from 400°C to 800°C, usually for 2 hours, to achieve various degrees of crystallinity in the form of rutile SnO$_2$. The resulting films were characterized and evaluated for sensor performance. A Lindberg furnace was used for air anneals with a ramp rate of 30°C per minute. No cooling mechanism was available so the furnace was allowed to cool due to natural radiation and convection to temperatures below 300°C before unloading the samples.

2.1.4 Electrode Definition

Finally, electrode metal consisting of a 100 Å titanium adhesion layer and 2500 Å of gold is evaporated in high vacuum ($10^{-6}$ Torr) in a Kurt J. Lesker electron beam evaporation system. Interdigitated electrodes defined by photolithography and lift-off processes were attempted in early experiments, but the sensing surface was found to be very susceptible to poisoning by the chemicals used and shadow mask deposition of simple square contact pads was determined to be a more reliable method. Fig. 2.3 shows a diagram of the sensor structure and a photo of the interdigitated electrodes.
2.2 Physical Characterization Methods

The ALD metal oxide films were investigated with a variety of material characterization methods to verify the quality of the film and the deposition process. The material analysis methods are described in this section.

2.2.1 Variable Angle Spectroscopic Ellipsometry (VASE)

Spectroscopic ellipsometry is an optical technique used to determine dielectric properties and thickness of thin films. In this technique, a beam of monochromatic light is incident on the sample and reflects either off the film surface or the underlying silicon substrate, depending on the wavelength and the transmission characteristics of the film. Polarization and phase shift data is collected for a range of wavelengths to determine the complex reflectance ratio of a material system. The complex reflectance ratio, \( \rho \), is composed of an s component, oscillating perpendicular to the plane of incidence; and a p component, oscillating parallel to the plane of incidence. In Eq. 2.1, \( \tan(\Psi) \) is the amplitude ratio upon reflection and \( \Delta \) is the phase shift.

\[
\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}
\]  

(2.1)

Ellipsometry measurements were used with a Cauchy model to determine the thickness of the deposited films and the bandgap of the crystal structure. A Woolam Variable Angle Spectroscopic Ellipsometer (VASE) was used to take measurements at an angle of 75° from the substrate normal over wavelengths from 500-750 nm (nanometer) for thickness measurements. Additional measurements using wavelengths of 191-1690 nm were used to evaluate bandgap information and verify previous results.
2.2.2 Grazing Angle X-Ray Diffraction (XRD) Analysis

X-ray diffraction is used to determine the crystalline structure of a material. Incident X-ray beams are diffracted from the atomic planes as the source is swept in an arc such that only X-rays from certain angles reflect from parallel crystal planes with constructive interference. This is governed by Bragg's law, Eq. 2.2, where \( d \) is the atomic spacing, \( \theta \) is the angle and \( \lambda \) is the X-ray wavelength. As each atomic plane has a unique \( \theta \) value corresponding to the reflected waves, the crystal structure and phase can be determined together. Grazing angle XRD involves using an incident beam that just grazes the surface of interest. This is required for very thin films where X-rays don't pass through enough physical material to create strong diffraction patterns.

\[
2d \sin \theta = n \lambda
\]  

The XRD analysis in this work was done in grazing angle mode using a Panalytical X’Pert PRO MRD HR XRD System. A Cu-K\( \alpha \) radiation source was used to generate X-rays at 45 kV and 40 mA with a wavelength of 0.15418 nm.

2.2.3 X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is a powerful technique for chemical and elemental analysis in thin films and on material surfaces. This technique involves an X-ray of known energy incident on the material surface such that the energy of the X-ray ejects core electrons from atoms within the sample. The ejected electrons are collected and counted as a function of kinetic energy in a cylindrical mirror analyzer. The total energy is expressed by Eq. 2.3 where \( h \nu \) is the photon energy, BE is the binding energy or the minimum energy required to break the chemical bonds and \( \phi_s \) is the spectrometer work function. The resulting spectrum of intensity vs. kinetic energy enables extraction of many material parameters [65].
\[ BE = h \nu - KE - \varphi_s \]  \hspace{1cm} (2.3)

The XPS analysis in this work is performed \textit{ex situ} using a Kratos Analytical Axis Ultra spectrometer using an Al K\textalpha\ radiation source (1486.6 eV) for X-ray generation with a 20 eV pass energy and the charge neutralizer on. Depth profiling was accomplished via argon sputtering. All spectra are referenced to the 284.5 eV peak of adventitious carbon to compensate for charging and calibration effects.

\subsection*{2.2.4 Scanning Tunneling Electron Microscopy (STEM)}

Transmission electron microscopy is an excellent tool for understanding and imaging materials at high spatial resolution down to the atomic level. In this technique, an electron beam is incident upon a very thin (less than 200 nm) prepared sample and electrons that pass through the sample are collected and analyzed. Energy Dispersive X-ray Spectroscopy (EDS) is one TEM technique that provides compositional information for elemental mapping.

In this work, STEM samples were prepared by Focused Ion Beam (FIB) milling and a Titan electron microscope with a beam energy of 200 kV was used to perform aberration corrected scanning tunneling electron microscopy with energy dispersive X-ray spectroscopy. This analysis was used to verify VASE film thickness measurements, crystallinity and obtain EDS elemental mapping data.

\subsection*{2.2.5 Time Of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)}

Secondary ion mass spectroscopy is a very sensitive surface analytical technique. Positive and negative mass spectra and spectral images are determined using a pulsed, focused ion beam and time-of-flight analyzer to determine composition of materials. Depth profiling was used to evaluate the film composition for impurities.
The TOF-SIMS analysis in this work was performed using a TOF SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a $\text{Bi}^{m+}_n$ ($n = 1 - 5$, $m = 1, 2$) liquid metal ion gun, $\text{Cs}^+$ sputtering gun and electron flood gun for charge compensation. Both the Bi and Cs ion columns are oriented at 45° with respect to the sample surface normal. For the depth profiles acquired in this study, 1 keV low energy $\text{Cs}^+$ with a current of 8 nA was used to create a 240 µm by 240 µm area, and the middle 100 µm by 100 µm area was analyzed using about 0.3 pA $\text{Bi}^+_3$ primary ion beam. The negative secondary ion mass spectra were calibrated using $\text{H}^-$, $\text{C}^-$, $\text{O}^-$, $\text{Sn}^-$ and $\text{SnO}^-$.

2.2.6 Rutherford Backscattering (RBS)

Rutherford Backscattering is an excellent material characterization technique for determining relative concentrations of atoms within a sample to determine stoichiometry. It is often used to analyze thin films for composition, thickness and uniformity with depth. In this analysis technique, an accelerated ion beam is directed onto the sample and a small fraction of the rebound off of the atomic nuclei to be caught in an energy sensitive detector.

The shape of the energy spectrum can be used to analyze a region near the surface, about one micron deep. The principles of conservation of energy and momentum are used to determine the mass and depth of the scattering atom with the number of rebound counts proportional to its concentration. The sensitivity is very high for heavy elements but very low for the lightest elements. The values returned for elemental concentration are absolute and require no calibration although the heavier elements crowd together at the upper end of the spectrum and can be difficult to distinguish.

The RBS analysis in this work was done by the Ion Beam Lab at the University of Albany. Due to the very thin dimensions of the films, the lab adopted the resonant RBS method to distinguish oxygen in the tin dioxide from the underlying silicon dioxide layer. The sample normal was tilted 70° off the beam incident to enhance the surface oxygen signals. Helium ions with an energy equal to the resonance energy for oxygen detection, 3.05 MeV, were used to bombard the sample and a
silicon particle detector was used to collect the backscattered ions at a scattering angle of 175°.

2.3 Electrical and Gas Response Characterization Methods

This section describes the measurements conducted on the ALD SnO$_2$ films to characterize their electrical properties and the methods used for gas exposure experiments and data acquisition.

2.3.1 Hall Effect Measurements

The Hall effect is the creation of an electric potential transverse to current flow through a conductor when there is a magnetic field perpendicular to the current flow as illustrated in Fig. 2.4, where $B_z$ is the magnetic field, $I$ is the current flow due to the electric field $E_x$, and $V_H$ is the hall voltage associated with the electric field, $E_y$. This phenomenon can be used to determine the carrier concentration, mobility and resistivity of a conducting or semiconducting material, and the polarity of the Hall voltage on a semiconductor indicates if it is n or p-type.

The Hall effect is a manifestation of the Lorentz force, which is a force applied to charge carriers in the circumstance of an electric current and a perpendicular magnetic field. The Lorentz force, $\vec{F}$, is given by Eq. 2.4, where $q$ is the elementary charge, $\vec{v}$ is the velocity of the charge carriers and $\vec{B}$ is the magnetic field.

$$\vec{F} = q \left[ E + (\vec{v} \times \vec{B}) \right]$$ (2.4)

The direction of the Lorentz force can be determined by using the right hand rule with the cross product $\vec{v} \times \vec{B}$ while keeping in mind that this is the direction of the force acting on a positively charged particle and a negatively charge particle will be pushed in the opposite direction. For n-type material in Fig. 2.4, this results in a build up of electrons on the left side of the conductor. At steady state conditions, the Hall voltage and electric field $E_y$ generated by the non-uniform charge distribution, exactly balances the Lorentz force so that the charge carriers move straight down the
The Hall effect measurements in this work were conducted using an Ecopia HMS-3000 Hall measurement system with a 0.57 T magnetic field applied. Gallium dots were pressed onto the sample to make contacts and the sample was mounted on an SPCB-2 spring clip board from Ecopia. The Ecopia system was used to run a current/voltage sweep to verify the contacts were ohmic and subsequently conduct the Hall measurement.

### 2.3.2 Gas Testing Chamber Design and Fabrication

This research was the first in the Misra group to explore the area of gas sensing and required development of the infrastructure for exposure of the fabricated sensors to harmful gases in a safe and controlled manner. A custom gas exposure testing chamber was designed by the author and commissioned for fabrication by the North Carolina State University Machine Shop. The chamber was composed of all ozone resistant materials: stainless steel, Teflon and silicone.
Cylinder sources for NO\textsubscript{2} (20 ppm in air) and CO (200 ppm in air) were diluted with zero grade synthetic air (80.5% N\textsubscript{2}, 19.5% O\textsubscript{2}) to achieve concentrations of interest. Early experiments used a custom built Mass Flow Controller (MFC) network designed by the author to dilute gases and a simple ozone generator that consisted of a small closed chamber with a UV lamp inside. An adjustable metal shield to cover a portion of the lamp enabled coarse control of the ozone output which was verified to produce a minimum value of 400 parts per billion (ppb) with an Alphasense OX-B431 electrochemical ozone sensor and low noise Individual Sensor Board (ISB).

Later experiments replaced the MFC network with a NIST (National Institute of Standards and Technology) certified Teledyne T700U gas calibration unit to dilute the gases sourced from cylinders and to generate ozone from the zero air carrier gas with an ozone range of several ppb to several part per million (ppm). A peripheral bubbler was later integrated to add humidity to the gas just upstream of the chamber. Since ozone is highly soluble in water, it was required to generate dry air with ozone and then mix it with humid air to obtain the desired test gas. A block diagram of the system is shown in Fig. 2.5.

2.3.3 Laboratory Gas Response Measurements

Gas response of the sensor in the form of resistance change of the SnO\textsubscript{2} film was measured in the laboratory testing chamber using a Keithley 4200 semiconductor parameter analyzer. A bias voltage, usually 100 mV, was applied across two metal contacts on the surface of the film and the current flow was measured at a sampling frequency, \( f_S \) to determine the resistance. The sampling frequency was typically set to 1 or 2 Hz for short measurements, which is more than sufficient. When longer measurements were conducted, \( f_S \) was decreased to 0.2-0.4 Hz because the Keithley Interactive Testing Environment (KITE) has rather strict limitations on the number of data points it will record. The built in Integrated Testing Modules (ITM) support collection of 4096 (\( 2^{12} \)) data points while the custom User Testing Modules (UTM) support collection of 32768 (\( 2^{15} \)) data points.

Sensor recovery was accomplished with illumination from an ultraviolet (UV) LED, usually
Figure 2.5 Block diagram of sensor testing setup including source gases, Teledyne T700-U gas calibration unit and ozone generator, testing chamber and data collection via Keithley parameter analyzer.
385 nm, to desorb gas species from the surface. The UV illumination began after completing a measurement sequence of 1-2 minutes and continued until the reset resistance was reached. The reset resistance value was determined by the oxidation rate due to gas chemisorption in the testing ambient. A higher reset resistance results in a lower oxidation rate and reduced UV power required for recovery. Early experiments utilized an ITM for resistance measurement and the UV LED was turned on and off manually using an external power supply. Later experiments were controlled by a UTM programmed in C by the author. The UTM adjusted the UV bias to maintain a recovery time of 5-10 seconds for short measurements. When the sampling frequency was reduced for longer measurements, a recovery time of 15-30 seconds was maintained in order to prevent reducing the surface too far and driving the resistance lower than the reset value.

2.3.4 Mobile Gas Response Measurements

The Health and Environmental Tracker (HET) was developed in conjunction with the testbed team to allow system integration and testing of new technologies as they come online. Many thanks go out to James Dieffenderfer, who did the lion’s share of the work on the HET platform.

The ALD SnO$_2$ gas sensor was integrated into the HET, shown in Fig. 2.6a. The sensor is mounted on the small daughterboard that faces down toward a UV LED for recovery on the motherboard. The resistance of the sensor is measured using a voltage divider circuit and an Analog to Digital Converter (ADC). The measurement circuit is illustrated schematically in Fig. 2.6b, where $R_S$ is the resistive gas sensor, $R_L$ is a load resistor with a value above but near the resistance of the sensor in typical indoor conditions (around 20 kΩ), $V_{DD}$ is 5 V, ADC is the analog to digital converter, and MCU is a microcontroller that collected the digital data and transmits it to a Windows application over Bluetooth Low Energy (BLE) communications. The operational amplifier between the voltage divider and the ADC is configured for unity gain to function as a voltage buffer, although the ADC likely has high input impedance rendering it redundant.
Figure 2.6 (a) Photograph of ozone sensor integrated into the Health and Environmental Tracker (HET) Testbed developed by James Dieffenderfer and (b) schematic of the sensor measurement circuit in the HET.
2.3.5 Gas Response Testing with the Environmental Protection Agency (EPA)

The laboratory testing chamber is small and directs a gas stream directly onto the sensor, which will not be the case in a wearable platform for personal environmental monitoring. To more accurately simulate field testing conditions, the Environmental Protection Agency was kind enough to allow the use their large ozone chamber with temperature and humidity control. This allowed gas to come into contact with the sensor through a diffusion process rather than a directed flow.

The EPA lab is located within the EPA Human Studies Facility on the campus of the University of North Carolina (UNC) at Chapel Hill. The facility is equipped with 12 environmental exposure chambers where human test subjects can be exposed to controlled ambient levels of air pollutants to measure associated health related effects.

Exposure tests were conducted in testing chamber LA75, which has a floor area of 29.7 m$^2$ with 3.3 m high ceilings. The chamber operates under a slight negative air pressure with a one-pass, 100% make up air flow from the ceiling to the floor. An adjacent control room houses pollution monitors and provides control over the flow rates to the chamber. All pollutant gases, and clean filtered air, are produced on the floor above and then delivered to the chambers. Ozone is generated by the silent arc discharge method using USP (United States Pharmacopeia) grade oxygen and delivered to the chamber by a custom hardware/software pollutant control system.

Air conditioning equipment removes air pollutants and maintains the temperature and humidity in the exposure chambers as specified by each research protocol and the environmental conditions are recorded as two minute averages in a data base.
CHAPTER 3

ALD SnO$_2$ CHARACTERIZATION

3.1 Introduction

Before the sensor functionality can be understood, it is important to understand the ALD SnO$_2$ (Atomic Layer Deposited tin dioxide) material properties and how they compare to other SnO$_2$ reports in literature. Many excellent material characterization techniques were used to study the atomic layer deposited SnO$_2$, as described in Chapter 2. This chapter (Chapter 3) presents the results of that characterization and compares the data to previously reported values.
3.2 Variable Angle Spectroscopic Ellipsometry (VASE)

With an ideal atomic layer deposition process, the thickness should be a linear function of the number of ALD cycles due to the self saturating nature of the deposition. Additionally, there exists an ‘ALD window’ of temperatures where the reactions should happen uniformly and the resulting deposition rate will be invariant.

An experiment was conducted to verify the ALD nature of the deposition process and to evaluate the effects of annealing temperature. Depositions of 50-500 cycles of ALD SnO$_2$ were performed at 200°C and annealed at 600°C in air for two hours to determine the deposition rate. Another group of 200 cycle depositions were done at temperatures from 150-250°C and then annealed at 0-800°C. Spectroscopic ellipsometry data was fitted to a Cauchy model (Eq. 3.1) to determine the film thickness and refractive index. The data from these experiments is plotted in Fig. 3.1.

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}
\]  

(3.1)

The film deposition rate is close to unity and constant with the number of deposition cycles, as seen in Fig. 3.1a, indicating a true ALD process. However, Fig. 3.1b reveals a minor increase in thickness with deposition temperature. This has also been reported in literature documenting ALD experiments of SnO$_2$ using the same precursor and reactants. The increased growth rate was attributed to thermal decomposition of the TDMASn precursor molecule at temperatures above 175°C [66]. This thermal decomposition could conceivably result in film impurities from the metal-organic precursor, and a higher than stoichiometric concentration of tin, leading to an increase of tin interstitials and oxygen vacancies. Film composition will be investigated in more detail later.

Examining the thickness with respect to the anneal temperature in Fig. 3.1b reveals a slight decrease in thickness after annealing at 400 or 600°C, and an increase upon annealing at 800°C. The decrease from the as deposited film thickness is expected due to densification of the film, and the
Figure 3.1 VASE measurement results: (a) 200°C SnO$_2$ annealed at 600°C thickness by number of ALD cycles and (b) thickness of 200 cycles SnO$_2$ by deposition and anneal temperature.
increase at higher temperatures is due to oxidation of the underlying silicon due to the atmospheric oxygen present during the anneal.

VASE measurements can also provide the complex dielectric function (Eq. 3.2) which is related to the optical band gap and index of refraction. The imaginary part of the dielectric function is plotted in Fig. 3.2a. By extrapolating the linear portion of the imaginary part of the dielectric constant down to \( y = 0 \), the band gaps were calculated to be 3.816 and 3.829 eV for the 150°C and 200°C deposited films, respectively. The index of refraction is plotted as a function of film thickness in Fig. 3.2b. Very thin films result in a reduced index but as the thickness climbs above 100 Å, the index saturates at accepted values for bulk SnO₂.

\[
\epsilon = \epsilon_1 + i\epsilon_2
\]  

(3.2)

These results agree well with literature. ALD growth rates for tin oxide using TDMASn have been reported as 1.2 and 1.25 Å/cycle using ozone and hydrogen peroxide as oxidizers, respectively [66, 67] and 1.4 Å/cycle using another tin precursor, Sn(II) (1,3-bis(1,1-dimethylethyl)-4,5- dimethyl-(4R,5R)-1,3,2-diazastannolidin-2-ylidene), and nitric oxide as an oxidizer [68].

The index of refraction is reported in the range of 1.77-2.0 and observed to decrease at low film thickness [66, 67, 68]. The commonly accepted value for the band gap is 3.6 eV although it has been reported at values from 3-4 eV [67]. It is known that the conduction band of SnO₂ is strongly dispersed, resulting in a strong curvature at the minimum. This can manifest as the Burstein-Möss effect. This results in an increase in the band gap as the carrier concentration increases and the semiconductor becomes degenerate. Excited electrons fill the sharply curved minimum of the conduction band and result in an increased energy needed to promote additional electrons from the valence band [27]. This phenomenon, illustrated in Fig. 3.3 may be the cause of the slightly higher than usual measurement for the band gap.
Figure 3.2 VASE measurement results: (a) extrapolation of $\varepsilon_2$ as function of energy for band gap determination. Films deposited at 150 and 200°C and annealed at 600°C, and (b) Index of refraction as function of film thickness.
Figure 3.3 Illustration of the increased optical band gap due to the Burstein-Möss effect. $E_g$ is the initial band gap, $E_F$ is the starting Fermi level. CBM and VBM are the conduction band minimum and valence band maximum, respectively.
3.3 Hall Measurements

Hall measurements were conducted on the SnO$_2$ films to evaluate the electrical properties as deposition and annealing conditions changed. Fig. 3.4a shows the carrier concentrations, Fig. 3.4b the mobility and Fig. 3.4c obtained from the Hall measurements as a function of deposition temperature on the left column and anneal temperature on the right.

Fig. 3.4a shows that carrier concentration is generally increased with deposition temperature which was also seen in literature and attributed to carbon impurities in the film at low deposition temperatures as a result of steric hindrance, or incomplete reaction of the precursor leading to ligands being trapped within [67, 66, 68]. The carrier concentration is also seen to decline with increasing anneal temperature in air. This can be explained by more complete oxidation of the SnO$_2$ and an associated decrease in the concentration of oxygen vacancies to act as donor sites.

The electron mobility for as deposited films 150°C is the lowest, as seen in Fig. 3.4b, but increases strongly with deposition or anneal temperature. This is not surprising as increasing the processing temperatures results in a more crystalline structure and less electron scattering. However, films deposited at 200 or 250°C show very high mobility as deposited and then lower values after annealing. The as deposited films in this case likely have some degree of crystallinity resulting in the high initial mobility. Additionally, if thermal decomposition of the precursor was significant, then increased tin content may have contributed to conduction band states in the as deposited films and then been oxidized during the anneal.

The resistivity falls sharply as the deposition temperature increases above 150°C. This is due to the previously mentioned high carbon content reported in films below 200°C which is appears to be associated with reduced carrier concentration and mobility [67, 66, 68].

Choi and Park [67] specifically mentioned choosing not to electrically characterize films deposited below 125°C. Experiments conducted during the course of this work revealed that films deposited at 100°C where too resistive to measure. Even an applied voltage sweep from -20 to 20 V
Figure 3.4 Hall measurement results by (left) deposition temperature and (right) anneal temperature: (a) carrier concentration, (b) mobility and (c) resistivity
barely produced any result more than pA level noise.

### 3.4 X-ray Diffraction (XRD)

Grazing Angle X-Ray Diffraction was used to verify that the annealed SnO$_2$ achieved the rutile crystal structure. XRD spectra are shown in Fig. 3.5. Fig. 3.5a displays as deposited films that received no anneal for several deposition temperatures. Fig. 3.5b shows the effect of a 400°C anneal with different deposition temperatures. Then Fig. 3.5c and Fig. 3.5d show the effect of different annealing temperatures for films deposited at 150 and 200°C, respectively.

The data in Fig. 3.5a shows that the as deposited films deposited at 150 and 200°C are mostly amorphous. It is interesting however that the (211) peak is always present, and to a lesser extent the (220) peak. Evidence for the presence of these planes has been observed in many XRD spectra recorded but not included in this report. This particular plane seems very likely to form without additional activation required from an anneal. Deposition at 250°C results in more crystalline features being detectable with the (110) plane being detected through a wide angle range.

In Fig. 3.5b, each of the deposition temperatures display some crystallinity after a 400°C anneal. The higher deposition temperature shows greater crystallinity, as expected. The strong narrow peak from the (220) plane appears to be primarily due to the deposition conditions for anneal temperatures of 400°C. The (101) plane only shows a strong signal in the 150°C deposition, which also displays a more well defined (101) plane than the 200°C deposition and has the most suppressed (200) plane of any deposition temperature. This seems to indicate that the structure and/or composition of the 200 and 250°C depositions encourage formation of the (200) plane parallel to the substrate which may also inhibit that orientation for the (110) plane. The carbon content in the film reported at temperatures below 200°C may be the cause of the preferential orientation of the crystal grains.

After annealing, the (110) peak dominates the spectrum in every test condition, indicating that the exposed surface is largely composed of this crystal plane. A photograph of an SnO$_2$ single crystal
Figure 3.5 Top: XRD scans for (a) as deposited and (b) 400°C annealed films deposited at 150, 200 and 250°C. Bottom: XRD scans for SnO$_2$ annealed at 600°C and deposited at (c) 150 and (d) 200°C.
grown by vapor phase transport with the low index planes labeled is shown in Fig. 3.6 [69], to provide some intuition on the relative angles between the crystal planes.

### 3.5 Scanning Tunneling Electron Microscopy (STEM)

STEM and Electron energy Dispersive Spectroscopy (EDS) was used to verify film thickness, crystallinity and do elemental mapping of the SiO$_2$, SnO$_2$ stack. Focused ion beam (FIB) milling was used to cut a very thin cross section from an oxidized wafer with ALD SnO$_2$, which was then imaged on the TEM. Fig. 3.7 shows the results of this analysis including an approximately 11 nm thick SnO$_2$ film on top of SiO$_2$ with good laminar structure. From the atomic image in the center the grain size is estimated to be on the order of the film thickness.
3.6 X-ray Photoelectron Spectroscopy (XPS)

XPS was used to analyze the chemical bonding and stoichiometry of the ALD SnO$_2$ films. All scans were calibrated to the 284.5 eV peak for adventitious carbon. The survey scan in Fig. 3.8a indicates SnO$_2$ with good stoichiometry.

3.7 Summary

In this chapter (Chapter 3) the ALD SnO$_2$ film material properties were characterized by ellipsometry and Hall effect measurements. TEM measurements confirmed thickness values from ellipsometry and crystallinity from XRD. XPS was used to evaluate the elemental composition and oxide quality. The deposition process has been verified to deposit SnO$_2$ at a linear rate of 1 Å/cycle with a weak dependence on deposition temperature due to precursor decomposition and steric hindrance. It was found that deposition temperature of 250°C or anneals of 400°C or more resulted in rutile crystalline structure that became more evident with increasing temperatures. The optical band gap and refractive index were found to be in good agreement with values reported in literature and it was discovered that increasing the deposition temperature increased the carrier concentration.
Figure 3.8 XPS (a) Survey, (b) Sn3d, and (c) O1s scans of SnO$_2$ deposited at 200°C, annealed at 600°C and treated with oxygen plasma for 5 minutes.
while the anneal temperature in air had an inverse effect due to further oxidation of the film and an associated decrease of oxygen vacancies. XPS studies revealed an oxygen deficient surface with large amounts of carbon which is attributed both to adventitious carbon and to impurities remaining from the tin precursor which increase with reduced deposition temperature.
4.1 Introduction

Chapter 3 characterized the Atomic Layer Deposited tin dioxide (ALD SnO$_2$), verified the quality of the films, and provided the material understanding required to evaluate the gas sensing transducer function effectively. This chapter (Chapter 4) will investigate the sensor response to ozone. Discussions will center around mechanisms related to the SnO$_2$ film properties and geometry that enable
gas sensing and recovery at low temperature.

### 4.2 Low Power Sensing Challenges and Strategies

Power consumption is the primary challenge of adapting metal oxide sensors to continuous, long-term, and portable monitoring. Commercial ozone sensors typically heat the sensitive layer to 300-500°C to facilitate rapid response and stable operation. Fabrication on a membrane or a micro-hotplate to reduce the thermal mass and power consumption is common [28, 70], but the sensors still consume up to 80 mW of thermally dissipated power, as discussed in the background information in Chapter 1. The obvious solution is to reduce the operating temperature of the sensor. This approach presents additional challenges as chemical reactions on the surface take a very long time as temperature decreases and the effect of adsorbed water vapor increases dramatically.

Recall from Chapter 1, that the transducer mechanism involves gas species adsorbing to the surface where they participate in ionosorption and the resulting charge transfer modulates the sensing layer’s conductivity. At low temperature, this reaction rate is very slow making it difficult to detect a signal, much less understand it. Sensor recovery suffers even more as the desorption reactions are endothermic and have a longer time constant than adsorption. Alternative energy sources may be considered, such as ultraviolet (UV) light, but the challenge of dealing with humidity effects remains. The impact of humidity is more pronounced at lower temperature where water molecules are not driven off by the heat [29]. This strongly impacts the adsorption kinetics at the surface and the sensor response. Additionally, carbon build up on the surface may degrade performance over time. A heated sensing film has some self cleaning properties through oxidation of carbon which is then desorbed as carbon monoxide or carbon dioxide gas.

The reduced response and reaction speed can be mitigated by enhancing the sensitivity, but this may also have drawbacks. Metal oxides are already known to have poor specificity and respond rather broadly to oxidizing gases, like ozone and nitrogen oxides, as well as reducing gases like
carbon monoxide. As such, it is difficult to enhance the sensitivity to a particular gas without also enhancing increasing response to interfering gases. If the specificity of the sensor isn’t understood, then the signal of interest may be lost among interfering signals. Reports in literature describe efforts to specifically identifying gases through use of an e-nose (electronic nose) system. Such systems are composed of at least several different sensors working together and pattern matching or classification algorithms that must be trained to effectively determine the identity and concentration of gases from the response signals [71, 72, 73, 74, 75].

Fig. 4.1 illustrates how the system inputs and outputs relate to the sensor function. Each of these components require investigation to understand how they effect the sensor. Mechanisms that enable room temperature gas response, including sensor geometry, film composition and crystallinity, are investigated in Section 2, the UV enabled sensor recovery mechanism in Section 3, and finally the unavoidable impact of humidity will be introduced in Section 4 before investigating it in more detail in Chapter 5. Experiments designed to evaluate the impact of each of these parameters on the sensor’s response to ozone have been conducted in a custom made flow through testing chamber using a NIST (National Institute of Standards and Technology) certified Teledyne T700U gas calibrator and ozone generator. The results will be explained with the help of the materials analysis techniques and knowledge from Chapters 2 and 3.

4.3 Ultra-thin SnO$_2$ Film Sensor: Room Temperature Ozone Response

Recall from Chapter 1 that the metal oxide sensing mechanism depends on the oxygen vacancies in the crystal structure. The oxygen vacancies act as donor sites, contributing electrons to the conduction band and increasing conductivity [76, 77]. Oxidizing gas molecules, such as molecular oxygen (O$_2$), ozone (O$_3$), or nitrogen oxides (NO$_x$) ionosorb to oxygen vacancy sites on the surface and trap electrons. This charge transfer results in a negative surface charge and upward bending of the energy bands. The region just below the surface is depleted of carriers, leaving behind a
space charge region of fixed positive charges and reducing conductivity. This is the basic transducer function of conductometric metal oxide gas sensors and is illustrated in Fig. 4.2 for n-type sensors. An expanded discussion of this topic, including p-type sensor response, can be found in Chapter 1.

The target analyte in this work, ozone, is highly reactive and readily donates an oxygen atom to free radical species. Additionally, it has a resonant structure resulting in a dipole with the center oxygen atom being positively charged and one of the terminating atoms negatively charged as illustrated in the Lewis Dot diagram in Fig. 4.3 [28]. These properties make the ozone adsorption process low energy resulting in strong sensor response, but also make the reactions less certain.

The main accepted mechanism involves dissociation of O$_3$ into molecular oxygen and a negatively charged atomic oxygen ion that may then react with the surface. However, a mechanism for molecular adsorption has also been proposed. The dipole of the ozone molecule could allow the negatively charged oxygen atom to associatively bond with a positively charged surface state.
Figure 4.2 Result of negative surface charge on an n-type semiconductor: (a) space charge region of depth $x_0$, (b) energy band bending, and (c) majority carrier concentration
and decomposition of the molecule may occur at a later time. The following reactions for both associative and dissociative ionosorption on the SnO₂ surface have been proposed. It is suggested that Eq. 4.1 is more likely at temperatures below 160°C while will dominate at higher temperatures [28]. However, additional factors that make Eq. 4.2 more likely to dominate will be discussed later.

\[
O_3(g) \rightarrow O_3(s) + e^- \rightarrow O_3^-(s) \quad (4.1)
\]

\[
O_3(g) \rightarrow O_3(s) + e^- \rightarrow O_2(g) + O^-(s) \quad (4.2)
\]

As the operating temperature of the sensor is reduced, the reaction rates for ionosorption decrease. In order to reduce the operating temperature as much as possible and still be able to detect a signal with a reasonable amount of time, the response from ionosorption induced charge transfer must be enhanced. Considering the issue as a signal to noise ratio (SNR) problem, one might intuit that sufficiently reducing the free carrier concentration in the film would allow changes from charge transfer to be more easily observed. This is the motivation for ultra-thin film based sensors. For thicker films, the conductivity of the sensing layer is dominated by the bulk characteristics where many conduction electrons exist and a large change is required to produce a measurable response. However, as the film thickness of the sensing material decreases, the resistance of the surface charge depleted region has more impact and trapping of electrons has a larger effect on the total resistance change [78, 56, 55, 27]. The critical dimension for this effect to occur is referred to as the Debye length and will be discussed in greater detail later in this chapter (Chapter 4).
The sensor response in Fig. 4.4 are from films approximately 24 nm thick, based on 200 cycles of ALD SnO$_2$. The films were tested for response to 400 ppb ozone at high temperature, 350°C, and room temperature, 22°C. The plot of resistance vs time can be seen in Fig. 4.4. This experiment predates the acquisition of the Teledyne T700U ozone generator. The ozone generator used for this experiment was a simple UV light with an adjustable metal sleeve that could be used to block a portion of the light from the ozone generation chamber. The minimum ozone concentration output from the generator was calibrated at 400 part per billion (ppb) using an Alphasense OX-B431 electrochemical ozone sensor and low noise individual sensor board.

The first experiments, conducted at 350°C, used a heated chuck in the testing chamber and demonstrated good response and fast recovery to 400 ppb ozone as shown in Fig. 4.4a. The response does not saturate completely although it more than doubles in less than 100s and then rolls off considerably. Many commercial heated sensors suggest operating the sensor at temperature for a burn in period of 48 hours to stabilize the surface, but this was not attempted because the zero grade air cylinders only last for about 16 hours of testing. Additionally, 350°C was the maximum temperature for the heated chuck and maintaining that temperature for extended periods of time resulted in a considerable increase in the testing chamber surfaces and surrounding area. The lack of burn time and operating nearly 100°C below commercial sensors is probably why the sensor response doesn't saturate and shows a decrease with each exposure. The baseline resistance here is very low, 250 Ω, due to the high operating temperature. At 350°C, 54 meV of thermal energy work to excite carriers from shallow donor levels created from oxygen vacancies. The net effect is many more free electrons and reduced resistance. This energy also provides energy to break the bonds of oxygen species that have ionosorbed, resulting in a fast recovery process. The response at room temperature, shown in Fig. 4.4, displays a much slower change in resistance and recovery did not occur on a reasonable time scale. The resistance here is quite a bit higher with less thermally excited carriers. Despite the recovery challenges, the results motivated further investigation into this low power mode of operation.
Figure 4.4 24 nm thick SnO$_2$ film response to 400 ppb ozone at (a) 350°C and (b) 22°C.
From this point on, all sensor resistance data is collected at room temperature operation and all gas exposure experiments were conducted using the NIST certified Teledyne T700U gas calibration unit with ozone generator. This instrument allows very fine control over ozone concentrations down below 10 parts per billion (ppb). The sensors discussed next were fabricated with 100 cycles of ALD SnO$_2$ and are about 12 nm thick, half the thickness of the previous sensors. The sensor resistance is plotted during 100 ppb ozone exposures at room temperature in Fig. 4.5a. The sensor was measured four different times with the same exposure pattern and shows consistent results.

Conductometric sensor response is traditionally measured as the ratio of the resistance in the presence of the target gas to that in clean air, but at lower temperatures the resistance change is considerably slower than with heated sensors and there is no clear point of saturation when the measurement can be concluded. The derivative of the resistance change with respect to time, $\frac{dR}{dt}$, has been shown to correlate with the concentration in literature and provides a method for measuring the sensor under these conditions [79, 80]. The reason for this correlation is that the adsorption rate is a function of the concentration of gas molecules in the air, as one might intuit, while the desorption rate is independent of the analyte concentration [81]. The change in band bending, and thus the change in resistance, is a function of the surface charge from adsorbed species. The derivative is plotted in Fig. 4.5b.

The sensors were tested for response to 25, 50, 75 and 100 ppb ozone to verify that the derivative increased with increasing ozone concentration. The measurement cycle was repeated five times and the results are shown in Fig. 4.6. The raw time response is shown in Fig. 4.6a and the derivative plot in Fig. 4.6b. A quadratic fit worked very well for these data points. An ideal sensor would have a linear response to concentration, however several mechanisms prevent that. The number of oxygen vacancies that can be occupied is limited by the Weisz effect, where electrostatic repulsive forces between ions on the surface limit adsorption [82]. Additionally, as more surface charge accumulates, the depleted space charge region grows and the energy bands bend further. This results in a larger potential barrier for conduction electrons to react with surface species. For heated sensors this is not
Figure 4.5 Repeatability of room temperature sensor response to 100 ppb O$_3$. (a) Resistance vs. time and (b) $\frac{dR}{dt}$ of the time signal
an issue, but at room temperature this barrier impedes surface reactions and slow the adsorption rate. No appreciable amount of ozone is desorbed in zero air phases of the exposure and so there are fewer active adsorption sites as time goes on. However, this data confirms that different concentrations of ozone in the ambient are distinguishable from the sensor response.

### 4.3.1 Film Thickness and the Debye Length

With careful attention to this figure, one may have noticed that the 12 nm thick films responded much stronger at room temperature than the 24 nm thick films. For the 24 nm thick sensors the resistance only increased about 20 Ω over 100 s while the 12 nm thick sensor increased by about 200 Ω. Chapter 1 discussed tailoring the film thickness to twice the Debye length for maximum sensitivity and the data presented here confirms the thickness related response amplification. This knowledge motivates the strategy to exploit the monolayer thickness precision intrinsic to atomic layer deposition to tailor the film thickness for maximum response.

As mentioned in Chapter 1, the Debye length is given by Eq. 4.3 where \( \varepsilon \) is the dielectric constant (13.5\*8.85\*10^{-12} F/m in SnO\(_2\)), \( k_B \) is the Boltzmann constant (1.38\*10^{-23} J/K), \( T \) is the absolute temperature (K), \( q \) is the elementary charge (1.6\*10^{-19} C) and \( n_c \) is carrier concentration in the channel. Ogawa, et al. [56] determined \( n_c \) in SnO\(_2\) to be equal to 3.6\*10^{18} cm\(^{-3}\) at 250 °C. This value yields 46 Å for twice the Debye length, however the number of carriers is highly dependent on the number of oxygen vacancies as discussed in Chapter 1. Hall measurements on ALD SnO\(_2\), summarized in Chapter 3, revealed carrier concentrations in the range of 10^{19} cm\(^{-3}\) - 10^{20} cm\(^{-3}\) which yields a value of 9-28 Å for twice the Debye length. Some sample calculations for the Debye Length in SnO\(_2\) at room temperature (300 K) can be seen in Table 4.1.

A thickness study to evaluate the impact of the Debye length was conducted on film thicknesses of 6, 12 and 36 nm. The deposition temperature was 150°C and the annealing conditions were 2 hours at 600°C in air. The sensor responses were measured for ozone concentrations from 50-300 ppb and the results are shown in Fig. 4.7. The response is again calculated as the derivative of the
Figure 4.6 Evaluation of room temperature sensor response to 25, 50, 75 & 100 ppb O$_3$. (a) Resistance vs. time and (b) $\frac{dR}{dt}$ of the time signal.
Table 4.1 Sample Debye Length Calculations

<table>
<thead>
<tr>
<th>n (cm⁻³)</th>
<th>Lₐ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0E+17</td>
<td>13.9</td>
</tr>
<tr>
<td>5.0E+17</td>
<td>6.22</td>
</tr>
<tr>
<td>1.0E+18</td>
<td>4.40</td>
</tr>
<tr>
<td>5.0E+18</td>
<td>1.97</td>
</tr>
<tr>
<td>1.0E+19</td>
<td>1.39</td>
</tr>
<tr>
<td>5.0E+19</td>
<td>0.622</td>
</tr>
<tr>
<td>1.0E+20</td>
<td>0.440</td>
</tr>
<tr>
<td>5.0E+20</td>
<td>0.197</td>
</tr>
</tbody>
</table>

\[ L_D = \sqrt{\frac{\varepsilon k_B T}{q^2 n_c}} \]  \hspace{1cm} (4.3)

resistance change with respect to time, but due to the large difference in baseline resistance with film thickness, normalization of the data was required. The response data was normalized by dividing by the baseline resistance measured just prior to the experiment to compare the percentage of resistance increase during exposure. It is clear that the 6 nm film is the strongest sensor by far as the relative resistance increase for the 12 and 36 nm films is barely visible at the bottom of the figure. This illustrates the impact of the Debye length effect on the strength of gas response and the advantage of very thin films over the more traditional thick film technologies.

Based on the first thickness experiment, and the Debye length calculations for room temperature SnO₂, it was decided to conduct another more detailed thickness study with finer thickness resolution centered around 6 nm to determine the optimal thickness for maximum sensitivity. SnO₂ films were prepared at four different thicknesses from 3 to 12 nm. The deposition temperature was 150°C and the annealing conditions were 2 hours at 600°C in air. The baseline resistances were measured just after fabrication and the average values are shown in Fig. 4.8. The 3 nm films turned out to be insulators, so that data was omitted. The error bars represent the standard deviation and the sample size is 8.

This data shows the decrease in resistance with increasing film thickness which is to be expected
Figure 4.7 Effect of SnO$_2$ film thickness on room temperature ozone response

Figure 4.8 Baseline resistance after fabrication as a function of film thickness. Films were deposited at 150°C and annealed for two hours in air at 600°C.
Figure 4.9 Normalized room temperature 50 ppb O₃ response as a function of film thickness. Films were deposited at 150°C and annealed for two hours in air at 600°C.

Based on the concept of the Debye Length, as the film thickness shrinks toward the Debye length, the charge carrier concentration in the crystal declines and the space charge region dominates the conductivity. The sharp increase in resistance as the film shrinks shows that this effect begins to dominate the resistance between 6 and 9 nm. The normalized responses for the sensors to 50 ppb ozone from both thickness studies are summarized in Fig. 4.9.

Fig. 4.9 confirmed that the 6 nm thick films gave the largest ozone response and that the response magnitude drops off rapidly with just a few more nm of film thickness. The 9 and 12 nm thick films displayed only 1-2% resistance increase with exposure while the 6 nm thick film exhibited a 40% increase indicating that at 6 nm thick, the depletion region defined by the Debye length is dominating the electrical characteristics of the film.

4.3.2 Impurities in the SnO₂ Film

Hall measurements, presented in Chapter 3, showed that the carrier concentration decreased with deposition temperature. This is also consistent with literature that cites reduced conductivity of
SnO₂ films with decreasing ALD temperature. The proposed cause of the reduced conductivity is increased carbon content and dimethylamino ligands left over from the TDMASn precursor molecule due to steric hindrance (incomplete removal of dimethylamino ligands during reactant exposure) [67, 66]. Based on the previous discussions of the Debye length and the Hall measurements of the SnO₂ films, it is expected to see increased sensor response correlate with decreased deposition temperature. The experimental data in Fig. 4.10 verifies this, showing the sensor response for films deposited at 150, 200 and 250°C.

Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) was used to investigate and quantify the carbon content in the films. Accurate quantification requires a reference sample with a known concentration to compare with, which presented a small problem. A carbon implant could provide the doping profile for reference, but an implant requires a minimum film thickness of 100 nm so that the implant peak can be distinguished from adventitious surface carbon. Additionally, it was suspected that the background carbon content in the film could be as much as several at.% based on deposition conditions and the implant dose must be an order of magnitude higher than...
background levels. Several samples were prepared using different treatments in an attempt to reduce carbon concentration before the implant.

Implant simulation of carbon in \(\text{SnO}_2\) was performed using SRIM (The Stopping and Range of Ions in Matter) software. Because the film was relatively thin for implant purposes, a low dose and energy were required to achieve a good profile. Carbon 13 isotope was chosen so that a lower dose would result in a visible doping profile. A simulated dose of \(5\times10^{14} \text{ cm}^{-2}\) at an energy of 25 keV resulted in a visible carbon peak about one order of magnitude greater than the background levels at a depth of 445 Å. These parameters were deemed satisfactory and film preparation began.

A "thick" film of approximately 1100 Å was deposited on oxidized silicon at 200°C and samples were subjected to several different conditions designed to eliminate carbon concentration before sending them off for a carbon implant. Each of the samples were annealed in air at 600 °C for crystallization. One was left in that crystallized state, another received a one minute, 600°C anneal in an \(\text{N}_2\text{O}\) ambient, and another was treated with a five minute oxygen plasma in a barrel asher at 300 W forward power. The \(\text{N}_2\text{O}\) anneal and the oxygen plasma experiment were designed to introduce atomic oxygen to the film in an effort to scavenge carbon that may desorb as CO. A 900 or 1000°C \(\text{N}_2\text{O}\) anneal would have been ideal as \(\text{N}_2\text{O}\), however the cooling water pump for the Heatpulse 610 Rapid Thermal Annealing (RTA) furnace was broken and the auto shutoff function prevented reaching the desired temperature. The samples were then shipped to Leonard Kroko, Inc. Ion Implantation Services who performed the implant.

Fig. 4.11 shows TOF-SIMS results for each of the treatments that attempted to reduce carbon concentration. The background carbon concentration was very similar across all the implanted samples indicating that the oxygen plasma and \(\text{N}_2\text{O}\) anneals did not scavenge appreciable carbon from the films. This is not surprising in retrospect, as the oxygen plasma did not heat the sample enough to activate the film and mobilize the carbon while the \(\text{N}_2\text{O}\) anneal was too low temperature to dissociate the \(\text{N}_2\text{O}\) effectively. However, the implant peak was sufficiently high compared to the background to quantify the carbon content.
The implanted reference samples were then used to quantify the carbon content in the films as a function of deposition temperature. The TOF-SIMS results can be seen in Fig. 4.12. From this data, it is seen that carbon concentration does increase dramatically as deposition temperature decreases, ranging from almost 2 at.\% at 100°C deposition down to 0.6 at.\% at 250°C.

This indicates that increased carbon content of the film is the physical cause for reduced carrier concentration. This may be due to carbon atoms replacing oxygen atoms in the crystal lattice, but may also be due to carbon content affecting the concentration of oxygen vacancies. To verify if the oxygen vacancy concentration was being impacted by the carbon left in the film, the samples were sent to the Ion Beam Laboratory at the University of Albany for Rutherford Backscattering (RBS) analysis. The RBS data is tabulated in Table 4.2. The oxygen deficient nature of the films is clear, but no trend in stoichiometry can be seen with deposition temperature, making it difficult to say if the carbon atoms are interstitial impurities or substitutional for tin or oxygen.

As both carbon and tin are group IV elements, one might expect any substitutional carbon to replace tin in the SnO$_2$ lattice, but the answer is not so simple. The combination of large electroneg-
Figure 4.12 TOF-SIMS analysis of carbon concentration vs deposition temperature.

Table 4.2 Stoichiometry results from Rutherford Backscattering analysis.

<table>
<thead>
<tr>
<th>Deposition Temperature</th>
<th>Anneal Temperature</th>
<th>Sn:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0</td>
<td>1:1.89</td>
</tr>
<tr>
<td>150</td>
<td>600</td>
<td>1:1.87</td>
</tr>
<tr>
<td>200</td>
<td>600</td>
<td>1:1.92</td>
</tr>
<tr>
<td>250</td>
<td>600</td>
<td>1:1.80</td>
</tr>
</tbody>
</table>
ativity difference and atomic radii differences means that substitution for carbon would cause large amounts of lattice distortion and have a high formation energy \[83\]. Additionally, research on carbon induced magnetism of SnO\(_2\) surfaces has been performed by Density Functional Theory (DFT) calculations which indicates substitutional carbon at oxygen sites on the (110) surface \[83, 84\].

The Hall measurements in chapter 3 showed decreasing carrier concentration with deposition temperature but increasing mobility, at least for as deposited samples. The increased lattice strain would reduce mobility, but the carrier concentration decreased by an order of magnitude which seems unlikely to have been caused by substitution for tin. Carbon substituting for oxygen would result in two fewer electrons to participate in bonding and potentially being conduction electrons. While carbon substituting for tin(IV) would not cause any change in carrier concentration as they have the same number of valence electrons. If the carbon were to substitute for a tin(II) atom then it could conceivably bond with two electrons that were going to be conduction electrons, but the likelihood of any particular oxygen atom bonding to a tin(II) atom is higher than any particular tin atom displaying the inert pair effect discussed in Chapter 1. The argument for substitution of oxygen atoms is convincing and would result in a greater carrier reduction on a large scale. Therefore, the most likely cause for the reduced conductivity is carbon substitutionals replacing oxygen atoms or oxygen vacancy sites.

To further support the body of evidence that carbon content left over from the precursor molecule is impacting the sensor response due to carrier modulation, another experiment was conducted to evaluate the effect of additional oxidation of the films through two different methods. The first method consisted of changing the tin precursor to ozone reactant ratio during the deposition process. The standard deposition recipe alternated precursor to reactant doses at a 1:1 ratio, but industrial applications of ALD often utilize multiple reactant doses for each precursor dose to limit steric hindrance and promote more complete oxidation. The deposition for this experiment used three ozone pulses for each tin precursor pulse.

In addition, sensors deposited with the standard recipe and then exposed to oxygen plasma were
investigated. In this case, the atomic oxygen plasma was expected to passivate oxygen vacancies on the surface, resulting in increased baseline resistance and perhaps a stronger ozone response due to the signal to noise ratio of the conduction electron modulation in the film. The normalized resistance of the films treated with three times the reactant dose during deposition and the films with the post deposition plasma treatment are compared to the standard recipe during ozone exposure in Fig. 4.13.

The deposition with triple reactant pulses displays a weaker ozone response than the standard film as expected. The additional ozone pulses result in fewer carbon impurities, higher carrier concentration, and a corresponding weaker ozone response. The oxygen plasma treated films exhibited a greatly increased baseline resistance and response to ozone. The data from the TOF-SIMS reference sample preparation has shown that the carbon content is unchanged by the oxygen plasma so this change is due completely to atomic oxygen passivating oxygen vacancy sites on the surface. As the oxygen vacancy concentration decreases, fewer donor sites result in a smaller carrier concentration. Recall that as the carrier concentration falls, the Debye length grows, resulting in
a higher signal to noise ratio and increased sensor response. In fact, the sensor response was so strong that even 25 ppb of ozone resulted in resistance too large to measure effectively. This is the cause of the noisy peaks of approximately equal amplitude for all four exposures of 25-100 ppb as the current levels approached the noise threshold of several pA. This holds interesting implications for part per trillion level detection of ozone.

### 4.3.3 SnO$_2$ Crystallinity: Impact of Annealing Temperature

The annealing process to crystallize the SnO$_2$ is another important step in determining the sensing characteristics of the ALD films. The surface structure of SnO$_2$ is complex, and especially the (110) surface is filled with high density defect terraces, steps, antiphase boundaries and metastable adislands of various configurations depending on anneal temperature [85]. Additionally, the crystal structure obtained upon annealing defines the band gap and the oxygen vacancy donor levels, which impact the sensor response significantly. Fig. 4.14a shows the baseline resistance plotted vs the annealing temperature for different film thicknesses and Fig. 4.14b shows the same data with film thickness on the x-axis and the anneal temperature represented by the different series. This is a superset of the data from Fig. 4.8 combined with additional annealing conditions.

Recall that the Hall measurement results in Chapter 3 showed decreasing carrier concentration with increasing anneal temperature. This plot is repeated in Fig. 4.15 for convenience. The increased conductivity may seem counter intuitive here but the anneal also enhances the crystallinity of the film. This removes point defects and broken bonds which reduces scattering and increases mobility so the increase in conductivity is not surprising.

What is surprising is the ozone response for each of the films. The normalized response to 50 ppb O$_3$ is plotted in Fig. 4.16 for each anneal temperature. The 800°C annealed films displayed weaker ozone response than the 600°C films and the as deposited films displayed very strong response.

It should be noted that an effort was made in this experiment to have a consistent reset resistance, $R_0$. The as deposited sample and the 400 and 600 °C annealed samples were tested with a reset
Figure 4.14 Effect of annealing temperature and film thickness on baseline resistance.
Figure 4.15 Carrier concentration by deposition and anneal temperature via Hall Measurements.

Figure 4.16 Effect of anneal temperature on room temperature 50 ppb O₃ normalized response.
resistance of 10 MΩ. The 800°C resistance was tested with a reset resistance of 1 MΩ because the starting baseline resistance was already lower than 10 MΩ. This required driving the resistance of the as deposited sample down significantly with UV light resulting in more vacancies for adsorption. Additionally, the amorphous films have many more defects and broken bonds to begin with so this explains the high response for the as deposited films. It should also be noted that this does not mean an amorphous film is a better sensor. The stochastic nature of the amorphous structure results in films that are difficult to reproduce and often too high resistance to measure effectively, especially when exposed to humid ozone conditions where adsorption rates increase dramatically. Finally, driving the resistance down enough to measure the film required long UV exposure and consequently high power consumption.

The decreased response at 800°C annealing conditions is likely due to increased oxidation of the surface during the anneal resulting in fewer oxygen vacancies, which will also contribute to the lower carrier concentration observed in the Hall measurements. On the other hand, recall that the Debye length is proportional to $\frac{1}{\sqrt{\pi}}$. This seems to indicate that the Debye length will increase with anneal temperature as the carrier concentration decreases, however no increase in response is observed. The effect of the Debye length amplification has been described as a signal to noise ratio problem in this work. As the space charge region begins to dominate the crystallite conductivity, any change in carrier concentration from ionosorbed gases should result in a larger change in resistance. A competing effect here may be the potential barrier between conduction electrons and the surface. As the Debye length grows, that barrier increases and fewer electrons arrive at the surface to interact with the gas species. Therefore, for high sensitivity, a balance must be found that approaches the Debye length to reduce carrier concentration enough for response amplification while maintaining sufficient carriers and oxygen vacancies to react with adsorbed gas species on the surface.
4.4 Sensor Recovery

The low temperature also impacts the application of the sensors due to slow desorption rates hindering sensor recovery. If the sensor cannot recover so that it can make another measurement then its utility is practically null. When ozone molecules ionosorb onto the surface, the trapped electrons occupy states within the band gap. To desorb these gas molecules, the trapped electrons must be excited back to the conduction band. Photo-excitation is an alternative to using thermal energy and can be finely tuned using light emitting diodes (LEDs) that emit a narrow band of wavelengths. The acceptor states (electron traps) associated with ionosorption are deep within the wide 3.6 eV band gap and so light in the near UV spectrum is required to excite them. A schematic of the band diagram in Fig. 4.17 shows the locations of the donor levels (E_D) from oxygen vacancies, acceptor levels (E_A) from ionosorbed gas species, and the Fermi level (E_F) relative to the conduction (E_C) and valence (E_V) bands.
Figure 4.18 25-100 ppb room temperature ozone exposure with UV assisted recovery between exposures.

The energy of a photon is expressed as Eq. 4.4 where $E$ is the energy, $h$ is Planck's constant and $\lambda$ is the wavelength of light. Solving for $\lambda$ if $E = 3.6$ eV yields a wavelength of 344 nm, well into the ultraviolet (UV) spectrum. In laboratory testing indium gallium nitride based LEDs with 405 nm (3.06 eV) and 385 nm (3.22 eV) light were used to desorb ozone and achieve sensor recovery as shown in Fig. 4.18. A wavelength of 385 nm resulted in a much faster and more efficient recovery as the higher energy enables exciting electrons from deeper traps to the conduction band as expected. Shorter wavelengths of 365 nm (3.39 eV), 340 nm (3.65 eV), and 325 nm (3.82 eV) light were also experimented with, however these wavelengths require aluminum gallium nitride which drives the cost up on order of magnitude or more. Additionally, they had significantly lower power output rendering them unsuitable for strong desorption rates.

$$E = \frac{hc}{\lambda}$$  \hspace{1cm} (4.4)
4.5 Effect of Humidity

4.5.1 Reduction of the Surface

Tin dioxide (SnO$_2$) exhibits high sensitivity toward water causing dramatic changes in sensor response. Literature reports decreased resistance and decreased response to oxidizing gas in the presence of humidity [86, 87, 88, 89] due to dissociation of water at the metal cation sites and reduction of the surface, although the exact mechanisms are under debate. The complex nature of polycrystalline samples prevents making a definitive statement on the nature of water adsorption reactions. Many theoretical and experimental studies have been performed to provide evidence that both molecular and dissociated water in the form of hydroxy groups exist on SnO$_2$ surfaces. Eq. 7.1 describes the basic dissociation of water into a hydroxy group and proton (hydrogen). Commercial sensors operate above 400 °C partly to combat the effects of water vapor by desorbing it from the surface.

\[
H_2O \rightarrow OH^- + H^+ \quad (4.5)
\]

Congruent with literature, the humidity response of freshly fabricated ALD SnO$_2$ sensors is strongly reducing as electrons are donated to the SnO$_2$ surface upon water adsorption and dissociation as seen in Fig. 4.19.

On a clean but defective surface, water dissociation is proposed by two different mechanisms. Eq. 5.3 shows the formation of a terminal OH group attached to a surface tin atom and a rooted OH group formed when the dissociated proton bonds to a neighboring bridging oxygen atom. The terminal group forms a dipole with only localized charge transfer and does not contribute to the conductivity but the rooted OH group ionizes and releases an electron to the conduction band. Eq. 5.4 shows another dissociation mechanism were two terminal dipole groups are formed by pulling lattice oxygen out to react with the proton. This leaves behind an oxygen vacancy which
becomes doubly ionized and releases two electrons to the conduction band.

$$\begin{align*}
H_2O(g) + Sn_{Sn} + O_O &\leftrightarrow (Sn^{\delta+} - OH^{\delta-}) + (OH)_O^+ + e^- \quad (4.6) \\
H_2O(g) + 2Sn_{Sn} + O_O &\leftrightarrow 2(Sn^{\delta+} - OH^{\delta-}) + V_O^{2+} + 2e^- \quad (4.7)
\end{align*}$$

4.5.2 Ozone Response in Humid Atmosphere

Evaluation of the sensor response to ozone in various humidity levels can be seen in Fig. 5.7a and Fig. 5.7b. The A transient strong oxidation effect upon humidity increase that slowly decays is visible here, superimposed with a more constant step like function of enhanced oxidation with humidity increase in the presence of ozone. Deferring discussion of the transient responses until Chapter 5, it is noted that each time the humidity increases, the ozone response does as well.

This may be counter intuitive based on the previous discussion. One would expect that the reducing effect of the humidity would offset the oxidation due to ozone exposure. This behavior indicates several mechanisms are modifying the surface charge. The reduction of the surface in
Figure 4.20 Room temperature sensor response to humidity in 100 ppb O₃: (a) time series resistance signal and (b) Derivative ($\frac{dR}{dt}$) magnitudes
humid zero air is apparent from the change in resistance in Fig. 4.19. However, when ozone is introduced with humidity then a synergistic effect causes clearly enhanced oxidation when compared to dry air with ozone.

One might suggest that the water and ozone molecules are competing for adsorption sites. Then when ozone is introduced to the H$_2$O saturated surface, it preferentially takes the place of water molecules, increasing the resistance [90]. However, this mechanism cannot explain the larger response to humid ozone over dry ozone.

The mechanism can be explained by the presence of dissociated water on the SnO$_2$ surface at room temperature. Takada et al. [91] showed that surface hydroxy groups act as catalysts for ozone decomposition. This results in a larger number of reactive oxygen species simulating a higher effective ozone concentration available to chemisorb to the surface.

This phenomenon of surface reduction in humid air and increased oxidation in humid ozone has also been observed by Korotcenkov et al. [89] on heated SnO$_2$ films from 150-300 °C. Korotcenkov observed a shift in the maximum ozone response from 350 °C to 250 °C. This likely has to do with the maximum concentration of hydroxy groups available on the surface as they begin to desorb at 250 °C.

However, the OH$^-$ enhanced ozone response may be problematic for ozone sensors' longevity. Stable chemisorbed OH$^-$ builds up on the surface resulting in drifting baseline resistance and reduced active sites for ozone adsorption [92]. Also, ozone and water molecules can react to form a stable H$_2$O-O$_3$ complex passivating the surface [93]. Molecular water begins to desorb at temperatures as low as 100 °C, which may be manageable as a duty cycled recovery option on the available power budget, but hydroxy groups are more stable. Hydroxy groups may begin to desorb at 250 °C but won't fully desorb until reaching 400-500 °C [89, 88] (which is, probably not coincidentally, the operating temperature of the commercial Sensortech ozone sensors). However, if the ratio of molecular water to hydroxy groups has some preferential ratio determined by the oxidation state of the surface (as will be see in Chapter 5), then molecular water may be driven off periodically by low heat and the
remaining hydroxy groups should rearrange themselves into a ratio of \( \text{H}_2\text{O} \) and OH groups.

### 4.6 Summary

In this chapter (Chapter 4) the basic sensor functionality of the ultra-thin SnO\(_2\) films has been investigated. Room temperature ozone response was shown and it was explained that the required sensitivity enhancement was due the surface electron depleted layer dominating the electrical characteristics as the thickness approached the Debye length. The sensor data exhibited repeatability of measurements and correlation of response to ozone concentration in the range of 25-100 ppb. The change in resistance and response amplification was investigated as a function of film thickness and both were found to increase sharply as the thickness decreased from 9 to 6 nm and the films became insulating at 3 nm.

Fabrication parameters were also considered for their effect on the sensor characteristics. In particular, the effects of deposition and anneal temperatures were investigated. Decreasing deposition temperature in the range of 150-250°C was found to be associated with decreased film conductivity, increased ozone response, and increased carbon content. It was explained that the carbon content was a result of steric hindrance during the deposition process and that the carbon is a substitutional impurity for oxygen in the crystal lattice. This results in the decreased electron concentration and increased ozone response.

Increasing the air anneal temperature in the range of 0-800°C was found to be related to increased conductivity up to the maximum anneal temperature, but ozone response demonstrated a maximum in as deposited films and a second peak at 600°C. The amorphous response is likely due to a large number of defects, broken bonds, and very high baseline resistance, while the reduced response at 800°C was attributed to increased oxidation of the surface resulting in fewer oxygen vacancy sites for reaction, fewer conduction electrons to react with surface species, and a large potential barrier for conduction electrons to reach the surface due to the increased Debye length. It was noted that
the amorphous material does not make a better sensor despite the increased response because of
the film resistance was too high to measure effectively and the high adsorption rate results in higher
power consumption for recovery.

Sensor recovery utilizing ultraviolet light was also demonstrated and it was explained that the
mechanism involved UV excitation of electrons trapped in deep acceptor states formed by the
adsorbed gas molecules. When the electron returns to the conduction band, the gas molecule is
able to desorb.

Finally, SnO$_2$ sensitivity to water vapor was introduced and it was shown that it results in a
reduced surface and increased conductivity. However, when humidity and ozone are both present,
an increased oxidation response over that of dry ozone was observed. This is due to dissociated water
on the surface catalyzing ozone decomposition and resulting in a larger effective concentration of
oxygen ions available on the surface for chemisorption. Interactions with humidity will be explored
in more depth in Chapter 5.
5.1 Introduction

Water vapor (H$_2$O) is well known in the sensor industry to impact the operation of metal oxide sensors [94, 89, 95]. In fact, tin dioxide (SnO$_2$) materials have been reported numerous times as conductometric humidity sensors in literature [92, 96]. The conductivity change in SnO$_2$ upon exposure to humidity is due to dissociation of molecular water into hydroxy groups, which occurs even at room temperature due to the defect rich surface. However, the mechanism of dissociation is complex still debated. Water vapor is more abundant in the air than any other molecule and will
always be present as a surface contaminant from the atmosphere or hydrocarbon oxidation [97]. In addition, the concentration can vary from 0 to 4% depending on location and time of day resulting in significant changes in the adsorption kinetics at the SnO$_2$ surface.

In Chapter 4, it was shown that the presence of humidity acted to reduce the SnO$_2$ surface and increase conductivity in zero air. However, if ozone was present with humidity then the oxidation effect of ozone was enhanced due to dissociated water species acting as catalysts for ozone decomposition in accordance with literature [86, 87, 88, 89]. The high operating temperature of commercial metal oxide sensors is required, in part, to reduce their sensitivity to humidity changes. Molecular water will dissociate at modest temperatures of 100-150°C, but the dissociated hydroxy groups are stable up to 350°C and won't fully desorb until 500°C. For this reason, sensors operating at room temperature require exceptional knowledge of the mechanisms of water on the surface. This chapter (Chapter 5) explores the impact of water on the room temperature sensor operation in more depth.

### 5.2 Water Adsorption: Impact of Temperature and Absolute Humidity

The amount of water that will physisorb onto a surface varies depending on the temperature and the amount of water, or vapor pressure, of water in the air. The maximum vapor pressure before water begins to condense on surfaces is referred to as the saturation, or equilibrium, vapor pressure and corresponds to 100% relative humidity. The saturation vapor pressure is a increasing function of temperature, as shown in Fig. 5.1, so warm air can hold more water vapor than cold air [98]. This concept is demonstrated by dew forming in the early morning. As the temperature drops and the vapor pressure remains constant, the saturation vapor pressure falls and the relative humidity increases. The vapor pressure is limited by the saturation pressure, so as the temperature falls further, water condenses on surfaces resulting in the morning dew. The dew point is a more common name for the saturation temperature, or the temperature at which a particular vapor pressure is equal to the saturation vapor pressure and water spontaneously condenses onto surfaces.
Figure 5.1 Saturation water vapor pressure in air as function of temperature. When the vapor pressure equals the saturation vapor pressure, the relative humidity is 100%.

At the saturation temperature, the saturation pressure is equal to the current water vapor pressure in the air. Below the saturation temperature, the vapor pressure is limited by the saturation pressure and excess vapor will condense. Above the saturation temperature, the amount of condensed on the surface is a function of the vapor pressure and the temperature of the surface. As the surface coverage increases, the effects of water on the conductivity and ozone response of the SnO$_2$ films increases, so it is important to understand this concept. These effects continue to become more dominant with increasing surface coverage until multiple layers of water condense onto a surface, at which point the sensing mechanisms change drastically [99]. Fig. 5.2 [99], shows how much water will adsorb onto the surface where $\Theta$ is the surface coverage in monolayers of water, $T$ is the surface temperature, $P$ is the vapor pressure, and $P_{max}$ is the saturation pressure assuming an atmosphere temperature of 300K (27°C).
Figure 5.2 Water coverage on the SnO$_2$ surface as a function of the ratio of vapor pressure to saturation vapor pressure for (a) $T > T_{sat}$ and (b) $T < T_{sat}$, reprinted from open access article [99]
5.3 Dissociation of Water on the SnO$_2$ Surface

Under energetically favorable circumstances, water may dissociate heterolytically, meaning that the hydroxy group keeps both of the electrons from the covalent bond with the other hydrogen atom. This results in a negatively charged hydroxy group (OH$^-$) and an ionized hydrogen atom (proton), as shown in Eq. 7.1. The term hydroxy group is defined as the negatively charged OH$^-$ molecule while the term hydroxyl refers to the neutral free radical, OH, according to the International Union of Pure and Applied Chemistry (IUPAC). Homolytic dissociation, where the hydrogen atom keeps one of the electrons from the broken bond, is also possible. This results in both dissociated parts becoming highly reactive free radicals and possessing $\frac{1}{2}$ of an electron pair. Free radicals are unstable due to their half filled electron orbital, meaning they will quickly react with other species and not remain in the free radical state for long. Interestingly, the hydroxyl radical is a very strong oxidizer with an oxidation potential of 2.70 V, even more so than ozone at 2.07 V [100].

$$H_2O \rightarrow OH^- + H^+ \quad (5.1)$$

As early as the mid 1970’s, coexistence of molecular water and hydroxy groups was found via transmission infrared (IR) spectroscopy at 47°C [101]. Additional studies used Temperature Programmed Desorption (TPD) and infrared spectroscopic methods to show that measurement features at temperatures below 162°C are attributed to molecular water, while higher temperature features are due to desorption [101], recombination [88, 102], or disproportionation [103] of hydroxy groups.

Caldararu et al. [97] also saw evidence of two different water desorption events at low and high temperatures. They found that molecular water desorbs up to 150°C, and then reappears upon exposure to air. The high temperature water desorption corresponded with a sharp increase of conduction in dry argon, which they attribute to water recombination and desorption as in Eq. 6.9.
After thermal cycling in a humid atmosphere, they noted higher temperatures of desorption. This indicates that water desorbed through thermal treatment may be replaced by more stable species upon cooling and that the ratio of molecular water to hydroxy groups depends on the history of the sample and the ambient humidity during cooling [97].

\[ 2OH^- \rightarrow H_2O + O^- + e^- \]  

(5.2)

However, more subtleties exist for these mechanisms depending on the crystal plane that the water is adsorbing to. These are summarized below for the two most common low index crystal planes. The reader is reminded that the X-Ray Diffraction (XRD) study presented in Chapter 3 indicates that the ALD film surface exhibits strong evidence for the (110) surface, while the peak for the (101) plane was significantly smaller. The XRD spectra are replotted in Fig. 5.3 for reference.
5.3.1 Water Adsorption on the (110) Surface

Theoretical calculations from literature show that full dissociation is the energetically preferred \( \text{H}_2\text{O} \) adsorption mechanism on \( \text{SnO}_2 \) [104, 105, 106]. However, molecular dynamics suggests that dissociative and associative states may exist in dynamic equilibrium due to the formation of strong hydrogen bonds between water and bridging oxygen atoms on the surface [107, 108]. Lindan et al. [105] performed first principles calculations with inter-molecular forces and found molecular water was only stable on the \( \text{SnO}_2 \) (110) surface when bound to a neighboring hydroxy group. As such, they deduce that at half mono-layer coverage, no molecular water was stable. At full coverage, a 1:1 ratio of dissociated to molecular water was found to exhibit only slightly lower adsorption energy when compared to the fully dissociated configuration. Later, Bates confirmed many of Lindan's conclusions for full monolayer coverage on the \( \text{SnO}_2 \) (110) surface [109].

Calculations by Sanatarossa [86] show that the oxidation state of the surface influences the proportion of water that will dissociate. At high oxygen content, the dissociated water is unstable resulting in a small average charge transfer to the surface. Reducing the surface enhances the dissociation and the charge transfer from \( \text{Sn}_5c \) atoms to the adsorbate. However, additional oxygen atoms on top (\( \text{O}_{ot} \)) of \( \text{Sn}_5c \) atoms promote the formation of hydrogen bonds between \( \text{H}_2\text{O} \) and \( \text{O}_{ot} \), stabilizing the adsorbate. This results in associative \( \text{H}_2\text{O} \) being the dominant water adsorption mechanism on more stoichiometric \( \text{SnO}_2 \) surfaces with few oxygen vacancies.

Experimental studies support these hypotheses. Gercher and Cox [103] performed Ultraviolet Photoelectron Spectroscopy (UPS) and temperature programmed desorption studies where desorption peaks at -73 and 27°C were attributed to molecular water desorption, while peaks at 162°C were assigned to hydroxy group disproportionation. They concluded 10-15% of water dissociated on stoichiometric reduced surface with all bridging oxygen atoms removed and on highly defective surfaces with many in plane oxygen vacancies. Interestingly, 35% of water dissociated on less defective surfaces. This finding suggests some finite number of in plane vacancies results in a maximum
of dissociated water and is shown qualitatively in Fig. 6.3.

Due to the complexity of the surface and the difficulty in quantifying defect structures, it remains unclear if the water dissociates only at the defect sites or if it also occurs on perfect surfaces. A downward band bending of 0.1 eV was observed in the form of UPS shifts of the O2p feature on stoichiometric (110) surfaces which was explained by electron transfer from water to the substrate, consistent with the reported conductivity increase of SnO$_2$ in humid atmosphere [110]. Finally, Yamazoe et al. [88] used TPD to show that molecular water did not contribute to the conductivity decrease but that dissociated OH groups did.

### 5.3.2 Water Adsorption on the (101) Surface

Water adsorption has been also studied on the stoichiometric and reduced SnO$_2$ (101) surface through Density Function Theory (DFT) calculations and UPS measurements [110]. In this case, the

---

**Figure 5.4** Percentage of dissociated water vs oxygen vacancy concentration at the surface.
stoichiometric surface exhibited signals attributed to dissociated water and the consequent band bending, while the reduced surface only showed weakly bound molecular water. This may be due to the lack of surface oxygen atoms to accept the proton from the dissociated water molecule [58]. These findings are consistent with earlier work suggesting the conduction change in SnO$_2$ is a result of dissociated water [88].

5.3.3 Reduction of SnO$_2$ Surface by Water Vapor

Hydroxy groups have several possible theoretical configurations on the SnO$_2$ surface which affect the electrical properties of the crystal in different ways. The OH$^-$ may bond to a surface tin atom, which is described as a terminal OH$^-$ group. Terminal groups take part in localized charge transfer which forms a dipole and does not donate an electron to the conduction band. Alternatively, hydroxy group may incorporate lattice oxygen and a proton which is known as a rooted OH$^-$ group. Rooted groups ionize and donate an electron to the conduction band, increasing the conductivity.

Three mechanisms have been suggested for increased SnO$_2$ conductivity upon H$_2$O adsorption: (i) simple H$_2$O dissociation with a donor electron coming from the rooted hydroxy group formed with the lattice oxygen, $O_O$, (Eq. 5.3)[111, 95], (ii) formation of oxygen vacancies where the ionized vacancy donates electrons to the conduction band (Eq. 5.4) [111, 90], and (iii) indirect paths with preadsorbed species [95, 111]. These mechanisms are still under debate, but each model involves H$_2$O dissociating into a terminal OH group and a proton.

In the first case, the terminal OH group (OH$_T$) binds to a surface metal cation, and the hydrogen atom (H$_R$) binds to a neighboring bridging oxygen anion to form a rooted hydroxy group (OH$_R^+$). This reaction is shown in Eq. 5.3 where $Sn_{Sn}$ and $O_O$ represent lattice ions of the surface, the $Sn^{δ^+}−OH_{T}^{δ−}$ represents the isolated terminal hydroxy group dipole, and $OH_{O}^+$ is the newly formed rooted hydroxy group on the bridging oxygen atom which ionizes and donates an electron [95].

The second reaction is shown in Eq. 5.4. Calculations by Santarossa et al. [86] indicate an electron is transferred from the rooted hydroxy group to the terminal group, rather than to the conduction
band. This implies that the conductivity change may be due to formation of oxygen vacancies. Here the hydrogen atom and lattice oxygen react to form a second terminal hydroxy group dipole which is bonded to a tin atom and the resulting oxygen vacancy ionizes to donate two conduction electrons [111].

\[
H_2O(g) + Sn_{Sn} + O_o \leftrightarrow (Sn_{Sn}^{\delta^+} - OH_{O}^{\delta^-}) + OH_{O}^+ + e^- 
\]

\[
H_2O(g) + 2Sn_{Sn} + O_o \leftrightarrow 2(Sn_{Sn}^{\delta^+} - OH_{O}^{\delta^-}) + V_o; \quad V_o \rightarrow V^{**} + 2e^- 
\]

It is likely that both mechanisms are possible, but which one dominates is dependent on the surface conditions. If the surface has many bridging oxygen atoms, then there are many sites for the dissociated proton to bond and Eq. 5.3 dominates. However, if there is no available site for the proton to bond, then the oxygen vacancy method in Eq. 5.4 is more likely. In either case, highly reactive protons are released from the dissociated water.

The third mechanism is an indirect effect and more complex. The hydroxy group or the proton from water dissociation could interact with an acid or base group which act as surface acceptor states. The interaction could alter the electron affinity, resulting in charge transfer [112]. With a sensor surface exposed to an unknown ambient atmosphere, knowing exactly what reactions are occurring on the surface requires advanced techniques that are impractical outside of a laboratory setting. Even within the laboratory, the results from these experiments are open to interpretation as evidenced by the literature collection on the subject.

Considering these reports from literature and the oxygen deficient nature of the ALD SnO_2 film by Rutherford Backscattering analysis (RBS) presented in Chapter 4, it is highly likely that the films are coated with some ratio of molecular water and hydroxy groups which depends on the temperature and surface conditions. The polycrystalline nature of the films and the instability of the (110) surface with many metastable oxygen deficient superstructures, makes quantifying the amount of dissociated water very difficult [85, 58].
5.4 ALD SnO$_2$ Sensor: Interactions with Humidity

In Chapter 4 it was shown that the ALD SnO$_2$ films displayed reducing behavior upon exposure to humidity when measured just after fabrication. However, after aging and ozone exposure, the sensors show some interesting behavior that does not appear to be documented in literature. The sensors in this chapter (Chapter 5) are 12 nm thick, deposited at 150°C and annealed for two hours at 600°C in air.

5.4.1 Water Vapor Response in Zero Air

Several long exposures to 25% humidity were taken intermittently over two months and are shown in Fig. 5.5. This sensor was exposed only to humid zero air over its lifetime, and was stored in a wafer box with desiccant packets between measurements. In Fig. 5.5a, measured just after fabrication on 4/1, the resistance is decreasing as the surface is reduced. This effect is well documented in literature and is attributed to electron donation during dissociation of water as discussed previously. After two weeks of storage in dry air, the sensor displayed unusual behavior with duty cycled humidity as shown in Fig. 5.5b. The short increase in resistance at $t = 1800s$ coincides with the beginning of the first humidity cycle. After the transient period, the known reducing behavior of water seems to take over. Then at $t = 3600s$, the exposure is changed back to dry air and the resistance increases again. The subsequent humidity exposures at $t = 5400s$ and 9000s show a sharp transient reducing behavior before settling to a more constant rate, but still display the same quick jump in resistance upon switching back to dry air. This response does not fit any existing model in the literature. It may be that the surface was populated with many physisorbed or chemisorbed O$_2$ molecules, but mostly devoid of water species due to the storage conditions in dry air. The rise in resistance from the first humidity pulse may be due to reaction with, and consumption of, these surface oxygen species.

Fig. 5.5c shows the same sensor exposed to constant humidity on 5/20 after another month of
storage in dry air. This time, the resistance increase is more noticeable as the experiment starts with humid air. After about 30 minutes, the oxidation process weakens enough for the resistance curve to roll over and start to decline again. This is likely the same mechanism shown in Fig. 5.5b but more pronounced due to increased storage time in dry air and immediate exposure to humidity.

Another sensor with a different history of exposures and storage was also tested for humidity response after reducing the surface with UV light, which may help to explain this oxidation mechanism. The data is presented in Fig. 5.6. This sensor had been previously exposed to ozone and in this experiment the surface was reduced with UV illumination so that a positive resistance response could be seen in zero air. Additionally, this sensor was stored in air without any desiccant and so was constantly in contact with typical indoor humidity levels. Under these conditions there should be many water species, both molecular and dissociated, on the surface which would enhance reaction with ambient ozone in the lab, resulting in more ionosorbed oxygen species occupying the vacancies. Upon every exposure to humidity, or increase in humidity in zero air, there is a transient anomaly in the form of a sharp oxidation effect where resistance increases for a short time before beginning to decrease. Fig. 5.6a shows the raw resistance measurement with respect to time while and Fig. 5.6b shows the response between UV resets in the form of the time derivative of the resistance \( \frac{dR}{dt} \).

The baseline resistance of the sensor in Fig. 5.6a in atmosphere was approximately 200 k\( \Omega \). UV light was used to desorb oxygen species, increase the number of active adsorption sites, and reduce the resistance to 80% of the baseline value so that a repeatable, increasing resistance response could be seen in zero air. The UV reset process creates active adsorption sites and carriers in the conduction band which facilitate \( O_2 \) chemisorption. During UV illumination, the oxygen chemisorption rate is increasing, but is still unable to compete with the UV induced desorption rate. Once the UV is turned off, adsorption dominates again and the resistance increases as the sensor tries to return to its previous stable condition. If the resistance rises above the reset value then UV illumination resumes after 60 seconds to reset the sensor again.

At \( t = 10 \) minutes in Fig. 5.6a, the air stream was changed to 25% relative humidity. The large
Figure 5.5 Room temperature sensor response to humidity in zero air: (a) Just after fabrication, (b) after two weeks storage in dry air, and (c) after another month of storage in dry air.
Figure 5.6 Room temperature sensor response to humidity in zero air: (a) time series resistance signal and (b) Derivative \( \frac{dR}{dt} \) magnitudes. Sensor was stored in regular air with ambient humidity.
spike here is the transient anomalous behavior. After this anomaly, the oxygen response of the sensor slowly decreases down to about half of its previous value. This decrease in oxygen response in the presence of humidity is congruent with reports in literature. At \( t = 20 \) minutes, the humidity was increased to 32%. At this point, there is another sharp increase in resistance before the expected reducing behavior takes over. At this higher humidity, the electron trapping due to \( \text{O}_2 \) ionsorption can no longer compete with the reducing effect from humidity. From this point on, the UV does not turn on again because the resistance does not rise above the reset value. At \( t = 26 \) minutes, humidity is increased to 43% and the resistance decreases at an even faster rate. Finally at \( t = 28 \) minutes, the humidity is reduced back to 0% and the resistance increases again as water desorbs and \( \text{O}_2 \) molecules can once again compete for adsorption sites.

### 5.4.2 Water Vapor Response in Zero Air with Ozone

Finally, a similar test exposure with 100 ppb ozone in various humidity levels was also conducted to observe any changes in the humidity response. The raw resistance vs time plot can be seen in Fig. 5.7a and the magnitude of the response is plotted in Fig. 5.7b.

The sensor data in Fig. 5.7 was shown in Chapter 4 to illustrate the increased response to ozone with humidity and the discussion of the transient behavior was deferred until now. The transient oxidation effect upon humidity increase that slowly decays is visible here, superimposed with the enhanced oxidation effect in humid ozone that has been attributed to dissociated water catalyzing rapid ozone decomposition. This sensor was also stored with desiccant so the surface should be populated with very few hydrogen terminated groups and many physisorbed and chemisorbed oxygen molecules.

### 5.4.3 Summary of Results in Humid Zero Air and Ozone

The behavior observed in Fig. 5.5, Fig. 5.6 and Fig. 5.7 indicates several mechanisms are modulating the charge carrier concentration in the film. In Fig. 5.5, the film displays textbook reducing behavior
Figure 5.7 Room temperature sensor response to humidity in 100 ppb O$_3$: (a) time series resistance signal and (b) Derivative ($\frac{dR}{dt}$) magnitudes
just after fabrication, where the reducing effect of water vapor donates electrons to the conduction band and reduces the resistance. Then after two weeks of dehydroxylation and oxygen adsorption, the strange transient oxidation effect upon humidity exposure appears.

In Fig. 5.6, reduction of the surface by UV light to approximately 80% of its baseline value results in a noticeable oxidation response from O$_2$ chemisorbed from the zero air stream. Then when humidity is introduced, the response increases briefly rather than immediately displaying the expected reducing behavior. As humidity increases to 32%, the reducing behavior of water easily overpowers the oxidation from zero air, but not before the sensor exhibits another transient oxidation process.

The humidity response in ozone shown in Fig. 5.7 is similar in that it also displays the transient oxidation effects, but in this case the water enhances ozone ionosorption at a far greater magnitude than it reduces the surface. Still, the superposition of the hydroxy group enhanced ozone response and the unexplained transient effect can be seen clearly.

The mechanism is certain to involve water and is more likely to involve the dissociated reactive species than molecular water. It was suggested earlier that the rise in resistance from humidity exposure may be due to reaction with surface oxygen species that had adsorbed to the surface during storage. The first transient response observed in Fig. 5.5b after dry air storage was very small and lasted for at least three minutes, although the signal appears to take upwards of 15 minutes to become linear. Additionally, only this first humidity increase in the experiment displays the oxidizing behavior while the subsequent humidity increases resulted in a reducing transient with a much shorter time constant. The reductions in humidity all display similar oxidizing transients with short time constants. This indicates some surface species is responsible for the oxidizing behavior, but is consumed relatively slowly during the first humidity pulse. Then some other faster mechanism is responsible for the reducing transients at the beginning of the subsequent humidity cycles and the oxidizing transient at the end of the humidity cycles.

When the same sample is exposed to humid air immediately upon removing from dry storage in
Fig. 5.5c, the longer lasting oxidizing transient lasts for about 30 minutes before rolling over. The curve takes another 30 minutes to linearize indicating the transient reactions are still occurring at a lower rate. This is in good agreement with the hypothesis of surface species being consumed. If it is indeed surface oxygen species, then the humidity response of a sample without oxygen exposure should display different behavior.

5.4.4 Water Vapor Response in Nitrogen

To test this theory, experiments were conducted with \( \text{N}_2 \) used as the carrier gas for the water vapor. By removing oxygen from the environment, the phenomenon will be better isolated to identify the cause. Additionally, a very small concentration of water was added to the \( \text{N}_2 \) stream to determine the sensitivity of the surface to this mechanism. Fig. 5.8 shows the response of a sensor stored in regular ambient humidity lab air which was then exposed to humidity in \( \text{N}_2 \). The transient oxidation response with a very short time constant is observed upon humidity exposure. This reveals that the transient oxidation response is not related to ambient oxygen in the carrier gas and so it must involve the water vapor in the carrier gas and the surface as it exists after aging.

To investigate the impact of surface oxygen species, another sensor was stored in a container continuously flushed with \( \text{N}_2 \) for over a week and tested with low humidity exposures in \( \text{N}_2 \) carrier gas. After storage in \( \text{N}_2 \), the sensor surface was very reduced and displayed a low baseline resistance. The reduced surface is also very reactive and some oxygen would have adsorbed during transfer from the storage container to the testing chamber, so it has not been eliminated entirely from the surface. This experiment also incorporates flow rate modulation of the carrier gas to determine if that is a factor in the observed behavior. The data from this experiment is shown in Fig. 5.9.

The results in Fig. 5.9 are particularly interesting for a number of reasons. First, there is an oxidizing behavior with a long time constant over the first 20 minutes, even though the sample is only being exposed to nitrogen. This response is attributed to surface species that physisorbed during sample transfer and are reacting with the surface for the first few minutes. Second, doubling
Figure 5.8 Aged room temperature sensor humidity response in N₂ carrier gas

Figure 5.9 Humidity and N₂ flow rate response of sensor stored in N₂ at room temperature.
Table 5.1 Summary of transient room temperature responses related to humidity exposure.

<table>
<thead>
<tr>
<th>Response</th>
<th>Speed</th>
<th>Catalyst</th>
<th>Storage</th>
<th>Surface</th>
<th>Surface Species</th>
<th>See in</th>
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</thead>
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<td>Medium</td>
<td>Humid Air</td>
<td>Dry Air</td>
<td>Equilibrium</td>
<td>Lots of $O_2$, $O_2^-$</td>
<td>Fig. 5.5b</td>
</tr>
<tr>
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<td>Fast</td>
<td>Dry Air</td>
<td>Dry Air</td>
<td>Equilibrium</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.5b</td>
</tr>
<tr>
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<td>Fast</td>
<td>Humid Air</td>
<td>Dry Air</td>
<td>Equilibrium</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.5b</td>
</tr>
<tr>
<td>Oxidizing</td>
<td>Slow</td>
<td>Humid Air</td>
<td>Dry Air</td>
<td>Reduced</td>
<td>Lots of $O_2$, $O_2^-$</td>
<td>Fig. 5.5b</td>
</tr>
<tr>
<td>Oxidizing</td>
<td>Medium</td>
<td>Humid Air</td>
<td>Air</td>
<td>Reduced</td>
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<td>Fig. 5.6a</td>
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<td>Air</td>
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<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
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<tr>
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<td>Fast</td>
<td>Humid $N_2$</td>
<td>Air</td>
<td>Equilibrium</td>
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<td>Fig. 5.8</td>
</tr>
<tr>
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<td>Dry $N_2$</td>
<td>$N_2$</td>
<td>Very Reduced</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.9</td>
</tr>
<tr>
<td>Oxidizing</td>
<td>Fast</td>
<td>Humid $N_2$</td>
<td>$N_2$</td>
<td>Very Reduced</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.9</td>
</tr>
<tr>
<td>Oxidizing</td>
<td>Medium</td>
<td>Humid $N_2$</td>
<td>$N_2$</td>
<td>Very Reduced</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.9</td>
</tr>
<tr>
<td>Reducing</td>
<td>Fast</td>
<td>Dry $N_2$</td>
<td>$N_2$</td>
<td>Very Reduced</td>
<td>$O_2$, $O_2^-$, $H_2O$, $OH^-$</td>
<td>Fig. 5.9</td>
</tr>
</tbody>
</table>

the flow rate of nitrogen in dry conditions at $t = 180$ s has a negligible effect on the sensor response. In humid conditions at $t = 1800$ s, a slightly more noticeable effect is observed that may be due to calibration of the Mass Flow Controllers (MFC) resulting in a slight change in the humidity levels. Third, the transient behavior on the edges of the humidity pulses is still visible and unchanged in magnitude, even after the proposed oxidation from physisorbed surface species dies out. This result shows that unreacted surface species are not a significant factor in the short time constant transient behavior but likely do impact the long time constant mechanism. Finally, during the first humidity pulse, the oxidation effect is observed to be stronger than any other point throughout the full humidity exposure.

5.5 Discussion of Results

The evidence accumulated on the nature of the strange transient behavior in humidity is now sufficient to explain the phenomenon. The findings are summarized in the order presented for convenience in Table 5.1.
To understand the transient behaviors associated with the humidity pulses, recall the previous discussion on water dissociation. Upon dissociation of molecular water, a hydroxy group binds to a surface metal cation and a proton (ionized hydrogen atom) remains that must be accounted for. In literature, these protons are assumed to bind to neighboring bridging oxygen atoms, forming an additional hydroxy groups. Certainly this cannot go on indefinitely as the surface would quickly become saturated and if the surface is very reduced then there are few bridging oxygen sites available. So what happens to the protons in these cases?

Pavelko et al. [113] studied hydrogen sensing with SnO$_2$ based sensors extensively. His results will provide valuable insight to help to explain the observations in this chapter (Chapter 5). Pavelko used H$_2$O and D$_2$O (heavy water with deuterium isotopes of hydrogen) exchange to study the kinetics of water adsorption on SnO$_2$ surface. In his studies, he observed a similar, but inverse transient response upon hydrogen exposure due to consumption of OH groups to form molecular water.

The dissociated protons are very mobile along bridging oxygen lines [113], so several reaction possibilities exist: (i) a reaction with atomic oxygen species to form molecular water as in Eq. 7.2, (ii) a reaction with O$^-$ or O$_2^-$ to form hydrogen peroxide as in Eq. 7.3, or (iii) a combination of two protons and two electrons into hydrogen gas as in Eq. 7.4.

\[
H^+ + H^+ + O^-(ad_s) + 2e^- \leftrightarrow H_2O \tag{5.5}
\]
\[
H^+ + H^+ + O^-(ad_s) + e^- \leftrightarrow H_2O_2 \tag{5.6}
\]
\[
H^+ + H^+ + 2e^- \leftrightarrow H_2 \tag{5.7}
\]

Each of these reactions takes electrons from the SnO$_2$ conduction band which would manifest as a resistance increase. Alternatively, the hydrogen atom could keep its electron and the hydroxy group would become a neutral hydroxyl radical. The hydroxyl radical is a very strong oxidizer, even stronger than ozone [100]. The hydroxyl radical would react with an oxygen vacancy and trap electrons at the
surface, also resulting in a resistance increase. The remaining hydrogen atom is also a free radical and very reactive, so the hydrogen reactions in Eq. 7.2 - Eq. 7.4 are still valid with some additional charge balancing. The sensor presented Fig. 5.5 that revealed the first transient responses was stored in dry air. This would result in few water species, but many physisorbed and chemisorbed O$_2$ molecules, so many protons are searching for a place to react during the first humidity pulse in Fig. 5.5b. In this scenario, the hydrogen processes dominate the resistance change until the surface oxygen is consumed. This mechanism is the cause of the slow oxidation reaction seen in the first humidity pulse of Fig. 5.5b and in the beginning of the constant humidity exposure in Fig. 5.5c.

As the adsorbed oxygen species are consumed, the reaction rates for Eq. 7.2 and Eq. 7.3 would slow and the reducing effect of water via oxygen vacancy formation would dominate again. This can be seen in the rolling off of the curves in Fig. 5.5b and Fig. 5.5c. This is also the cause of the steeper downward slope of the resistance in subsequent humidity pulses of Fig. 5.5b.

After the surface species are consumed, exposure to dry air results in evaporation of molecular water from the surface and recombination of the OH groups to maintain the energetically preferred ratio of molecular to dissociated water. Of course this results in electrons previously donated from ionized rooted hydroxy groups being taken from the conduction band, which explains the fast oxidizing effect observed in Fig. 5.5b upon changing the exposure from humid air to dry air. The inverse reaction explains the fast reducing effect observed upon humidity exposure after the surface oxygen species have been consumed.

The sensor shown in Fig. 5.6a was stored in regular lab air with ambient humidity and exposed to zero air with humidity while being kept at a slightly reduced state by UV illumination. In this case there were likely many molecular and dissociated water species on the surface resulting in many oxygen atoms already being hydrogen terminated. The reduced surface is more reactive and ionizes O$_2$ molecules from the zero air stream. In this case, the hydrogen reactions dominate again but decay more slowly due to a higher O$_2$ adsorption rate replenishing the surface species.

In the humid ozone exposure test of Fig. 5.7a, a similar oxidation effect superimposed over the
ozone response is evident but it seems to trail off slower than the exposures in humid zero air. As ozone decomposes at the SnO$_2$ surface, it forms O$_2^-$ and O$^-$ anions. This results in a steady generation of reactive oxygen species at the surface that react with run away protons. Upon humidity increase, the sudden influx of protons results in the rapid oxidation of the surface through the hydrogen reactions, but the surface oxygen is consumed more slowly as decomposing ozone continues to replenish it. This is the reason for the longer time constant for stabilization as opposed to the humid zero air case.

The sensors tested in humid N$_2$ were shown in Fig. 5.8 for the sensor stored in air and Fig. 5.9 for the sensor stored in N$_2$. Both of these sensors displayed fast transient oxidations upon humidity exposure and reductions when switching back to dry air, which are explained by the rapid generation and consumption of protons as the ratio of dissociated to molecular water stays constant while the surface water coverage is modulated with changing humidity.

The final unexplained mechanism is the slow oxidation response seen in Fig. 5.9 for the sensor stored in N$_2$ and tested for response in humid N$_2$.

During his studies, Pavelko found evidence for water oxidation of SnO$_2$ through oxygen assisted water adsorption. Pavelko described a reduced surface with sparse bridging oxygen atoms from dissociated O$_2$. Of course, the process of oxidizing the heavily reduced surface would be much faster in the presence of ozone as described in Fig. 5.10a. Exposure of the still heavily reduced surface to water vapor can then lead to formation of two rooted hydroxy groups per water molecule and further oxidize the surface, as shown in Fig. 5.10b.

If the surface is already very reduced, as would be the case for films stored in N$_2$, then this process continues until water dissociation is no longer favorable. Of course, it is known from previous discussion that the percentage of water that will dissociate decreases as the surface becomes very reduced [86, 103]. This means that as the surface oxidizes, a greater percentage of the adsorbed water is dissociated, extending the oxidation period. Once the surface has oxidized considerably, the dissociated water percentage begins to saturate. Then, the better understood regime takes
Figure 5.10 (a) Ozone ionosorption on reduced (110) surface and (b) oxygen assisted water adsorption mechanism adapted from [113]
over where the surface oxygen is mostly hydrogen terminated and dissociated OH\(^{-}\) groups donate electrons to the SnO\(_2\) surface through oxygen vacancy formation as described previously in Eq. 5.4. At this point the resistance begins to fall again.

It is the author's opinion that all of these process are occurring. The presence of reactive oxygen species on the surface is likely in practically all circumstances, and the dissociated protons must react with something. Perhaps prolonged strong illumination of high energy UV light in an inert atmosphere could remove all adsorbed oxygen species. If the oxidation effect still occurs upon humidity exposure in N\(_2\) with all oxygen species desorbed, then that would be strong evidence that hydrogen gas production is occurring. If in fact, hydrogen gas is being generated, then several other interesting reactions may be occurring. Pavelko documents a water formation cycle involving consumption of OH groups by the hydrogen gas and associated oxygen vacancy generation. In fact, hydrogen gas may also be forming through another mechanism described by Pavelko in Eq. 5.8.

\[
H_2O + e^- \leftrightarrow H_2 + O_{ads}^- \quad (5.8)
\]

Upon consuming surface oxygen, few oxygen atoms that are not already hydrogen terminated are available to accept protons from water dissociation and Eq. 5.9 shifts its equilibrium to the left. This results in the consumption of two hydroxy groups and the bridging oxygen atom as one ionized oxygen atom is left behind.

\[
H_2O + 2SnSn + O_{ads}^- \leftrightarrow 2Sn - OH + e^- \quad (5.9)
\]

### 5.6 Summary

This chapter (Chapter 5) has investigated the impact of humidity on the SnO\(_2\) surface and ozone sensing conditions. Water coverage was explained as a function of temperature and absolute humidity and the effects of water dissociation were explained as follows:
Dissociated water may form terminal and rooted hydroxy groups if there are available sites to accept the proton released during dissociation. Rooted hydroxy groups form from the proton and a bridging oxygen atom. The rooted groups ionizes and donates one conduction electron to the surface. Terminal groups bond to surface tin atoms and participate in localized charge transfer only. This forms a dipole and does not contribute to the conductivity of the material, but modifies the work function and charge transfer kinetics. In other material systems dipoles typically increase the work function although there are subtleties that may lead to a decreased work function.

If there are not available sites for proton bonding, then the dissociation could result in the extraction of lattice oxygen to react with the proton to form two terminal OH groups and an oxygen vacancy. The vacancy can then doubly ionize and contribute 2 conduction electrons.

Fast and slow finite oxidizing reactions were discovered upon exposure to humidity in certain circumstances. Protons released during water dissociation react with each other and/or surface species to form hydrogen gas, hydrogen peroxide or recombine into molecular water. Each of these reactions oxidize the surface, but with different results depending on the surface state of the film as follows:

A sensor stored in dry air has many surface oxygen species, but few hydrogen terminations. In this case, humidity exposure displayed a slow oxidation response as protons have the option of bonding to lattice oxygen or consuming surface species.

A sensor stored in humid air has both surface oxygen species and hydrogen terminated groups. The protons have fewer options and consume the surface species faster, resulting in a stronger faster oxidation.

In a humid ozone environment, the same surface conditions result in an extended oxidation period that decays slower due to the surface species being replenished by ozone decomposition.
A sensor stored in nitrogen is heavily reduced and has almost no sites for the protons to react, although the surface oxygen species are also low in concentration. Additionally, proton mobility on the surface is along lines of bridging oxygen atoms that are not present on the reduced surface. In this case, any existing surface species that adsorbed during sample transfer are quickly consumed if water is able to dissociate near them. Once they are gone, protons can only react with each other, recombine into molecular water, or not dissociate in the first place. This offers another explanation as to why the amount of water that dissociates decreases as the surface becomes very reduced, as observed by Gercher and Cox [103] and demonstrated theoretically by Santarossa et al. [86].

An additional slow oxidation effect, known as oxygen assisted water adsorption, was observed on the very reduced surface stored in nitrogen. The dissociated water fills oxygen vacancies with rooted hydroxy groups and the proton bonds surface oxygen producing another rooted group until water dissociation is no longer favorable. The oxidation period is extended as more oxygen vacancies are filled, some protons are removed through hydrogen reactions, and the percentage of water that dissociates increases.

Each of these transient reactions continue until the reagents are depleted, or it is no longer energetically favorable for more water to dissociate. At this point, the well known reducing effect of water vapor takes over.
6.1 Introduction

Stability is an important metric when evaluating sensor technology. Drift of the baseline resistance and response over time is a well known issue for metal oxide sensors due to changing structural and electrical properties as the sensors age [114, 115, 116, 117, 118]. The SnO$_2$ (110) surface is unstable with many point defects, low formation energies for oxygen vacancies, and corresponding fluctuations in the oxidation state of the tin cations. There are many metastable, oxygen deficient superstructures that transform as oxygen atoms move around on the surface [85, 58].
With heated sensors, the thermal energy associated with the high temperature operation activates the film and allows reactions to happen more quickly. This applies both to gas response and to the movement of oxygen atoms (and vacancies) as the metastable superstructures evolve on the surface. This means the heated surface is able to reach a quasi-steady state condition in a constant atmosphere reasonably quickly. At room temperature, the gas reaction mechanisms slow down considerably and the surface structure evolution may become practically frozen with the exception of oxygen vacancy formation due to water dissociation discussed in Chapter 5. This is the reason the derivative of the resistance change was used to evaluate ozone concentration in Chapter 4 and is the one source of the long time constant for stabilization after a humidity change that was observed in Chapter 5. It is reasonable to assume that other unknown, long term drift mechanisms exist for metal oxide films at low temperatures that are dependent on the sensor's exposure history.

For the aforementioned reasons, understanding the state of the surface over time is critical for obtaining meaningful data from the sensor's gas response. Therefore, to fully understand the evolution of the sensor surface, and evaluate its potential as a long term continuous environmental sensor, long exposures must be performed to monitor any changes in the response. This chapter (Chapter 6) will describe the results from experiments designed to investigate these mechanisms and determine their impact on the sensor as it ages.

6.2 Humid Gas Exposure Data Correction

It should be noted that a portion of the humid air and ozone exposure data collected required correction due to an incorrect configuration of the system plumbing and exhaust. Ozone has high solubility in water, so an air/ozone mix bubbled through water to add humidity will lose ozone in the process. To maintain desired concentrations, the dry air/ozone output from the Teledyne T700U ozone generator and the humid air output from a Mass Flow Controller (MFC) and water bubbler were routed to a mixing chamber upstream of the testing chamber as shown in Fig. 6.1.
Figure 6.1 Block diagram of the testing setup including T700 ozone generator, mass flow controller (MFC), water bubbler, mixing chamber and testing chamber. The overflow vent on the T700U manifold is labeled.

When the T700U is used with Teledyne gas analyzers, the T700U is set to generate a greater flow rate than required and each of the gas analyzer instruments uses a pump to control their input flow rate. An overflow vent on the T700U is routed to an exhaust vent to eliminate excess gas flow. This is how the instrument was set up in the lab initially, but the testing chamber in this work is a flow through design and not equipped with a pump. The resistance to gas flow due to the tubing geometry resulted in a lower flow rate delivered to the testing chamber than expected.

For dry gas mixtures this is not a problem because all of the gas mixing takes place inside the T700U before reaching the output manifold and the overflow vent. In this case the flow rate to the chamber is reduced, but the gas concentration remains constant. The results from a variable flow rate experiment were presented in Chapter 5 and showed that modulation of the flow rate has a negligible impact on the sensor output. However, for humid gas mixtures, the humid air from the MFC and bubbler branch maintains a constant flow rate while the dry air/ozone mixture overflowed through the manifold vent. This results in unknown relative humidity (RH) and ozone (O₃) concentration delivered to the testing chamber.

The initial flow rate ratios for desired humidity levels were calibrated with a Honeywell HIH-4010 humidity sensor in the mixing chamber when it was disconnected from the testing chamber and the overflow vent was uncapped. When the testing chamber was added to the system, the building
exhaust resulting in a slightly lower pressure at the chamber output which pulled more air from the T700U manifold and partly compensated for the reduced flow.

This means that the air delivered to the chamber was lower humidity than expected because the dry air flow rate was during humidity calibration was less than that during sensor testing. For the same reason, the ozone concentration was lower than expected. However, the change in the ratios of humid air to dry air and ozone/air to zero air were not identical because the ozone concentration was calculated based volume ratios of the expected flow rate from the T700U and the known flow rate from the bubbler. An additional factor is the strength of the building exhaust fluctuates slightly, which perturbed the ozone and humidity levels as it modulated the gas flow from the T700U. This exhaust modulation is impossible to correct for but is also less significant because it is a small perturbation added onto a larger constant difference, or an small alternating current (AC) signal with a direct current (DC) bias to use an electrical engineering analogy.

To correct the data, a new humidity sensor was placed in the testing chamber with output correction factors for the voltage supply and temperature to accurately measure the testing environment. The humidity levels were measured using the calibration flow rate ratios with the overflow vent open to determine the actual humidity level of the experimental tests. Then the humidity was measured again with the vent capped. With no overflow route available, the actual flow rate ratio of dry air to humid air was known from the MFC readings. This, coupled with a measurement of 90% humid air being delivered from the bubbler, enabled determining the true volume ratios of dry and humid air obtained during previous experiments. From there, volume ratios were used again to determine the actual ozone concentration in the chamber during the initial tests. Finally, the exhaust was rerouted to a chemical hood rather than directly to the building exhaust to eliminate pressure fluctuation.

The math used to correct the data is shown in Eq. 6.1 - Eq. 6.3 and Table 6.1 shows the target and corrected values for flow rate, humidity, and ozone concentration. The subscripts on the Flow variables denote if the air is the programmed flow from the T700, the T700 overflow through the vent, or the humid air flow through the bubbler. \( RH_{(T C)} \) and \( O_{3(T C)} \) denote the relative humidity
Table 6.1 Corrected values for exposures in April

<table>
<thead>
<tr>
<th></th>
<th>Flow Ratio Dry:Humid</th>
<th>RH (%)</th>
<th>Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>2.4:0.6</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>Actual</td>
<td>1.4:0.6</td>
<td>25</td>
<td>87.5</td>
</tr>
</tbody>
</table>

and ozone concentration in the testing chamber, respectively.

\[
\text{Flow}_{\text{total}} = \text{Flow}_{T700} - \text{Flow}_{\text{vent}} + \text{Flow}_{\text{bubbler}} \tag{6.1}
\]

\[
RH_{(TC)} = 0 \left( \frac{\text{Flow}_{T700}}{\text{Flow}_{\text{total}}} \right) + RH_{\text{bubbler}} \left( \frac{\text{Flow}_{\text{bubbler}}}{\text{Flow}_{\text{total}}} \right) \tag{6.2}
\]

\[
O_3_{(TC)} = O_{3,T700} \left( \frac{\text{Flow}_{T700}}{\text{Flow}_{\text{total}}} \right) + 0 \left( \frac{\text{Flow}_{\text{bubbler}}}{\text{Flow}_{\text{total}}} \right) \tag{6.3}
\]

It should also be noted that the environmental control in the lab was essentially non-existent until May, which was also when the flow rate problems were corrected. The chillers in the air handler were broken resulting in temperature swings of up to 10°C and relative humidity swings of 10-15%. As such, the data from after the correction should be the primary indicator of mechanisms on the surface with earlier data serving to cautiously confirm trends with the knowledge that there are some additional unknowns. The figure captions will denote if the data required correction.

6.3 ALD SnO₂ Sensor: Interactions with Humidity and Ozone

In Chapter 5, it was shown that exposure to humidity will decrease steady state resistance of SnO₂ films as it reduces the surface. If ozone is present with humidity, the effect is reversed. Molecular water physisorbs onto the surface and dissociates, leaving behind hydroxy groups (OH⁻). These hydroxy groups act as a catalyst for ozone decomposition, resulting in higher effective concentration of ionized oxygen species on the surface and increased response [86, 87, 88, 89].
This section investigates the effect of long term exposure to humid ozone without UV illumination to determine how the film might change during exposure to these conditions. For additional insight, films that were stored in dry air, ambient humidity air and N₂ (nitrogen) flushed inert environments were evaluated to determine what effect the surface species and the oxidation state of the surface has on the interaction with water vapor.

6.3.1 Response of Sensor Stored in Ambient Lab Atmosphere

Fig. 6.2 shows the resistance change due to humid ozone exposure of a sensor that was stored in a wafer box with ambient lab air and humidity. Recall the Weisz limit states that only 1% of the oxygen vacancies may be occupied due to repulsive electrostatic forces between adsorbed ions, so the sensor surface in this case would be slightly reduced [82]. Fig. 6.2a shows the sensor resistance change over three hours in 25% humidity with 87.5 ppb O₃. The humidity and ozone concentration were corrected using the methods in Section 6.2.

The results in Fig. 6.2a are not remarkable. The resistance increases from 200 kΩ to 600 kΩ over three hours as the surface is oxidized. As time goes on and more charge is trapped at the surface, the electron depleted space charge region and the potential barrier for conduction electrons to be trapped at the surface increases. This coupled with the repulsive electrostatic forces cause the adsorption rate to decrease as more oxygen species chemisorb and the Weisz limit is approached [28, 119, 120].

The longer exposure on 5/24, shown in Fig. 6.2b, is more interesting. The exposure conditions were 25% RH and 100 ppb O₃ for 10.3 hours. Here, the resistance also increases to just above 600 kΩ, but at a slower rate. Then, the resistance begins to fall despite no change in the testing environment. The surface appears to have oxidized to some saturation point and then began reducing as other mechanisms took over.

Two mechanisms are likely to be involved here. Humidity adsorption has been shown to cause a decrease in work function and an increase in electron affinity on metal oxide surfaces. Terminal
Figure 6.2 Room temperature sensor response to constant ozone and humidity in zero air: (a) 3 hour measurement on 4/5 that required data correction and (b) 10 hour measurement on 5/24
hydroxy groups on the surface from water dissociation form dipoles that result in localized charge transfer and do not directly effect the carrier concentration of a semiconductor. However they do result in a large surface potential change over a short distance and an associated work function change [119]. If the work function decreases but the electron affinity increases, then the energy between the Fermi level and the conduction band increases. This results in a larger potential barrier for electrons to be trapped by adsorbed molecules and a corresponding decrease in the adsorption rate.

When water dissociates on the surface, it may form a rooted and a terminal (dipole) hydroxy group if there is oxygen available to capture the proton. The chemical reaction is shown in Eq. 6.4. Alternatively, if the surface is heavily reduced or all oxygen is already hydrogen terminated, it may form two terminal groups and an oxygen vacancy as shown in Eq. 6.5. The latter case becomes more likely with increasing exposure as water dissociates and the surface becomes saturated with hydrogen terminations.

\[
\begin{align*}
H_2O(g) + Sn_{Sn} + O_O & \leftrightarrow (Sn^{\delta+} - OH^{\delta-}) + (OH)^{+}_O + e^- \quad (6.4) \\
H_2O(g) + 2Sn_{Sn} + O_O & \leftrightarrow 2(Sn^{\delta+} - OH^{\delta-}) + V_O; \quad V_0 \rightarrow V^{**} + 2e^- \quad (6.5)
\end{align*}
\]

Increasing the oxygen vacancy density would increase the ozone adsorption rate but would also have a non-linear effect on the amount of water that dissociates on the surface. Fig. 6.3 illustrates the possible relationship between oxygen vacancy density and water dissociation based on several data points from literature [86, 103].

If oxygen vacancies are formed in sufficient numbers, the percentage of water that dissociates on the surface may begin to reduce. This would also reduce the ozone reaction rate as fewer hydroxy groups exist on the surface to catalyze ozone decomposition. Eventually, the adsorption rate decreases enough that desorption and/or the reducing effect of water vapor takes over and the
resistance begins to fall as seen in Fig. 6.2b.

6.3.2 Response of Sensor Stored in Nitrogen

This section investigates the influence of existing surface oxygen species by exposing a sample stored in an N$_2$ environment for one week to the same exposure conditions of the previous section, 25% RH and 87.5 ppb O$_3$. Fig. 6.10 shows the results from an exposure test of 100 ppb O$_3$ in 0% humidity on one such sample.

The exposure data for the sensor stored in N$_2$ is presented in Fig. 6.4. Storage in a non-oxidizing N$_2$ ambient results in a very reduced surface with lots of oxygen vacancies, high conductivity and high reactivity. The resistance of the 10 nm thick SnO$_2$ films stored in N$_2$ was typically in the range of 20-21 kΩ although it was observed to reach as low as 15 kΩ after prolonged storage. The reactive surface immediately begins oxidizing upon exposure to atmosphere and the resistance increases.
The resistance of the N\textsubscript{2} stored sensor increased almost 600\%, nearly double the change of the sensor stored in air due to the high reactivity of the surface. The plot does not exhibit any peculiar characteristics, but the sensor has not seen the exposure dose that the previous sensor has.

For this very reduced surface there are likely very few or no bridging oxygen atoms. In this case dissociated water tend to form in plane oxygen vacancies, or shed protons through hydrogen reactions. The formation energy of in plane oxygen vacancies of an already reduced surface is higher than at bridging sites, and with ozone present, many O\textsuperscript{-} and O\textsuperscript{2-} ions are present. In this case, the oxygen assisted water adsorption process, described by Pavelko [113] and illustrated in Fig. 6.5, and the hydrogen reactions in Eq. 6.6 and Eq. 6.7 will dominate, taking electrons from the surface and enhancing the oxidation rate while additional vacancy formation is limited. However, over time the dissociated water molecules will result in more surface dipoles, so it is likely that a longer exposure of this surface would reveal the same behavior.
6.4 Impact of Humid Ozone Adsorption and UV Desorption Over Time

Evaluation of the sensor evolution during normal operation with UV recovery in the presence of humidity and ozone is the final step in understanding sensor aging and changing surface properties. In this experiment sensors stored in ambient humidity and N$_2$ were investigated under UV illumination.

6.4.1 Response of Sensor Stored in Ambient Lab Atmosphere

The response magnitude for the three hour exposures to 25% humidity and 87.5 ppb ozone on 4/2 are shown in Fig. 6.6 for samples stored in wafer boxes with ambient lab air and humidity. The concentration values for this experiment were corrected using the methods described in Section 6.2. The surface in this case is slightly reduced and populated with both oxygen and water species.

This experiment shows markedly stronger ozone response than that of the dry ozone test as expected due to hydroxy groups catalyzing ozone decomposition as discussed in Chapter 5, but
even more interesting behavior is observed as the experiment continues. The response increases steadily for about 10 minutes before reaching a maximum and beginning to decrease again. The response then continues to decrease for approximately 2 hours before stabilizing.

Several mechanisms are in action here. The test air is only 25% humidity while the ambient lab air is typically around 40-50%, so the water coverage on the surface should decrease which eliminates increased hydroxy catalyzed ozone decomposition as a possibility. After storage in humid air, most of the lattice oxygen should be hydrogen terminated and the surface is populated with water and oxygen species. This results in the hydrogen reactions discussed in Chapter 5 and repeated in Eq. 6.6 - Eq. 6.8 to dominate the charge transfer on the surface. Additional deposition of oxygen ions due to ozone decomposition sustains these reactions for a short time. As hydrogen atoms are consumed, they eventually become the limiting reagent in the reactions and the increasing ozone response in the first 10 minutes of Fig. 6.6 dies out.

At this point, the balance of the dissociated to molecular water equilibrium takes over. As
water evaporates from the surface, OH\(^{-}\) groups recombine to molecular water to maintain the energetically favorable ratio. As molecular water desorbs or a rooted OH\(^{-}\) recombines and leaves an oxygen vacancy behind, the newly available adsorption site may be occupied and passivated by an atomic oxygen species. When this occurs, the number of vacancies decreases, which on a slightly reduced surface, would result in a reduction of the percentage of dissociated water on the surface. It is easy to imagine that this stochastic process would be slow to reach equilibrium, which agrees well with the data in Fig. 6.6.

6.4.2 Response of Sensor Stored in Nitrogen

The sensors stored in nitrogen display an opposite response when exposed to 25% humidity and 87.5 ppb ozone. These concentration values were corrected using the methods in Section 6.2. The raw resistance vs time graph is shown in Fig. 6.7a and the magnitude of the derivative in Fig. 6.7b. The discontinuity in the measurement is due to insufficient UV recovery illumination as the oxidation rate increases. At \(t = 115\) minutes, the measurement program was stopped and reprogrammed to drive the UV LED with 3.6 V as opposed to 3.3 V. The measurement was then restarted without opening the testing chamber.

After storage in N\(_2\), the surface is heavily reduced with few oxygen and water species and many bridging oxygen vacancies. This is evident from the low baseline resistance and strong ozone response. The baseline resistance was 21 kΩ, but the ozone response was too strong for the UV assisted desorption to overcome, so the reset resistance was allowed to rise to 35 kΩ. In these experiments, the oxidation response continues to increase over time, which cannot be explained by steady state ozone adsorption and desorption rates.

When water dissociates on the heavily reduced surface, dissociated protons have nowhere to bond, as discussed previously, so electron donation from ionized rooted hydroxy groups will be at a minimum unless a proton sink can be found. Alternative reactions involve water dissociating to two terminal hydroxy groups by pulling a lattice oxygen atom and forming an oxygen vacancy, or the
Figure 6.7 (a) Resistance vs time and (b) \( \frac{dR}{dt} \) room temperature response of N\(_2\) stored sensor to 25% humidity with 87.5 ppb O\(_3\) that required data correction.
dissociated protons react with the oxygen species from the decomposed ozone. However, the high proton mobility on the surface is due to travel along lines of bridging oxygen atoms. For the heavily reduced surface with no bridging oxygen atoms, proton mobility is limited.

The rapid increase in response over the first 10-20 minutes provides a clue. It would seem that a fast oxidizing reaction, like the hydrogen reactions, is occurring but at a slightly slower rate than observed in samples stored in air where the reaction involved consumption of existing surface species. This may be due to the concentration of available oxygen species being limited by ozone decomposition.

Fig. 6.8 shows a proposed mechanism for molecular ozone ionosorption in dry air and subsequent dissociation. For the heavily reduced surface, a small percentage of water would be dissociated and the majority of the surface would simulate dry air conditions. As the resonant ozone ionosorbs due to its dipole, and subsequently decomposes, it leaves behind the surface oxygen species, $O^{-}$. Now a new site for proton reaction has been generated and a water molecule nearby can dissociate to terminal and rooted hydroxy groups. As this process continues, a water molecule can theoretically dissociate for every ionosorbed ozone molecule. This results in oxygen vacancies being filled and a larger percentage of water that prefers to dissociate, contributing additional catalysts for ozone decomposition. When enough oxygen atoms exist on the surface to satisfy the amount of hydroxy groups that would energetically like to exist, the process saturates and rolls off. The continued steady increase is still related to increasing number of dissociated water molecules, but the rate of increase in the percentage of dissociated molecules slows as more oxygen vacancies are passivated and the limit is approached.

6.5 Impact of Dry Ozone Adsorption and UV Desorption over time

Evaluation of the sensor response over time as the response/recovery cycle executes will reveal the complexities of the sensor’s proposed method of operation. This section describes the results
of experiments designed to determine the effects of ozone adsorption coupled with UV assisted desorption. Dry air with ozone was used to expose sensors that were stored in dry air with desiccant packets to reduce the impact of humidity on the experiment. Additionally, exposures were performed on samples stored in N\textsubscript{2} to evaluate the influence of surface oxygen.

### 6.5.1 Response of Sensor Stored in Dry Air

The ozone response magnitude of the sensor stored in dry air is plotted over a three hour exposure in Fig. 6.9. The surface is slightly reduced due to oxygen vacancies and there are few water species on the surface after storage in dry air. The response is reasonably flat with the exception of the discontinuity at \( t = 80 \) minutes. This 3 hour segment was split into two parts due to running out of zero air during the test. The first portion of the experiment was conducted in the early morning and the second portion was conducted later in the afternoon, after fresh cylinders of zero air were delivered. The steady state resistance before the first measurement segment was 63 k\( \Omega \) but fell to 61 k\( \Omega \) in the afternoon. This is likely due to the 9°C increased ambient temperature and 10% higher afternoon humidity in the lab as the chillers in the air handler were down at this time.

Adsorbed ambient humidity resulted in dissociated hydroxy groups on the surface during sample transfer between the two segments of the experiment. This amplified ozone response over the few minutes and at \( t = 80 \) minutes. As surface molecular water evaporates in the dry air stream,
some hydroxy groups recombine to maintain the equilibrium balance as in Eq. 6.9, resulting in the response decay. The sensor stabilizes at a lower baseline resistance for the afternoon portion of the experiment due to the increased temperature in the lab causing an increased desorption rate and increased thermally excited carriers.

$$2OH^- \leftrightarrow H_2O + O^- + e^-$$  \hspace{1cm} (6.9)

### 6.5.2 Response of Sensor Stored in Nitrogen

The influence of existing surface oxygen was analyzed by running the same experiment on a sample stored in an N$_2$ environment for 1 week before measuring. The surface in this case would be heavily reduced after storage in a non-oxidizing ambient, which is evident by the low starting resistance of 22 kΩ and the fast increase in resistance upon exposure. Fig. 6.10 shows the results from an exposure test of 100 ppb O$_3$ in 0% humidity.
Figure 6.10 100 ppb ozone room temperature response ($\frac{dR}{dt}$) of N₂ stored sample in 0% humidity over three hours

The discontinuities at $t = 125$ and 170 minutes are due to the probe tips losing contact with the sample and the measurement being stopped while the chamber was opened and the probe tips re-positioned. At the beginning of each of these segments, and at the start of the experiment, the sample was briefly exposed to the humid lab environment. Each time the chamber was opened, the surface hydroxy groups are replenished and the ozone response is amplified temporarily. When the experiment continues in dry air, hydroxy group coverage decreases and the ozone response trends back toward its stable value. The desorption of water does make more adsorption sites available to ozone and cause a slight increase in adsorption, but a fewer number of catalytic hydroxy groups on the surface dominates the change in response. This resulting in far fewer $O^-$ and $O_2^-$ ions from dissociated ozone and explains the decrease in response over time.
Selectivity, or cross sensitivity, is an important characteristic for evaluating a sensor’s utility. The gold standard for selectively identifying gases is gas chromatography mass spectrometry (GC/MS). It is often used in analytical chemistry for analyzing compounds that are sufficiently volatile to be present in vapor or gas form and for separating impurities to prepare pure materials from mixtures [122]. Some sensor types, such as electrochemical and optical sensors, display strong selectivity. However, metal oxides do not fall into this category and tend to respond more broadly to oxidizing or reducing gases in general [123]. Application of metal oxide sensors in electronic nose applications make use of multiple different kinds of sensors in conjunction with pattern matching algorithms, such as principle component analysis or linear discriminate analysis [124]. These techniques can certainly be applied to the room temperature sensors as well, but some interesting side effects of room temperature operation were discovered when examining the cross sensitivity to common interfering gases. Response to nitrogen dioxide and carbon monoxide were evaluated based on their potential to interfere with ozone detection and their abundance in the atmosphere.

Nitrogen dioxide (NO$_2$) is a byproduct of combustion, so higher concentrations are found near highways, airports, rail yards and wood burning fires, among other sources. Additionally, it is a precursor to ozone formation and one of the Environmental Protection Agency’s (EPA) six criteria pollutants for air quality evaluation. The EPA’s current National Ambient Air Quality Standard (NAAQS) annual average for NO$_2$ is 53 parts per billion (ppb) while the 1 hour standard is set at 100 ppb [3].

Carbon monoxide (CO) is another widespread pollutant that can cause symptoms such as fatigue, impaired vision, reduced coordination, or even death, depending on exposure level. Higher concentrations of CO are found in homes with gas stoves and near fires [125]. The Occupational Safety and Health Administration (OSHA) limits permissible exposure to CO at 50 part per million (ppm) as an 8 hour average, while the National Institute for Occupational Safety (NIOSH) recommends
a 35 ppm 8 hour limit and an absolute ceiling of 200 ppm. Incidentally, the levels in homes with poorly adjusted gas stoves can reach 50 ppm [126].

For N-type semiconductors, an oxidizing gas species ionosorbs to the surface and forms an acceptor state that traps an electron in the band gap. This results in charge carrier modulation and a decrease in conductivity. Reducing gases behave similarly, except they are interact with oxygen that has already been adsorbed on the surface. The surface species oxidize the reducing gas molecule which donates electrons to the sensitive layer, increasing conductivity.

The primary differences in the reactions of various gases is the amount of energy required for the chemical reaction for adsorption, the amount of charge transfer, and the binding energy that must be broken for desorption. Some researchers have performed first principles calculations using density functional theory to determine binding energy and net charge transfer on various crystal planes for oxygen ($O_2$), carbon monoxide (CO) and various nitrogen oxide (NO$_x$) species. For example, many NO$_x$ species and oxygen vacancy configurations were calculated to have binding energies of 10-20 or even up to 30 kcal/mol while neutral physisorbed $O_2$ molecules displayed a much weaker binding energy at 1.4 kcal/mol [127].

Ozone is a special case in that the reaction involves dissociation of the O$_3$ molecule into an O$_2$ molecule and atomic oxygen such that the reactive species is actually O$^-$ ions. Ozone is highly reactive and decomposes easily, which is a great advantage for SnO$_2$ based ozone sensors operating at room temperature. The thermal energy of commercial sensors is not required to complete the chemical reaction at the surface, as evidenced by the results in Chapter 4. Additionally, other common interfering gases that are less reactive, do not adsorb at sufficient rates to cause substantial interference in the ozone response signal.

As mentioned previously in this chapter (Chapter 6), the EPA's air quality standard annual average for NO$_2$ is 53 ppb while the 1 hour standard is set at 100 ppb. CO safe limits are set at 50 ppm over 8 hours by the Occupational Safety and Health Administration (OSHA) and 35 ppm by the National Institute for Occupational Safety (NIOSH) with an absolute ceiling for instantaneous exposure of
The sensors in this work were tested for response to 50-100 ppm CO and 100-300 ppb NO\textsubscript{2} and found that the sensor exhibited very small response at these concentrations, directly contrasting the strong ozone response at very small concentrations of 25 ppb. The magnitude of the response to CO and NO\textsubscript{2} is shown in Fig. 6.11.

Addition of humidity to the air stream reduced resistance substantially again, but no amplified response was seen from high concentrations of NO\textsubscript{2} or CO. In fact, the humidity response was so strong that the signal from CO and NO\textsubscript{2} exposure was drowned out and not visible. This verifies that the increased response from ozone in the presence of humidity is due to catalytic decomposition of O\textsubscript{3} due to dissociated hydroxy groups.

### 6.6.1 Catalytic nanoparticles

Many works exist in the metal oxide sensor literature on modification of sensor response by doping, creating p-n junctions, catalytic nanoparticles or blends of metal oxides. Nanoparticles of noble
metals, such as Pd, Pt, Ag or Au, act as catalysts to promote the dissociation of oxygen and other gases at low temperatures. This results in faster response times and modified sensitivity and selectivity. For instance, Ag surface modification of SnO$_2$ has been shown to increase the response to CO while decreasing the response to O$_3$. In heated sensors, these surface treatments have also been shown to shift the operating temperature for maximum gas response to lower values [128, 129]

Using an ALD platinum (Pt) nanoparticle (NP) deposition process developed by Novak et al. [130], platinum was deposited on top of the ALD SnO$_2$ films to evaluate the effect on sensitivity and selectivity at room temperature. The films were deposited at 150$^\circ$C, annealed at 600$^\circ$C and 12 nm thick. The catalytic activity of the nanoparticles enabled detection of CO in concentrations of 200 ppb in air at 0, 20 and 40% relative humidity. The results of this experiment can be seen in Fig. 6.12.

Response to ozone was evaluated as well to see if the nanoparticles catalyzed reaction with ozone. Two sensor samples were fabricated together in the same film deposition, anneal and contact deposition steps. Then one received 30 cycles of ALD platinum. The comparison of the sensor response to 50 ppb ozone can be seen in Fig. 6.13.
Figure 6.13 Comparison of 50 ppb O₃ 0% RH response of pure SnO₂ and platinum nanoparticle decorated SnO₂.

6.6.2 SnO₂ -TiO₂ Composite Films

Using a combination of sensors made from different materials is a common approach for achieving different selectivity patterns in electronic nose applications. For example, sensors made from SnO₂, ZnO (zinc oxide), WO₃ (tungsten oxide), or In₂O₃ (indium oxide) all display different magnitude responses to various gases. By combining them and using pattern matching algorithms, a more accurate determination of gas mixtures can be accomplished. In addition, varying the material composition within a single sensor can result in increased selectivity for particular gases. For example, it has been shown that the addition of titanium (4.6 at.%) can reduce influence of humidity on sensor response [131]. Atomic layer deposition is an excellent tool for depositing films of several materials with varying composition. An ALD TiO₂ precursor (TDMATi) was used to fabricate SnₓTi_{1-x}O₂ films for gas sensing, where x is between one and zero. For example if x = 0.95 then the film is 95 at.% SnO₂ and 5 at.% TiO₂.
Lindan compared water adsorption energies for SnO$_2$ and TiO$_2$. He suggests 5% larger lattice constant of SnO$_2$ is significant because the water molecules on TiO$_2$ are more tightly packed. This makes formation of hydrogen bonds to neighboring water molecules more stable and reduces the tendency of water to dissociate. The mixed and molecular adsorption states have 0.1 eV higher adsorption energy compared to fully dissociated states. [105].

The composite film experiments in this work included films with x = 0.95, 0.9 and 0.8. The films with x = 0.8 and 0.9 were too highly resistive to measure, even with voltage sweeps from -20 to 20 V. The increase in resistivity is not surprising, based on literature and previous work with pure ALD TiO$_2$ films used for sensing NO$_2$ [132]. The films with x = 0.95 proved to be more interesting. The ozone response was significantly increased compared to the pure SnO$_2$ sensor, although the baseline resistance also increased substantially. After normalizing each sensor response to their baseline values, the composite films displays a higher percentage change in resistance during exposure to the same ozone concentration as shown in Fig. 6.14.

It was hypothesized that the combination of a smaller lattice constant and a larger electronegativity difference for TiO$_2$ ($\Delta \chi = 1.9$), and SnO$_2$ ($\Delta \chi = 1.46$) could cause a higher density of oxygen
Table 6.2 Composite Sn-TiO\textsubscript{2} film stoichiometry results from Rutherford Backscattering analysis.

<table>
<thead>
<tr>
<th>Deposition Temperature</th>
<th>Anneal Temperature</th>
<th>Sn:Ti:O ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>600</td>
<td>1:0:1.92</td>
</tr>
<tr>
<td>200</td>
<td>600</td>
<td>1:0.07:1.91</td>
</tr>
</tbody>
</table>

Figure 6.15 Comparison of room temperature humidity response in 100 ppb O\textsubscript{3} for pure SnO\textsubscript{2} and Sn\textsubscript{0.95}T\textsubscript{i0.05}O\textsubscript{2} films.

Vacancies and result in stronger ozone response. Composite film samples were sent to the Ion Beam Laboratory at the University of Albany for Rutherford Backscattering (RBS) analysis to determine the stoichiometry, however, the RBS results in Table 6.2 do not indicate substantial change in oxygen content of the films.

The humidity response with 100 ppb O\textsubscript{3} was also evaluated, to determine if the addition of titanium worked to mitigate the humidity response as reported by Tricoli et al. [131], but this effect was not observed. The normalized resistance vs time graph comparing the composite film with pure SnO\textsubscript{2} can be seen in Fig. 6.15.

The pure SnO\textsubscript{2} sensor displayed minor response changes of less than 1% for relative humidity changes of 10% while the composite sensor response increased 3 to 4% for the same humidity changes.
Figure 6.16 Room temperature NO\textsubscript{2} response in dry air for Sn\textsubscript{0.95}Ti\textsubscript{0.05}O\textsubscript{2} composite films. At t=21 minutes, 27% humidity is added to the gas stream, overpowering the NO\textsubscript{2} response.

changes. It should be noted that changing the ozone levels in dry air also causes a much larger change in the composite film resistance than the pure film which may be partly due to some chemical effect on the surface, but is certainly largely impacted by the change in baseline resistance. The SnO\textsubscript{2} sensor was easily set to a baseline of 130 k\(\Omega\) while the composite sensor was over an order of magnitude higher at 2 M\(\Omega\). Recalling the equation for the Debye Length, Eq. 6.10, it can be seen that a smaller number of charge carriers results in a larger depleted region, which enhances the sensitivity to ozone and to water vapor. The composite films appear to have low carrier concentration that would be reduced even further by charges trapped at the surface, which may be the primary cause of the change in response.

\[
L_D = \sqrt{\frac{\varepsilon k_B T}{q^2 n_c}} \tag{6.10}
\]

Finally, the composite sensor was tested for NO\textsubscript{2} response in dry air and humid air. A small response was visible for 200 and 500 ppb NO\textsubscript{2} in dry air, but addition of humidity to the gas stream overpowered this signal easily. The results can be seen in Fig. 6.16.
6.7 Power Consumption

Ultra-low power consumption has been a main driving force in the development of this work to enable portable, continuous, and personal environmental monitoring without having to worry about the charge left on a battery. In this work, the sensors were typically biased at 100 mV with 1 \( \mu \text{A} \) of current flow amounting to 100 nW of power dissipated in the sensing film.

The UV LED takes up the bulk of power consumption, but was still kept to very low average power values. For a 385 nm UV LED and appropriately high reset resistance, the average power consumption over a response/recovery cycle in 50 ppb dry ozone was as low as 100-200 \( \mu \text{W} \). Of course, it has been shown that humidity would increase the adsorption rate of ozone and so would require more power to be consumed by the UV light to maintain the same reset resistance. However, if the reset resistance is chosen at a higher value, then the increased power consumption can be offset.

Several heater options are also considered for comparison of power consumption. Heated membranes with a low thermal mass were characterized for power consumption before depositing \( \text{SnO}_2 \) to test the sensor response. The power consumption is very high as seen in the plot in Fig. 6.17, requiring 25 mW of power just to get to 100°C. The voltage for the temperature range plotted spanned from 15-30 volts. This is completely unsuitable for portable applications, but sensor fabrication was attempted regardless to evaluate the performance of the ALD \( \text{SnO}_2 \) on a hotplate with a very short time constant.

Unfortunately, attempts to fabricate sensors with these membranes were not successful. The electrode traces broke and migrated during the 2 hour anneal in air and the metal pads oxidized heavily. Reducing the thermal budget or annealing in an inert ambient might allow the contacts to survive. A final option would be annealing the film with the hotplate itself. The thermal isolation of the membrane may be enough to protect the contacts from oxidizing. However, the membranes were only characterized to 550°C and no data on how long they can withstand that temperature was
The lowest power consumption micro-hotplate found in literature is quite a bit more impressive, with a thermal time constant of 1.5 ms and requiring just 8.9 mW of power to heat to 400°C. Elmi et al. [133] fabricated the suspended hotplate by oxide-nitride-oxide (ONO) deposition and reactive ion etching (RIE). The electrodes and heater were then deposited in a single layer. Electrical isolation was accomplished with spin on glass and low temperature oxide with a wet etch for contact openings. Finally, a TMAH wet etch was used to remove the silicon under the hotplate. A Scanning Electron Microscope (SEM) image and plot of temperature vs. power consumption for several different geometries from their publication is shown in Fig. 6.18.

This would likely be suitable for a portable application if the heat was duty cycled and measurements were not taken too frequently. However, the micro-hotplate fabrication technology is significantly more involved. The three mask, front-side bulk silicon micromachining process used would increase the cost per sensor while decreasing the yield due to broken plates. The fragility of the hotplates is also important to consider. The device would have to be evaluated to determine if it available.

Figure 6.17 Power consumption for membrane hotplates.
would hold up under consumer use.

6.8 Summary

This chapter (Chapter 6) has investigated the sensor reliability by evaluating the response stability over longer term exposures of from 3-10 hours in humid ozone without UV illumination, humid ozone with UV illumination and dry ozone with UV illumination. Exposures were carried out on samples stored in humid or dry air, depending on if they were used to study humid or dry ozone effects, and nitrogen so that the impact of the starting surface species could be investigated. The impact of interfering gases nitrogen dioxide and carbon monoxide was also investigated and compared on standard recipe SnO$_2$, platinum nanoparticle coated SnO$_2$ and composite Sn-TiO$_2$ films. Finally, the use of heat for recovery was considered and compared to UV power consumption.

In addition to observing more evidence of some of the mechanisms described in Chapter 5, the following conclusions were made:

i Extended exposure to humid ozone without UV illumination resulted in a saturation of the
ozone oxidation effect followed by a reducing mechanism. Over time, without UV desorption, an increasing amount of terminal hydroxy groups on the surface form dipoles decreases the work function and the increase the electronegativity. This causes the Fermi levels to drop, resulting in a larger potential barrier for electrons to react with surface species and decreasing the ionosorption rate.

ii For samples exposed to humid ozone and UV, it was observed that the response decayed significantly after the transient oxidation processes described in Chapter 5. This was expanded on by proposing that over the course of many response and recovery cycles, the relative concentrations of oxygen and water species slowly trends toward steady state.

iii For humid ozone exposure of reduced surface stored in nitrogen, the hydrogen based oxidation reactions and oxygen assisted water adsorption described in Chapter 5 were observed, but at a slower rate. The lack of bridging oxygen for protons to bond to resulted in a longer transient process before reaching steady state.

iv The sensors display excellent cross sensitivity for ozone detection:

- The standard SnO$_2$ recipe responses to NO$_2$ and CO were very small at the concentrations tested and undetectable when coupled with humidity response.
- Platinum nanoparticle decorated SnO$_2$, a weak response to CO was observable in 0, 20 and 40% humidity, but the response to ozone was also enhanced significantly, dwarfing any contribution from CO.
- The Sn-TiO$_2$ films showed enhanced sensitivity to ozone, and very small response to NO$_2$

v Power consumption at levels amenable to portable device applications were achieved.

- With optimized parameters, UV power consumption averaged over the response/recovery cycle reach a low of about 150 $\mu$W.
• characterization of heated membrane sensors revealed power consumption of 25 mW to reach a modest temperature of 100°C and over 100 µW for 400°C.

• The best micro-hotplates in literature consuming 8.9 mW of power at 400 °C and just 2.5-3 mW at 100°C. Heating to modest temperatures of around 100°C before each ozone measurement could significantly stabilize humidity related effects and drops down to an average power on the order of 100 µW at a 3% duty cycle.
7.1 Introduction

The data and discussion in the previous chapters has enabled greater understanding of the material and sensing properties of the ALD SnO$_2$ (Atomic Layer Deposited tin dioxide) films. Ozone response has been investigated in a small flow through exposure chamber where the sensor consists an oxidized silicon wafer with an ALD SnO$_2$ sensing film and metal electrode pads. In the
experiments described so far, contact to the sensor electrodes was made using probes attached to a Keithley 4200-SCS parameter analyzer in the lab at North Carolina State University. However, the ultimate goal of the ASSIST (Advanced Self-powered Systems of Integrated Sensors and Technologies) Nanosystems Engineering Research Center is to develop wearable technologies for continuous monitoring. This requires integrating the sensor technology into a small independent system that is capable of collecting and transmitting data for analysis. This chapter (Chapter 7) describes testing and evaluation of the sensor functionality from a systems and application driven point of view.

### 7.2 Portable Gas Sensing System Evolution and Sensor Integration

The ASSIST Center is a systems driven engineering effort with technology testbeds that are intended to provide feedback and guidance on the development of devices and testing methodologies to better enable the parallel development of technologies that will ultimately be integrated together. The testbeds include hardware platforms that are composed of commercial technologies were appropriate, and technologies developed by the ASSIST center are integrated as they mature. The Health and Environmental Tracker (HET) testbed is the system designed to drive and support the development of sensor technologies produced by the ASSIST Center. The HET has been redesigned through several iterations as system specifications and technologies were chosen or evolved. The evolution of the HET are described below.

#### 7.2.1 HET Generation -1

The very first ASSIST system, shown in Fig. 7.1a, was built by the author before any fundamental research had been completed. The goal was to begin to understand the requisite thought processes and system level approach to the problem. This system was built entirely with Commercial Off The Shelf (COTS) components and is composed of a Texas Instruments MSP-430 Launchpad microcontroller development kit, switching buck converters for power management, Honeywell temperature
and humidity sensors, and e2V Sensortech metal oxide sensors for ozone (O\textsubscript{3}) and nitrogen dioxide (NO\textsubscript{2}). Four different voltages were required to power the microcontroller, the sensor voltage dividers and the sensor heating elements. The buck converters were chosen for their low power operation but required external capacitors and inductors and take up a lot of space. Approximately 80% of the footprint shown in Fig. 7.1a is devoted to power management.

### 7.2.2 HET Generation 0

The second iteration of the system was developed by Dr. Ryan Hodges in 2014 and is shown in Fig. 7.1b. This version of the testbed featured surface mount devices on a custom FR-4 printed circuit board and integrated the first functional ASSIST gas sensor, which is packaged in the TO-4 metal can on the lower right side of the picture. The sensor was mounted on the package base and secured with silver paste. Ball wire bonding was used to connect the sensor pads to the package pins with some difficulty. Despite the gold contact pads being a quarter micron thick and including a titanium adhesion layer between the gold and the SnO\textsubscript{2} surface, the metal easily pulled off of the metal oxide. After many attempts with the tireless help of Joe Matthews, the sensor was successfully wire bonded to the package base. The metal cap was then carefully placed over top of the sensor to protect the wire bonds and secured with more silver paste.

It was quickly decided that this was not the best way to integrate the sensors due to the difficulty in mounting, wire bonding and securing the cap to protect the bonds. Additionally, low volume quantities of the package base and caps were unavailable from commercial sources and typically were designed for hermetic sealing with no opening for gas to diffuse through. The cap used in the system pictured in Fig. 7.1b has a mesh top for gas diffusion, but this cap was actually cut off of an existing commercial sensor and was likely custom made. All commercially available caps found were either solid metal, or had a clear window for use with light emitting diodes (LEDs). Finally, sealing and attaching the package caps to the base requires expensive, specialized machinery which was suited more for high volume manufacturing than for research and development. For these reasons,
alternative methods for future system integration were considered.

### 7.2.3 HET Generation 0.1

The subsequent iterations of the HET were designed and built primarily by James Dieffenderfer, working under Dr. Alper Bozkurt. Design decisions were made with the help of regular meetings of the testbed team development team and researchers working on the related technologies. The next version of the HET was completed in 2015 and is shown in Fig. 7.1c. This version incorporated a new packaging method with a socket and drop-in chip carrier that could easily be swapped out for another. This aided in evaluation of multiple sensors, but the socket was very bulky and still not ideal. There is no cover to protect the wire bonds using this method, but the chip carrier was recessed deep into the socket which protected it from most disturbances. This generation of the HET also included a small solar panel which was able to power the measurement circuit in sunlight although indoor light was not always sufficient.

### 7.2.4 HET Generation 1 with UV Enabled Recovery

The next version of the HET, officially dubbed Generation 1.0, is shown in Fig. 7.1d. This is the first system to incorporate an ultraviolet (UV) LED for sensor recovery. The LED used in this system emits light with a wavelength of 385 nanometers (nm). As described in previous chapters, the UV light excites the electrons trapped during ionosorption of ozone, which allows the oxidizing gas molecule to desorb and recover the sensor resistance to the starting reset resistance value. The UV LED is mounted face up on the main circuit motherboard while the sensor was mounted to the small, removable daughter board that faces downward. The sensor chip was secured directly to the daughter board using double-sided tape and wire bonds were made from contact pads on the sensor to the contact pads on the circuit board. This iteration of the HET is the platform used in all of the ozone and humidity tests described in this chapter (Chapter 7).
7.3 Simulated Field Testing: Experimental Procedure

This section is qualified as "simulated" field testing because a chamber with a controlled environment is still used, but the experiment more accurately simulates the use case scenario where the sensor is worn on the body in an unknown ambient atmosphere. The flow through testing chamber used for the experiments in previous chapters was small and directed a gas stream directly onto the sensor. To more accurately simulate field testing conditions, the Environmental Protection Agency
EPA was kind enough to allow use of their large ozone chamber which allows gas to come into contact with the sensor through a diffusion process rather than a directed flow. The chamber is described briefly below.

EPA testing chamber LA75 has a floor area of 29.7 m$^2$ with 3.2 m high ceilings. The chamber operates under a slight negative air pressure and incorporates temperature, humidity, and pollutant control systems. Ozone is generated by the silent arc discharge method using USP (United States Pharmacopeia) grade oxygen. The environmental conditions inside the chamber are recorded as two minute averages and stored in a database. The HET and the integrated gas sensor are placed on a table in the chamber for the duration of the experiment, which was typically 7-8 hours, and the data was transmitted in real time to a laptop outside of the chamber.

The HET platform used in these experiments is programmed to record resistance and continuously cycle through a response measurement and recovery cycle. The sensor measurement circuit is a voltage divider shown in Fig. 7.2 where $R_S$ is the gas sensor resistance, $R_L$ is a load resistance, $V_{DD}$ is five volts, ADC is an analog to digital converter and MCU is a microcontroller that receives and transmits the digital data. The operational amplifier between the voltage divider and the ADC is configured for unity gain as a voltage buffer.

During response measurement, the UV LED is off and the voltage across the load resistor is measured. From this measurement and the known value of $R_L$, the sensing film resistance is calculated. After recording the increasing resistance values for a specified time (2 or 3 minutes), the recovery period begins and the UV LED turns on. During recovery, gas species desorb due to the energy of the UV light and the resistance drops. When the previously specified reset resistance is reached, the UV turns off and the measurement period starts again. The reset value was initially chosen to be slightly lower than the baseline resistance of the sensor indoors to ensure adequate response (rate of resistance increase) during testing. Later it was increased due to the strong response during experiments, which will be discussed in the next section.

Several different sensors were tested using the HET testbed system. They are identified through-
out the chapter with the HET name and a subscript. For example, HET\textsubscript{1} is the first sensor tested in this manner. The sensor denoted HET\textsubscript{1} was fabricated in August of 2016 and is a 24 nm thick film. This is considerably thicker than the films tested to obtain much of the experimental data presented in previous chapters. HET\textsubscript{2} and HET\textsubscript{3}, which were fabricated early in 2017, and are composed of 12 nm thick films.

### 7.4 Simulated Field Testing: Results and Discussion

#### 7.4.1 HET\textsubscript{1} Data: October 10\textsuperscript{th}, 2016

Data from the first test of the 24 nm thick HET\textsubscript{1} integrated gas sensor in the EPA testing chamber was collected on October 10\textsuperscript{th}, 2016. This data is shown in Fig. 7.3.

The top part of the figure shows the resistance of the sensor plotted vs. time. The reset resistance for this experiment was about 13.3 kΩ. The shaded regions of the plot show when the UV LED is turned on. The bottom part of the figure shows the sensor response for each exposure period.
between the UV resets in the form of the magnitude of the time derivative ($\frac{dR}{dt}$). In the bottom half of the figure, the actual measured values of ozone, humidity and temperature are plotted while Table 7.1 summarizes the planned exposure. It is important to remember that there is a time constant associated with stabilization of each of these variables inside the chamber. Ozone concentration in the chamber stabilizes relatively quickly in about 8 minutes, but humidity takes about 10 minutes to ramp up and typically overshoots by a few percent before stabilizing after another 10 minutes. The temperature can take an hour or longer to stabilize, and changing the temperature and the humidity at the same time is difficult.

With careful examination of Fig. 7.3, the reader might notice a slight downward trend in the reset resistance over the course of the test. This is due to an insufficient system power supply. When the UV LED turns on, the power rails for the system drop. This results in some noise from a slightly unstable microcontroller and an approximately square wave of increased resistance superimposed on the resistance plot. The sensor element is in series with a load resistor and when the power supply drops...
Table 7.1 HET

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>O₃ (ppb)</th>
<th>Relative Humidity (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
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<tr>
<td>0</td>
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<td>3</td>
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<td>3</td>
<td>32.5</td>
</tr>
<tr>
<td>300</td>
<td>120</td>
<td>3</td>
<td>32.5</td>
</tr>
</tbody>
</table>

the voltage being read across the load resistor also drops, resulting in an artificially high calculated value for the sensor resistance. These square pulses were subtracted from the resistance plots shown. However, the downward trend is still visible because voltage drop becomes larger as the battery drains, which may be noticeable in a small step down of the reset resistance after the long UV pulse in Fig. 7.3.

The first 100 minutes of the test go very well. The chamber is filled with dry air/ozone and the sensor response \( \frac{dR}{dT} \) tracks changes in the ozone concentration as expected. Approximately 110 minutes into the test, the humidity is increased to 40%. Chapter 5 discussed the influence of water vapor on the ozone sensor and concluded that water vapor in the air adsorbs to the SnO₂ surface dissociatively, resulting in hydroxy groups (OH⁻) at many of the active adsorption sites. The hydroxy groups act as a catalyst for ozone decomposition, which increases the effective concentration of O⁻ ions available to ionosorb at the SnO₂ surface and the sensor response. As the reactive oxygen species become more abundant, the adsorption rate increases while the UV induced desorption rate remains constant. As the UV works to desorb species from the surface, more active adsorption sites become available and further increase the adsorption rate. At approximately 135 minutes,
the surface reaches an equilibrium where the adsorption and desorption rates are equal and the resistance curve flattens out. Shortly after, at \( t = 140 \) minutes, the ozone level reduces from 120 ppb to 100 ppb. This reduces the adsorption rate and a corresponding decrease in the resistance is observed as the surface reaches a new equilibrium. However, the UV illumination is still insufficient to fully recover to the reset resistance. At \( t = 175 \) minutes, the ozone concentration drops to 60 ppb, and the adsorption rate finally decreases enough for the UV induced desorption to dominate and the sensor is reset. The time required for the three recovery periods before the humidity reduces back to zero shows that even 60 ppb of ozone results in very high adsorption rates in humid air with this system configuration. Finally, at \( t = 200 \) minutes, the temperature is increased from 24°C to 32.5°C. The response from the sensor at this point is slightly higher than in the beginning of the test due to the increased thermal energy and also due to residual OH\(^-\) groups that remain on the surface, both of which accelerate the ozone decomposition and ionosorption rates.

### 7.4.2 HET\(_1\) Data: November 18\(^{th}\), 2016

The next test of HET\(_1\) was conducted on November 18\(^{th}\), 2016. During the interim, the sensor was exposed to an uncontrolled ambient atmosphere inside an office building with no special storage considerations or monitoring. The sensor recovery specifications were modified in this experiment in an attempt to overcome the recovery failure exhibited in the October 10\(^{th}\) experiment in humid ozone. More specifically, the reset resistance was increased to approximately 16.6 kΩ.

During sensor recovery, adsorption processes are still occurring. In the previous experiment, the adsorption rate was so fast that even with the UV illumination enhancing the desorption rate, gas molecules could not be desorbed fast enough to drive the sensor to the reset resistance in humid ozone conditions. Recall that the adsorption rate slows as more vacancies are occupied. This motivated the choice to increase the reset resistance so that the UV light would be able to more effectively recover the sensor.

The results from this experiment and the testing profile can be seen in Fig. 7.4 and Table 7.2.
Similar to the previous experiment, the atmosphere is cycled through several ozone levels in dry air and 40% humid air. Additionally at $t = 220$ minutes the temperature is increased from 24°C to 32.5°C.

Again the response tracks the changes in ozone concentration, but this time the sensor recovery does not fail when the humidity increases. The lower adsorption rate in this experiment manifests in smaller slopes during sensor response which can be seen in the magnitude of $\frac{dR}{dt}$. Under these conditions, the UV recovery desorption rate is sufficient to overpower the adsorption rate in 120 ppb ozone at 40% humidity, where it failed in the previous test.

At $t = 220$ minutes, the humidity has fallen back to 0% and the temperature increases to 32.5°C. A small increase in the sensor response to 60, 100 and 120 ppb ozone can be seen showing that the increased temperature increases the ozone decomposition and ionosorption rates. When the humidity rises again at $t = 310$ minutes, the combined adsorption rate increases from the water vapor and the temperature result in the UV recovery failing again as the desorption rate is unable to

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>O$_3$ (ppb)</th>
<th>Relative Humidity (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
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<tr>
<td>450</td>
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<td>0</td>
<td>22.5</td>
</tr>
</tbody>
</table>
to overcome the adsorption rate. When the ozone level drops to 60 ppb at \( t = 400 \) minutes, the adsorption rate is low enough that the UV is able to recover the sensor again. Driving the sensor resistance down this far results in a surface that is too reduced and too reactive for the UV energy to be effective at higher concentrations.

### 7.4.3 HET\(_1\) Data: February 8\(^{th}\), 2017

Several changes were made to the experimental setup for the next test. It was decided to repeat test conditions more consistently in order to better understand the sensor response and evaluate its consistency. The ozone cycle was standardized to 30 minute increments of 60, 80 and 100 ppb with alternating humidity levels of 0 and 40% for each ozone cycle. The humidity response was deemed more complex and more important to understand than temperature, and so the chamber was held constant at 24\(^\circ\)C to simplify the experiment and reduce the number of changing variables.

The HET platform was reprogrammed for several changes as well. The results of the previous
experiments and failed recovery periods prompted the addition of dynamically adjustable reset resistance to the HET platform. With this addition, the reset resistance can be increased if the UV assisted desorption rate is insufficient to recover the sensor. Additionally, the measurement time between UV recovery cycles was decreased from three minutes to two minutes. Reducing the measurement time allows more response cycles to be measured and enhancing the resolution of transient effects due changes in the ambient. The sensor response and actual measured values of the atmospheric conditions are shown in Fig. 7.5 and the ozone and humidity profiles can be seen in tabular form in Table 7.3.

The irregularity in the reset resistance is due to manually changing the resistance value where the UV turns off. Recall that the sensor resistance while the UV LED is turned on is artificially high in the raw data, and that the jump in resistance increases as the battery drains. This means that the only way to adjust the reset resistance at this point is to approximate the resistance drop from the data being plotted in real time and add that value to the desired reset resistance. Then the HET will
Table 7.3 HET₁ Testing Conditions: 2/8/2017

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>O₃ (ppb)</th>
<th>Relative Humidity (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60</td>
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<tr>
<td>420</td>
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<td>2</td>
<td>24</td>
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</table>

Turn off the UV at this artificially high resistance and the resistance will fall to its true value.

The large spike in the sensor response when the humidity increases is another manifestation of the transient humidity response discussed in Chapter 5. Recall that water exists on the SnO₂ surface in both molecular form (H₂O) and dissociated. When water dissociates it forms hydroxy groups (OH⁻) and ionized hydrogen atoms, or protons (H⁺), as shown in Eq. 7.1.

\[ H₂O \rightarrow OH^- + H^+ \]  \hspace{1cm} (7.1)

The cause of the transient response spike is rapid dissociation of water molecules on the surface. The excess protons are very reactive and mobile along lines of bridging oxygen atoms. As such, the protons may react with negatively charged oxygen species to form water or hydrogen peroxide, or with other protons to form hydrogen gas. Each of these reactions trap electrons, as shown in Eq. 7.2 - Eq. 7.4, resulting in the observed response increase. As the surface species are consumed, the
reaction rates slow and the response decays toward steady state values. A more detailed discussion of this effect was presented in Chapters 5 and 6.

\[ H^+ + H^+ O^- \text{(ad s)} + e^- \leftrightarrow H_2 O \]  (7.2)

\[ H^+ + H^+ O^- \text{(ad s)} + e^- \leftrightarrow H_2 O_2 \]  (7.3)

\[ H^+ + H^+ + 2e^- \leftrightarrow H_2 \]  (7.4)

The reader may have noticed by this point that the sensor response is fairly stable throughout the several hour test data shown, which is summarized for each wet and dry cycle of the February 8th experiment in Fig. 7.6. However, the response has been decreasing between the experiments. This is partly due to increasing the reset resistance with each experiment to enable the UV recovery mechanism in higher concentrations of ozone and humidity. Another contributing factor is prolonged exposure to humid atmosphere resulting in many dipoles from dissociated water on the surface. Chapters 5 and 6 discussed modification of the SnO\textsubscript{2} work function and electron affinity under these circumstances, which results in an increased potential barrier for ionosorption at the surface.

This, is the last dataset from HET\textsubscript{1}. As the response decreased, the data processing required to remove the voltage rail fluctuations became more difficult. HET\textsubscript{2} and HET\textsubscript{3} were fabricated to replace HET\textsubscript{1}. At half the film thickness, the response is stronger due to the surface electron depleted region dominating the electrical characteristics of the film and the voltage rail artifacts are more easily separated from the sensor response. After removal from the HET testbed, the HET\textsubscript{1} sensor was tested in the smaller testing chamber described in Chapter 2. Unfortunately, during one of those experiments, the wire bonds were caught on the probe tips and ripped off. This greatly increased the contact resistance of the contact pad on the sensor surface and rendered the sensor nonfunctional.
Figure 7.6 EPA test Feb. 8 2017: Response vs. Concentration

7.4.4 HET$_2$ Data: March 15th, 2017

This section begins the story of HET$_2$, which was tested once a week in the EPA exposure chamber for six weeks. After testing the dynamic reset resistance and reducing the measurement period from three minutes to two minutes, the change in resistance during exposure decreased substantially. This called attention to decline in the reset resistance over time due to the voltage rail drop during UV illumination, as described earlier. Sending new values of the artificially high 'UV off' resistance more frequently, resulted in the choppy resistance plot previously illustrated in Fig. 7.5. To eliminate these fluctuations, the HET was reprogrammed to measure the first post recovery resistance value after manually entering a 'UV off' level. As the battery drains, and the post recovery resistance begins to decrease, the 'UV off' resistance is automatically increased so that the sensor is consistently reset to the same level.
Table 7.4 HET$_2$ Testing Conditions: 3/15/2017

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>O$_3$ (ppb)</th>
<th>Relative Humidity (%)</th>
<th>Temperature (°C)</th>
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<tbody>
<tr>
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<tr>
<td>420</td>
<td>100</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

In hindsight, entering the reset resistance instead of the "UV off" resistance and performing a resistance check against that value before turning the UV on would have been a better solution. As it stands, the UV turns on briefly every two minutes and then checks the resistance level. This results in unnecessary UV pulses during the initial ramp up of resistance at the beginning of each experiment, which slightly delays reaching the desired resistance level.

The first EPA exposure experiment for HET$_2$ took place on March 15$^{th}$th. The nominal ozone and humidity profiles for the experiment are shown in Table 7.4. Fig. 7.7 shows the data collected from HET$_2$ and the measured values for the chamber conditions during the experiment.

In this experiment it was attempted to reduce power consumption and enhance the response where needed by modifying the reset resistance based on the humidity level. It is known that a lower UV reset resistance will cause increased adsorption rate and this means that adjusting the reset resistance can enable the sensor to adapt to changes in the environment. For example, if the
adsorption rate becomes very high, the required power to reset the sensor increases. By allowing the resistance to rise and more adsorption sites to be occupied, the adsorption rate and the response decrease. Likewise, the power required for recovery is also reduced. Conversely, if the response is not strong enough, or if the UV reset is too powerful and overshoots the reset resistance, then a lower reset resistance can be set to increase the adsorption to desorption ratio resulting in a stronger response.

The HET\textsubscript{2} sensing film is about half the thickness of the HET\textsubscript{1} film. From discussion in Chapter 4 and 5, this thickness is much closer to the Debye length. Recall that the Debye length is the thin layer just below the surface that is depleted of electrons due to the negative surface charge that has been trapped by ionosorbed oxygen species. As such, the film characteristics are more strongly influenced by the depletion region. With fewer carriers available for conduction, the signal to noise ratio is increased and any charges trapped or released by adsorbing or desorbing gas species will result in a larger percentage resistance change. This is well illustrated in the data where the response in 40\% humidity ranges from around 20-35 \Omega/s. This is nearly an order of magnitude higher than the
24 nm thick HET$_1$ response from 2/8/17. The dry ozone response is also amplified by the thickness effect. Response in the range of 10 $\Omega$/s is seen in HET$_2$ while 1.5 $\Omega$/s is more representative of the HET$_1$ response.

Fig. 7.8 shows a zoomed in view of the final dry ozone response portion of Fig. 7.7. The response to dry ozone is still tracking the ozone concentration, although it takes about 30 minutes to stabilize after the change in humidity and reset resistance. The response in both the wet and the dry conditions appear to stabilize faster after the first humid ozone cycle completes. This another indication that humidity changes have long lasting effects on the sensor surface and highlights the importance of understanding the exposure history of the sensor.

The key findings here are that increasing the reset resistance for power savings is only beneficial if it is expected to be maintained at that level for an extended period of time. Maintaining a constant reset resistance results in more stable measurements. In addition, determining the ozone concentration during the settling time requires greater understanding of the sensor surface evolution over long periods of time in the absence of UV illumination. This was explored to an extent in Chapter 6.
and it was determined that molecular water may evaporate from the surface when humidity drops and some dissociated hydroxy groups recombine to maintain an energetically favorable ratio of molecular to dissociated water. Investigation of adsorption and desorption rates using quartz crystal micro-balances could offer insight here.

On the other hand, the settling time for changes in ambient humidity is on the order of 15 minutes, so if humidity data from peripheral sensors in the HET system is used to determine reset resistance changes, then the settling time for the two variables overlaps considerably. This sort of transition may occur when moving from indoors to outdoors and should be apparent from the humidity and temperature sensors on the HET. In this scenario, it may be worthwhile to adjust the baseline resistance if power consumption is a concern.

### 7.4.5 HET\textsubscript{2} & HET\textsubscript{3} Data: March 20\textsuperscript{th}, 2017

Beginning in this section, HET\textsubscript{3} joins HET\textsubscript{2} for simultaneous data collection from two sensors exposed to the same conditions. The two HET platforms were placed side by side in the ozone testing chamber for data collection.

Due to the long settling time required when adjusting the reset resistance, future experiments were designed to identify and maintain a stable resistance level where response and recovery were both attainable. Additionally, the time between humidity changes and ozone changes was increased from 30 to 60 minutes to allow extra time for sensor response and humidity in the chamber to stabilize. This provides more data points that can be compared per experimental condition (ozone and humidity level) and also maintains consistent conditions to compare exposure data from one week to the next as the sensor ages. An effort was made to maintain the reset resistance from week to week to better track the sensor performance over time. This worked well with HET\textsubscript{2} but HET\textsubscript{3} experienced significant baseline resistance drift that will be explained below.

The data for the March 20\textsuperscript{th} experiment is shown in Fig. 7.9. At this point it was decided that there was enough data collected for dry ozone exposures both in the EPA labs and the North Carolina
State labs, but the humidity effect was still not fully understood. For this reason, the remaining experiments will not include 0% RH test conditions. The reset resistance was chosen to achieve UV illumination reset times of 5-10 seconds. When reset times become shorter than this, the HET sampling rate may not be fast enough to prevent significant overshoot of the reset resistance. If the reset time is much longer, the battery drains more quickly and fewer data points are obtained per experimental condition. Under these constraints, the reset resistances for HET\textsubscript{2} and HET\textsubscript{3} were set to approximately 63 $k\Omega$ and 54 $k\Omega$, respectively. The data transmission from HET\textsubscript{3} stopped at around $t = 360$ minutes due to an error in the Bluetooth transmission, or perhaps crashing of the HET or the data receiving application.

Once stabilized, both HET\textsubscript{2} and HET\textsubscript{3} appear to track the ozone concentration fairly well. HET\textsubscript{2} took about one hour to reach 63 $k\Omega$. At approximately the same time, the humidity increased from 40% to 60%.

The long response time to humidity changes can be seen well here. From the work presented in Chapters 4 and 5, it is known that humidity reduces the SnO\textsubscript{2} surface and lowers the resistance. However, in the presence of ozone it enhances the oxidation response. After the humidity level in the chamber saturates at $t = 80$ minutes, the response of HET\textsubscript{2} to 60 ppb O\textsubscript{3} continues to increase, indicating that the adsorption rate is still increasing. The cause of this is the increasing concentration of hydroxy groups on the surface, resulting in the increased ozone response. Literature has suggested the hydroxy group concentration has a maximum at some finite concentration of oxygen vacancies \cite{103}. Additionally, some suggest that water dissociation on the surface may be a formation route for oxygen vacancies. This could explain response drift after humidity changes in the atmosphere. If the surface had been exposed to dry ozone for some time, then there are likely few oxygen vacancies. As hydroxy groups react to generate oxygen vacancies, more water can dissociate, resulting in a positive feedback loop. However, at some critical concentration, producing further oxygen vacancies decreases the percentage of water that dissociates on the surface.

The dashed line shows the chamber humidity level took 20 minutes or longer to stabilize, but
Figure 7.9 HET$_2$ and HET$_3$ response to ozone testing at the EPA on 3/20/17.
the response continues to drift upward indicating the adsorption rate is still increasing. This may be due to the partial recovery and response cycles resulting in slow stabilization of the relative concentrations of hydroxy groups and oxygen species on the surface. During response, the ratio of molecules that adsorbs to the surface depends on the concentrations in the atmosphere. However, the ratios desorbed during recovery depend on the relative amounts adsorbed to the surface. This may be the mechanism behind increasing response after the 60% RH stabilizes and a slight downward trend in the response at 100 ppb in 40% RH around $t = 275$ minutes.

The second 60% humidity cycle starting at 300 minutes shows an increased response to the same levels of ozone when compared to the first cycle. The upward response drift seen in the first 60% humidity cycle followed by the downward response drift in the 40% cycle from 200 to 300 minutes is another manifestation of the long response time to stabilize hydroxy groups after humidity changes. When the humidity increases, the surface slowly becomes more saturated with hydroxy groups and then when the humidity drops, the equilibrium amount of dissociated water also falls. HET$_2$ seems to be particularly sensitive to the humidity induced drift in this experiment, although again it appears to decrease as time goes on.

The transient spikes with increased humidity are not apparent in these plots. Recall in Chapter 5, the spikes in resistance upon humidity exposure were attributed to rapid dissociation of water and reaction of excess protons to form hydrogen gas, water or hydrogen peroxide. The absence of these transient effects is a result of the synchronous changing of environmental variables. Every time the humidity increases, the ozone concentration falls from 100 to 60 ppb, hiding the previously observed behavior.

7.4.6 HET$_2$ & HET$_3$ Data: March 27$^{th}$, 2017

The next week, on March 27$^{th}$, HET$_2$ and HET$_3$ were again tested in the EPA ozone chamber. The data from these exposures can be seen in Fig. 7.10. The testing profile in this experiment is essentially the same with cycles of 60, 80 and 100 ppb ozone repeating with the humidity oscillating between
40 and 60%. In this experiment, both of the HET platforms seem to exhibit upward drift in response magnitude as time goes on. The response of HET\textsubscript{2} is fairly flat during any particular ozone and humidity combination, but the change with each humidity cycle is less well behaved. The change in $\frac{dR}{dt}$ with ozone is slightly smaller in lower humidity, but increases to higher values with each humidity cycle. Conversely, HET\textsubscript{3} has a gentle upward drift in response through nearly the entire experiment. Also interesting is that the average magnitude of the response has dropped considerably.

On March 20\textsuperscript{th}, the strongest responses were in the 65-70 $\Omega/s$ range while a week later the same conditions result in 30-40 $\Omega/s$ response.

### 7.4.7 HET\textsubscript{2} & HET\textsubscript{3} Data: April 3\textsuperscript{rd}, 2017

On April 3\textsuperscript{rd}, another exposure was conducted. This one used the now familiar 60, 80, 100 ppb ozone profile, but the humidity started at 70% and stepped down 10% with each full ozone cycle. The response data from HET\textsubscript{2} and HET\textsubscript{3} can be seen in Fig. 7.11. The first humidity step of 70% was unstable in the chamber, which can be seen in the oscillation of the measured RH signal and the ozone response. This highlights a challenge for this sensor that was alluded to previously. With large changes in humidity levels, the data from the sensor has high variability due to a long time constant of the humidity response. If useful ozone measurements are to be made in these types of conditions, transient humidity response must be understood and characterized which may prove very difficult to do in the face of evolving surface conditions.

Additionally, the data from HET\textsubscript{2} in Fig. 7.11a reveals long term drift in the sensor response. In the first half of the experiment, an upward slope can be seen in the response during the steady state conditions. This indicates that the adsorption rate in high humidity has not stabilized, even after three hours, and continues to increase until the humidity level drops to 50%. The signal from HET\textsubscript{2} at 60% RH looks very much the same as the signal at 50% RH. The expected reduction in response does not begin to manifest until the 100 ppb exposure. Finally, at the end of the experiment the response begins to reduce as expected.
Figure 7.10 HET₂ and HET₃ response to ozone testing at the EPA on 3/27/17.
Figure 7.11 HET$_2$ and HET$_3$ response to ozone testing at the EPA on 4/3/17.
This result is likely due to the ratio of oxygen vacancies occupied by water vs. oxygen. In high humidity, each UV cycle desorbs trapped oxygen species, likely including hydroxy groups, and then they are rapidly filled again. During the recovery stage, the amount of vacancies that are filled by dissociated ozone, molecular water or dissociated water depends on the decomposition rate of ozone, which is determined by the number of surface hydroxy groups available to catalyze decomposition. In the beginning of the experiment, it appears that the number of hydroxy groups is increasing, which in turn increases the ozone decomposition rate and the response of the sensor. An extended strong UV exposure early in a high humidity experiment may be able to stabilize this by accelerating the water and gas exchange on the surface.

$\text{HET}_3$ also displays instability in Fig. 7.11b, but for a different reason. In the previous week, $\text{HET}_2$ was involved in another experiment not documented here. It used in an experiment at the EPA testing facility that involved a long exposure to filtered clean air and humidity only. This resulted in reduction of the surface for several hours which appears to have had a long lasting effect on the sensor. Prolonged operation of the sensor through response and recovery cycles would reduce the $\text{SnO}_2$ surface, removing many of the oxygen species. The humid, ozone free atmosphere would result in a surface heavily populated with molecular and dissociated water. In literature, a heavily reduced surface has been reported to allow greater relaxation of the (110) surface as the neighboring tin atoms are able to squeeze closer together resulting in the in-plane oxygen atoms bulging out from the surface plane by about 0.4Å [134]. The result of this is a change in the electron affinity as the surface potential is spread over a larger distance which impacts the adsorption kinetics.

The response was considerably weaker at typical reset resistances than expected, so a lower value was used to restore the signal. Each time the humidity dropped, the adsorption rate decreased significantly, required another reduction in the reset resistance to maintain a clear signal. Finally, during the second half of the experiment the reset resistance was reduced enough to allow a more stable signal to be seen. This is an interesting phenomenon and should be explored in more depth. A fundamental changing of the surface morphology resulting in a more stable reduced surface could
have implications in application of the sensor at low temperatures if the surface state is not reversed easily. The signal at the end of the experiment looks to be very good quality.

7.4.8 HET\textsubscript{2} & HET\textsubscript{3} Data: April 10\textsuperscript{th}, 2017

The exposure experiments conducted on 4/10 use the same ozone profile, but an inverse step up humidity profile. The humidity was increased every two hours, when the ozone cycle restarts, starting at 40% and ending at 70%. The experiment results are plotted in Fig. 7.12. The results are more stable than the last experiment. The HET\textsubscript{2} response in Fig. 7.12a shows increasing response with ozone and amplified ozone response with increasing humidity as expected, although the response change between 40% and 50% RH is small compared to the other humidity steps. It is possible that the prolonged high humidity exposure from the previous week resulted in water species on the surface that have not desorbed resulting in reduced sensitivity to lower range humidity changes. It does seem that desorption of water species is more difficult than oxygen species. This is another interesting result that should be investigated in more detail. Perhaps prolonged exposure to very high humidity could increase stabilization of the sensor after the surface reactions saturate and intermittent heat treatments can be used to more fully desorb water species.

The reduced baseline resistance of HET\textsubscript{3} due to the long clean air and humidity exposure of the previous week appears to have persisted, again indicating that desorption of water species is difficult with ultraviolet light. Based on those results, a lower reset resistance of 32 k\textohm{} was chosen so that it wouldn't have to be changed during the experiment. An upward drift during the steady state exposures is evident in 40 and 50% humidity which levels off at 60%. This is likely due to a combination of the surface change from high humidity clean air exposure and the high humidity ozone exposure of the previous week. If many water species exist on the surface in molecular form, then an oxygen atom from decomposed ozone creates a new bonding site for a proton enabling further dissociation of water and a corresponding increase in ozone response.
Figure 7.12 HET\textsubscript{2} and HET\textsubscript{3} response to ozone testing at the EPA on 4/10/17.
7.4.9 HET\textsubscript{2} & HET\textsubscript{3} Data: April 17\textsuperscript{th}, 2017

The final experiment in the EPA lab was conducted on 4/17. This experiment returned to the alternating 2 level humidity cycle, but this time from 40 to 70% and back again. Additionally, the one hour steady state ozone concentration previously started at the same time as the changes in humidity to allow extra stabilization time. In this experiment the one hour steady state ozone level was shifted to 100 ppb ozone and straddles the step in the humidity levels to better highlight the results of constant ozone but a change in humidity. The results from this experiment can be seen in Fig. 7.13. The discontinuity in Fig. 7.13b is due to a glitch in the communication from HET\textsubscript{3}.

The results from this experiment are reasonably consistent. In both HET\textsubscript{2} and HET\textsubscript{3}, an upward drift is displayed in the beginning of the experiment when the high humidity first begins, but seems to stabilize relatively quickly. The lower humidity level responses look particularly good, although when the humidity returns to 70%, the response is stronger than in the first cycle due to changing concentration of hydroxy groups on the surface as shown previously.

7.5 Summary

This chapter (Chapter 7) has presented a lot of experimental evidence evaluating the stability of the SnO\textsubscript{2} sensor at room temperature. Many of the mechanisms discussed in previous chapters have been observed in this chapter, verifying that they are not an artifact of the testing chamber and processes used in the North Carolina State University lab.

In the experiments with alternating humidity levels, exposure to an extreme humidity level results in significant response drift and the sensor takes a long time to reach steady state conditions. Additionally, each alternating humidity experiment shows change in response when returning to a previously tested humidity level. From week to week there are significant changes in the sensor response as well. Finally, the response of HET\textsubscript{3} reduced significantly after long exposure to air with water vapor but without ozone. The variation and drift observed in these experiments is attributed
Figure 7.13 HET$_2$ and HET$_3$ response to ozone testing at the EPA on 4/10/17.
to the following mechanisms:

i Partial UV recovery and response cycles result in slow stabilization of the relative concentrations of surface hydroxy groups and oxygen species. During response, the ratio of molecules that adsorbs to the surface depends on the concentrations in the atmosphere. However, the ratios desorbed during recovery depend on the relative amounts ionosorbed on the surface.

ii Over time species may build up on the surface despite the appearance of complete recovery. As oxygen atoms from ozone molecules fill vacancies and trap electrons, they facilitate additional dissociation of molecular water and form new rooted hydroxy groups that may then ionize and donate electrons. In this scenario, two surfaces with different amounts oxygen and hydroxy groups may appear identical from a resistance measurement, but have significantly different ozone decomposition and ionosorption rates.

iii Additional terminal hydroxy will also form at under coordinated tin atoms due to the previous mechanism. These form dipoles which may decrease the work function and increase electron affinity, as described in Chapter 6, leading to a decrease in the adsorption rate.

iv The hydrogen reactions from Chapter 5 further complicate things by providing a route for hydrogen removal and reversal of impact from hydroxy groups.

This data shows the importance of understanding the evolution of surface properties and oxygen vacancy occupancy in the presence of both ozone and humidity. As the vacancies are continuously occupied and evacuated during the response/recovery cycle, the ratio of water species to oxygen species occupying the vacancies changes depending on at least the last few hours of humidity and ozone concentrations, if not more. The time constant for this change with respect to concentration levels and the corresponding change in ozone response must be known to obtain meaningful data from the sensor. Coupled with the work function changes and simultaneous build up of ionosorbed ozone and hydroxy groups, the SnO$_2$ surface becomes a very complex system that may appear
constant from the resistance measurement point of view but has significantly different surface properties and adsorption kinetics.
CHAPTER

8

CONCLUSIONS AND FUTURE WORK

The following presents the key conclusions from this work, followed by a brief summary of the current state of the technology. Finally, future work is proposed from the device and the data perspective.

8.1 Conclusions

8.1.1 Atomic Layer Deposited Tin Dioxide Properties

i The deposition process for ALD SnO₂ (Atomic Layer Deposited tin dioxide) using TDMASn (tetrakis(dimethylamino)tin(IV)) precursor and ozone reactants has been characterized as depositing good quality SnO₂ at a rate of 1Å/cycle.

ii The effects of deposition temperatures (150, 200 & 250°C) on the physical and electrical properties
were investigated. It was determined that deposition at 200°C and below resulted in amorphous films while 250°C deposition showed evidence of rutile phase SnO$_2$. Increasing the deposition temperature increased the carrier concentration and mobility due to crystallization.

iii Annealing temperatures in air (0, 400, 600 & 800°C) were studied for changes in the film properties. Annealing of films at 400°C resulted in crystallization of amorphous films. Increasing anneal temperatures resulted in more well defined crystal structure and decreased the carrier concentration due to more complete oxidation of the film, although films deposited at 150°C showed increased carrier concentration, likely due to oxygen scavenging of carbon from the film during the anneal.

iv The composition of the film is oxygen deficient with a Sn:O ratio in the range of 1:1.8 to 1:1.92 and included carbon impurities whose concentration increased an order of magnitude with decreasing deposition temperature from 250 to 150°C.

### 8.1.2 Gas Response Sensitivity to Ozone and Interfering Gases

The room temperature gas response of the ALD SnO$_2$ films was investigated for low power environmental monitoring.

i Gas response to ozone concentrations from 25-300 ppb (parts per billion) was investigated, emphasizing the 25-100 ppb range, with respect to the physical and electrical properties of the film. Film thicknesses from 3-36 nm were evaluated and it was determined that 6 nm thick films deposited at 150°C and annealed at 600°C provided the strongest response by far. The derivative of the resistance change is correlated to the ozone concentration enabling fast measurement at low temperature.

ii No response was evident to 50 ppm (part per million) carbon monoxide (CO) or 100 ppb nitrogen dioxide (NO$_2$), which are well above typical atmospheric concentrations. Increasing concentra-
tions to 200 ppm and 500 ppb resulted in small response, dwarfed by that of ozone. Addition of platinum nanoparticles enhances CO sensitivity but also enhances O₃ sensitivity significantly more.

iii The optimal thickness was attributed to film dimensions approaching the Debye length, resulting in carrier depletion enhancing the charge transfer signal to noise ratio from ozone ionosorption.

iv Deposition at 150° resulted in increased carbon content and reduced the carrier concentration. This increases the Debye length and enhances the response amplification.

v The optimal anneal temperature is a balance of crystallization and preventing over oxidation during the anneal from reducing the concentration of oxygen vacancies, which are integral to the transducer mechanism involved in gas sensing.

8.1.3 Sensor Recovery and Power Consumption

i Ultraviolet (UV) light was demonstrated as an alternative recovery mechanism to heated sensing films. The mechanism is the excitation of an electron trapped by an ionosorbed gas molecule back to the conduction band.

ii UV energy of 3.06 eV, 3.22 eV and 3.39 eV

iii Power consumption utilizing UV recovery averaged over response/recovery cycles reached as low as 150 µW by optimizing sensor and system level properties.

8.1.4 Impact of Humidity

i Humidity was demonstrated to reduce the Sn₂ surface resulting in increased conductivity due to dissociation of water. The likely mechanisms for different surface conditions were discussed.

ii Oxidizing response of ozone was amplified in humid air due to dissociated water catalyzing ozone decomposition on the SnO₂ surface.
iii The number of dissociated water molecules depends on the water coverage and the number of oxygen vacancies at the surface. The water coverage is a function of temperature and absolute humidity. The ratio of water species to oxygen species occupying the vacancies changes slowly over many response/recovery cycles resulting in slow drift of the response.

iv Fast and slow oxidizing reactions upon exposure to humidity in certain circumstances were discovered. Protons released upon water dissociation may react with each other and/or surface species to form hydrogen gas, hydrogen peroxide or recombine into molecular water, all oxidizing reactions. A sensor stored in dry air with many oxygen species but few hydrogen terminations displays a slow response as protons have the option of bonding to lattice oxygen or consuming surface species. A sensor stored in humid air has both surface oxygen species and hydrogen terminated groups so protons consume the surface species faster, however in ozone the surface species are replenished at the same time, extending the reaction. A heavily reduced surface has nowhere for hydrogen to bond and surface species are consumed very fast.

v Over time, oxygen and water species may build up on the surface despite the appearance of complete recovery. As oxygen atoms from ozone molecules fill vacancies and trap electrons, they add bonding sites for protons from dissociated water. This facilitates additional dissociation and formation of rooted hydroxy groups that may then ionize and donate electrons. In this scenario, two surfaces with different amounts oxygen and hydroxy groups may appear identical from a resistance measurement, but have significantly different ozone decomposition and ionosorption rates.

8.1.5 Sensor Stability

i Sensor response displays minor drift in steady state dry conditions

ii Drift in humid stead state conditions is more substantial
iii Transient humidity levels result in long time constant changes in the response. So far, these changes are not quantitatively predictable.

8.2 Summary

Room temperature operation of SnO$_2$ ultra-thin films has been demonstrated to display resistance changes that correlate with ozone concentration, modified by humidity levels. Over time, exposure conditions cause changes in the reactivity of the sensor surface which have been investigated in this work. Currently, the changes are not quantitatively predictable. Without *ex tempore* knowledge of the reactivity of the surface, only qualitative measures of ozone change relative to previous levels are possible.

Six nm thick films deposited at 150$^\circ$C and annealed in air at 600$^\circ$C were identified as the most sensitive to ozone. However, the sensitivity of the films was stronger than required and from a system and application standpoint, other conditions may be preferable. For instance, Annealing at 800$^\circ$C results in finer crystal structure and more efficient UV recovery which would reduce power consumption. Additionally, thicker films with lower sensitivity will likely display reduced drift in response.

8.3 Future Work

Much remains to be learned about the surface reactions of SnO$_2$. Characterization of the surface reactivity evolution over time with controlled environments would enable predictive models to determine the reactivity by analyzing past data.

The change in work function and electronegativity due surface dipole formation and surface relaxation is very significant as this effects the potential barrier to ionosorption.

From a device perspective, *in situ* Kelvin probe measurements taken simultaneously with conductivity measurements will reveal the magnitude of these effects and enable better prediction of
the reactivity. Additionally, \textit{In situ} Hall measurements to measure carrier concentration, mobility and resistance change during exposure and recovery will also provide valuable information about the nature of the surface reactions with respect to material properties. Decomposition of the resistance signal into exponential functions and evaluation of the time constants of each component in conjunction with the Kelvin probe and Hall measurements will provide detailed information for determining the limiting reactions and reaction rates in different environments. Quartz crystal microbalances could be utilized to determine limits of water adsorption and if ozone exposure promotes water dissociation and allows additional water to adsorb.

From a data perspective, combinations of machine learning and forecasting techniques could prove capable of determining how reactive the surface is based on the time lagged data from humidity and temperature sensors along with the resistance changes from the SnO$_2$ film. With continuous data over long periods of time and using estimated values of ozone in certain low concentration situations, for example at home in the night, a figure of merit for the reactivity could be determined every night that would serve as a coarse calibration. Combined with Internet connectivity, location data and more accurate stationary bay stations located in the home or around a city would further improve the learning and calibration process.

Finally, integration of micro-hotplates to pulse temperatures of 100-150°C could be accomplished with just 3 mW of instantaneous power consumption [66]. Driving this with a 3% duty cycle to drive off physisorbed water would still result in less than 100 $\mu$ of average power and should stabilize the humidity effect and enable further investigation.


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