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Physical and Electrical Characterization of Triethanolamine
Based Sensors for NO₂ Detection and the Influence of
Humidity on Sensing Response

by

Zachariah Marcus Peterson

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science
in
Physics

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ABSTRACT

Triethanolamine (TEA) is a semiconducting polymer which exhibits a resistance change when exposed to various gases. The polymer also exhibits a number of reactions with nitrogen dioxide, with the reaction products being heavily dependent on the presence or absence of water vapor. Previous studies have attempted the incorporation of a TEA-carbon nanoparticle composite as the active sensing layer in a chemresistive sensor for detection of NO_2 . The incorporation of carbon nanoparticles in the polymer nanocomposite was thought to amplify the sensor's response. There are a number of chemical reactions that can occur between TEA and NO_2 , with the reaction products being heavily dependent on the presence and amount of water vapor in the environment. Because of this influence, it becomes necessary to know to what degree the presence of water vapor interferes with the sensing response.

In this work we show that the sensor exhibits a reversible resistance change as background humidity changes. This sensitivity to humidity changes is so large that it renders undetectable any resistance change that could be caused by the reaction of TEA with NO_2 . Furthermore, we show that the presence of low levels of NO_2 do not interfere with adsorption of water vapor. The detection mechanism is based on measuring resistance changes in the TEA film due to the adsorption/desorption of water vapor. The sensing response can be described by Langmuir adsorption by using a site-based model for the polymer film resistance. Breakdown of the polymer film over time due to continuous adsorption of water vapor, as well as photodegradation of the polymer film, will be discussed. SEM images will also be presented showing growth of crystallites on

the electrode walls, as well as experimental results demonstrating degradation of the sensing film during sensor operation.

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CHAPTER 1

INTRODUCTION

Triethanolamine (TEA) is a semiconducting polymer which has been employed as the active layer in a new chemiresistive sensor for detection of nitrogen dioxide (NO_2). The polymer is in liquid state at STP, and exhibits specific adsorption/desorption reactions with various gases. The polymer also exhibits a number of chemical reactions with NO_2 , and one of these reactions has been used to develop passive diffusion based sensors for measurement of large scale NO_2 concentrations. Dinitrogen tetroxide (N_2O_4) has also been suggested as a participant in a separate reaction with TEA to form nitrate and nitrite. [1]

Currently, numerous solid-state devices are used for accurate monitoring NO_2 at high concentrations (10-100 ppm). [2, 3] The current EPA-approved chemiluminescence equipment is capable of measuring NO_2 with sensitivity of 1 parts-per-billion by volume (ppb). These instruments detect photons emitted from NO_2 as a result of the reaction between NO and O_3 , and uses the reaction to distinguish between NO_2 and NO . However, these instruments are expensive, heavy, require auxiliary equipment, and use ~230 W of power. This allows accurate monitoring of NO_2 on large spatial scales at only a small number of monitoring sites, thus increasing the reliance on modeling to determine the local spatial distribution of NO_2 . This situation increases the need to develop cost-effective monitoring equipment in order to meet regulatory standards.

In the 1970's, a passive sensor was built which attempted to monitor the reaction between NO_2 and TEA on large time scales. NO_2 in the air is allowed to react with TEA

by diffusing through air in a cylindrical tube into the TEA film, and the concentration of nitrite among the reaction products is measured with a spectrophotometer. [4] Glausius later determined the reaction products using mass spectrometry. [5] The presence of water vapor in the ambient environment greatly influenced the overall stoichiometry of the reaction, as well as the amount of nitrite present in the reaction products. [1, 4, 5]

Aoyama and Yashiro (1983) later detected N-nitrosodiethanolamine (NDELA) among the reaction products when the reaction was allowed to take place in dry air. In this reaction, N_2O_4 was thought to play a significant role. [1] A chemiresistive sensor was recently developed by Meka et. al [6] which used TEA doped with carbon nanoparticles as the active sensing layer with the intent of measuring the reaction progress and the formation of NDELA electronically. The resistance of the sensor decreased over time when the sensor was exposed to NO_2 mixed with dry air, and it was observed to be sensitive down to ppb levels. This study has been the first attempt to replicate this data.

The sensor prototype is compact, inexpensive, has simple circuitry, and has the capability of being integrated into handheld devices, making it a viable candidate for detection of NO_2 . However, as it has been confirmed that water vapor greatly influences the products generated in the reaction between NO_2 and TEA, it becomes desirable to know to what degree ambient humidity interferes with the sensing response to NO_2 .

The purpose of this report is to characterize the new sensor introduced by Meka et. al. [6] which uses TEA doped with nanoparticles as the active sensing layer. Since it is known that the presence of water vapor can influence reactions between NO_2 and TEA, it also seemed important to determine how water vapor interferes with the electrical sensing response to NO_2 . Sensors based on TEA doped with carbon nanoparticles were developed

to study the effect of humidity on the sensitivity to NO₂. Sensing response data will be presented for sensors exposed to different combinations of humidity and NO₂ gas. A number of models for describing the sensing response will also be presented. SEM images will be presented showing the nanocomposite film morphology as well as a comparison of used versus unused sensors.

CHAPTER 2

INTERACTIONS BETWEEN GASES AND THIN FILMS IN SENSORS

The first step in detection of gas species in thin film sensors is typically adsorption of the analyte onto the film surface. Following adsorption, the interaction between the adsorbed species and the sensing species can take place. Sensors based on conducting polymers for detection of a specific species can have weak interactions with other gases in the ambient environment which can interfere with detection of the intended gas species. These interactions may involve surface adhesion of the analyte to the film surface, swelling of the sensing layer, or other effects. In some sensors, these interactions can be so powerful that they can mask the sensing response to the intended species. [7, 8]

2.1: Physisorption and Chemisorption in Gas Sensors

Physisorption is the first step of the association of the gas species with the sensing layer, which is an exothermic adsorption process which is mediated by Van Der Waals forces. [9] Depending on the combination of sensing layer material and adsorbed analyte, chemisorptions can occur. Chemisorption involves exchange of electrons between the adsorbed species and the sensing layer, and is an endothermic process. Chemisorption requires some activation energy to occur, be it thermal, photonic, or energy from some other source. As a result, physisorption dominates at low temperatures and chemisorption is dominant at high temperatures. The sensing characteristics of some gas are closely related with chemisorbed water vapor and oxygen; adsorbed oxygen can affect the concentration of oxygen vacancies. In metal oxides and solids, fluctuations in the

concentration and the charges of oxygen vacancies can interfere with the expected sensing response. [8, 10]

2.2: Langmuir Adsorption in Gas Sensors

Reversible adsorption of target gas molecules into the sensing film surface has been widely interpreted as the sensing mechanism in many reversible sensors. Langmuir adsorption is a model used to describe a chemical equilibrium between the number of gas analyte molecules adsorbed on the sensing film surface, the remainder of the analyte molecules in the surrounding environment, and the number of vacant adsorption sites. The equilibrium is based on a reversible process described by the following equation:

In the above equation, $\mathbf{A}$ is the analyte gas, $\langle \text{site} \rangle$ is an unfilled adsorption site, and $\langle \mathbf{A} \rangle$ is an adsorption site that has been filled with a molecule of species $\mathbf{A}$; let K_{eq} be the equilibrium constant for the adsorption process in equation 1. [7]

Bartlett, et. al., has shown that the Langmuir adsorption process in gas sensors can be derived from simple diffusion. Their derivation assumes that the sensor configuration consists of a thin uniform polymer film of thickness L lying on top of a pair of coplanar electrodes deposited on an insulating substrate. A schematic is shown in figure 1-a below. They also derived a modified diffusion equation in dimensionless form governing the adsorption process, as shown in equation 2.

$$\frac{\partial^2 \gamma}{\partial \chi^2} - \frac{\partial \gamma}{\partial \tau} = \frac{\eta}{\lambda} \frac{\partial \theta}{\partial \tau} \quad (2)$$

In equation 2, χ is the dimensionless distance parameter (x/L), τ is the dimensionless time parameter (Dt/L^2 ; D = Diffusion coefficient), γ is the normalized gas concentration (a/a_∞), and a_∞ is the external gas concentration. λ and η which depend upon material properties such as the equilibrium constant K_{eq} and the density of sites N . The rate of change of occupied adsorption sites in the sensing film, θ , is also governed by the following sorption kinetics equation:

$$\eta \frac{\partial \theta}{\partial \tau} = \kappa \lambda \gamma (1 - \theta) - \kappa \theta \quad (3)$$

Here, κ is a parameter which is equal to the ratio of forward reaction-rate to diffusion-rate, ($k_f N L^2 / D$). This system of equations can be solved to obtain the normalized adsorbed gas concentration, $\gamma(\chi, \tau)$, and the site occupancy concentration, $\theta(\chi, \tau)$, under a variety of limiting cases and boundary conditions (see [11] and [12] for a full treatise). [7, 13]

Figure 1: a) Device configuration investigated by Bartlett to investigate adsorption of analyte molecules on the film surface. b) Equivalent sensing film circuit developed by Hwang and Lin. [7]

Bartlett's equations are too complex to be directly applied to understanding the sensing response in the dynamic case, and there are other theories which connect surface adsorption with the sensing response based on Langmuir adsorption. The equilibrium (steady-state) case was studied by Hwang and Lin, who developed an equivalent circuit

for the sensing film; the circuit is shown above in figure 1-b. The overall film resistance can be thought of as n conductive layers, with each layer consisting of m adsorption sites. Empty sites have resistance r_0 , and filled sites have resistance r_1 , and the concentration of occupied sites can be determined by taking the limit $t \rightarrow \infty$ in equation 3. Solving for θ and given that each film layer has resistance $m(1-\theta)r_0 + m\theta r_1$, the sensing response when the film is exposed to gas concentration C_0 is given by equation 4:

$$\Delta R_t = (r_1 - r_0) \frac{m}{n} \frac{K_{eq} C_0}{1 + K_{eq} C_0} \quad (4)$$

K_{eq} is the equilibrium constant for the equilibrium in equation 1. Typically, the surface coverage is defined in terms of the gas pressure P , however, one can easily convert gas pressure into gas concentration. Upon exposure to an adsorbing species, the direction of resistance change (either positive or negative) depends upon the quantity $(r_1 - r_0)$; the quantity is just difference between the resistance of a filled and unfilled site. This equation has been used to explain many experimental results observed during experimentation of gas sensors. [7, 14] If we define a new constant $\beta = (r_1 - r_0)(m/n)$, and invert equation 4, one can obtain a linear equation relating the resistance change and concentration:

$$\frac{1}{\Delta R_t} = \frac{1}{\beta K_{eq} C_0} + \frac{1}{\beta} \quad (5)$$

The equilibrium constant can be determined by plotting experimentally measured values of $1/\Delta R_t$ versus $1/C_0$ and determining $1/(K_{eq}\beta)$ from the slope and $1/(\beta)$ from the y-intercept. It is also common practice to multiply equation 5 by R_0 (the resistance at zero gas concentration), which allows one to plot change in sensitivity versus gas concentration. Equation 5 is then only modified by simply taking the product of the

constant R_0 with the other constant $1/\beta$, which can then be redefined as a new constant, say, $\beta^* = \beta/R_0$. [7]

One of Langmuir's original assumptions on the nature of adsorption is that gas molecules only adsorb into a single molecular layer. In his original paper on adsorption he writes: *Molecules striking a surface already covered also condense but usually evaporate much more rapidly than from the first layer. Hence except when the vapour is nearly saturated, the amount of material adsorbed on a plane surface rarely exceeds that contained in a layer one atom (or molecule) deep.* [15] Hence in our above model, we can assume the constant $n \sim 1$; there is no effect on the formulation of the equilibrium constant and equations 4 and 5 are still valid.

Equations 4 and 5 only apply to gases which do not require dissociation in order to be adsorbed, however the Langmuir model readily extends to dissociative adsorption with little modification. In dissociative adsorption of a homonuclear polyatomic molecule of order i , A_i , equation 1 must be modified to include i as the stoichiometric coefficient for the $\langle \text{site} \rangle$ and $\langle A \rangle$ terms. As a result, the equilibrium constant becomes proportional to θ^i and $(1-\theta)^{-i}$. To determine the equilibrium constant in this case, a plot of $1/\Delta R_t$ versus the i th root of $1/C_0$ and interpolating the slope and y-intercept just as in the case of adsorption without dissociation. [9]

2.3: Important Parameters in Gas Sensors

There are a number of parameters that are important in characterizing any gas sensor, and the parameters are specific to the target analyte, detection method, and materials used in sensor fabrication. For sensors which lack selectivity to the target

analyte, concentration of any background or potentially interfering gases becomes an important parameter in characterizing the sensing response. Some sensors only have stability over short time scales, due to degradation of the active layer when left in some environments. [7] Since the conductivities of some sensing materials are directly related to stoichiometry, material defects can play a large role in characterizing sensors. Adsorbed water or oxygen on the sensing material surface can also drastically alter the sensing response, thus humidity and oxygen content of the background gas become important parameters. [8]

The four important parameters for characterizing any conductometric sensor are sensitivity, response and recovery time, and limit of detection (LOD). The definition of sensitivity depends on whether the compound to be measured is an oxidizing or reducing gas. For oxidizing gases, sensitivity is defined as the ratio of the device's resistance when exposed to target compound to that in ambient air, R_g/R_a (where R is resistance, the subscript 'g' represents target gas, and 'a' represents ambient air); if the target species is a reducing gas, it is defined as G_g/G_a (G is conductance). [7, 8] Response time is defined as the elapsed time required for the device resistance to change from 10% to 90% of the value in equilibrium upon exposure to the species of interest. Recovery time is defined as the time required for resistance to go from 90% to 10% of equilibrium resistance value when the target species is removed from the sensor environment. Typically, the LOD is determined experimentally, although according to its definition, the approximation of LOD is done via extrapolating the R_g/R_a versus concentration curve to $3\sigma/R_a$ (σ is the standard deviation of R_a). [8]

Stability is another important parameter in characterizing gas sensors, especially in sensors which employ a polymer as the active layer. All polymers undergo degradation processes which occur on different time scales; thus the distinction between a degradable and non-degradable material is arbitrary. The process of ‘degradation’ typically results from the alteration of bonds, for example bond cleavage – during which polymer chains are cleaved to form oligomers and finally to form monomers. ‘Erosion’ refers to the loss of material owing to monomers and oligomers leaving the polymer bulk. Polymers can degrade by photo, thermal, mechanical, chemical, or even ultrasonic processes; enzymatic reactions become very important in biological systems. All polymers exhibit marked degradation when illuminated with UV light or γ -rays. Uptake of water vapor by passive hydrolysis can also cause degradation in hydrophilic polymers; however, the degradation rate is determined mainly by the type of bond within the polymer backbone. [16] With all of these processes taken into consideration, it becomes important for the present study to determine if and how TEA degrades during use as the active layer in a sensor.

CHAPTER 3

NITROGEN OXIDES

NO₂ is an air pollutant produced by a number of anthropogenic processes (i.e. combustion). NO₂ forms an equilibrium mixture with N₂O₄ according to the following equilibrium equation:

Higher temperatures push the equilibrium more towards higher NO₂ levels. This means that N₂O₄ will inevitably be present in smog containing NO₂. [17] Previous studies have shown that high levels of NO₂ in the environment can cause harm to human health and ecosystems. [18-22] Air quality regulations regarding atmospheric NO₂ levels have created the need for new cost-effective monitoring systems which can be deployed over large areas.

Following passage of the Clean Air Act in 1963 by the United States, the Environmental Protection Agency was established in order to monitor and regulate a number of pollutants and harmful compounds. The EPA has set specific standards on six areas of air quality: ozone (O₃), particulate matter, carbon monoxide (CO), sulfur oxides (SO_x), nitrogen oxides (NO_x), and lead (Pb). [22] As a result, numerous sensors and detection methods have been developed for determining NO₂ concentrations.

3.1: Detection of NO_x by Chemiluminescence

The EPA's current "gold standard" for measuring NO and NO₂ is a chemiluminescence instrument such as the Thermo Environmental Instruments Model

#42C. The instrument has the ability to distinguish between NO and NO₂ with very high accuracy. The instrument detects photons that are emitted as products of the following reaction:

While sample air is continuously pumped into the instrument, it first measures the amount of NO by measuring the intensity of light produced from the reaction between NO and ozone. Next, the instrument runs the sample air through a high temperature apparatus to break two NO₂ molecules in the sample flow to two NO and one O₂ molecule. The sample of NO plus converted NO₂ (called NO_x) is then measured for NO content. The amount of NO_x minus the amount of NO yields the concentration of NO₂ in the sampled air. The sensitivity and selectivity of these instruments are very good although significant chemical interferences have recently been identified for NO₂ in urban environments. [23]

3.2: Detection of NO₂ by Reaction with TEA

Numerous reaction schemes have been proposed governing the reaction between TEA and NO₂. Palmes, et. al., were the first to investigate the diffusion of NO₂ into an absorber film through cylindrical tubes for use as a personal monitor for workplace NO₂ concentrations. This was soon developed into a simple monitoring device. A schematic is shown in the figure below:

Figure 2: Diagram of the Palmes diffusion tube. [18]

NO_2 in air diffuses into the cylindrical tube and is absorbed by the TEA film. For a cylindrical tube with a diameter d and length l , and with a perfect absorber at one boundary, Fick's first law can be used to calculate a theoretical sampling rate (the rate of net flow of a gas through the tube) as:

$$F = -D \cdot \pi d^2 / 4l \quad (8)$$

Where F is the sampling rate ($\text{m}^3 \text{s}^{-1}$) and D is the diffusion coefficient of NO_2 in air ($\text{m}^2 \text{s}^{-1}$). [1] Palmes and his colleagues made numerous theoretical assumptions regarding which they outline in detail in their original publication. The most important assumption they made regards the efficiency of the absorbent medium, which they assumed to be very close to 100% due to lack of evidence to the contrary. [1, 4] These samplers are cost effective and accurate down to ppb levels, although the major drawback to these sensors is that they need to be exposed to ambient air for weeks at a time. Typical studies use 2 or 4 week exposures, during which time NO_2 diffuses into the TEA film to form nitrite. The amount of nitrite in the film is then measured by absorption spectroscopy. [4, 5]

A “lab-on-a-chip” device has also been developed for NO_2 detection at levels under 100 ppb which uses a similar spectrophotometric method. A small piece of quartz glass acts as the substrate and contains small channels which are injected with a TEA solution in water. In this device NO_2 absorbs into the sensing channel through a porous glass plate and reacts with TEA. The mixture is then reacted with 2,3-diaminonaphthalene (DAN) in acidic solution to produce the fluorescent species 1H-naphthotriazole (NTA). NTA is then excited with 370 nm light from a UV-LED to produce fluorescence. [24]

For some time, it was only known that the reaction between NO_2 and TEA produced nitrite, among other compounds. Perhaps the most important observation made by Palmes and his colleagues is the 1 to 1 conversion ratio between NO_2 and nitrite ions in moist air. [4] Aoyama and Yashiro (1983) detected N-nitrosodiethanolamine (NDELA, chemical formula $\text{NO}-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$) among the reaction products between NO_2 and TEA in dry air. [8] However, TEA-nitrate and TEA-nitrite ions were identified as the major reaction products in a subsequent study, with N_2O_4 suggested as a reactive intermediate, yielding a conversion ratio for both NO_2 :nitrite and NO_2 :nitrate of 2 to 1. [1]

It was the intent of Meka et. al. [6] to detect the progress of the reaction forming NDELA electrically rather than spectroscopically. This was attempted by fabricating a thin film chemiresistor from TEA doped with carbon nanoparticles on a printed circuit board (PCB) substrate with interdigitated electrodes. It was argued that the addition of carbon nanoparticles to the mixture supposedly increased the sensitivity. While there

were some results published, the effect of humidity on film resistance was not investigated experimentally.

TEA and NO₂ react in solution as well, with the reaction products depending on the solvent used. Mixing gram quantities of NO₂ and TEA in water produces equimolar amounts of NO₂⁻, NO₃⁻, and dissociated TEA. Similar results can be obtained with other polar solvents. At temperatures lower than -5 °C, the reaction between TEA and NO₂ in a polar solvent other than water produces the nitroso-ammonium salt ⁻O₃N⁺ON—N(CH₂CH₂OH)₃. [1]

During a study of nitrogen dioxide concentrations in Denmark, Glasius, et. al. [5] identified different reaction products when TEA and NO₂ are allowed to react in humid air. They proposed the following reaction scheme between absorbed NO₂ and disassociated TEA to form TEA N-oxide and nitrite:

Hydroxyl-ions in the reaction are present due to the dissociation of TEA in water, and this reaction will therefore not take place in completely dry air. This is supported by the observations from Palmes and Johnson. One possibility for the dissociation of TEA is that the TEA film adsorbs some water vapor when exposed to humid air. The reaction in Eq. 9 was performed experimentally and measured with a gas chromatograph-mass spectrometer, which showed a peak with molar mass of 166. This can only be explained by the presence of TEA N-oxide as a reaction product. [5] The conversion ratio from NO₂ to nitrite was found to be 2 to 1 in this case. If a large amount of water is present in the TEA film due to improper drying, this reaction will inevitably take place. [1] A summary of these reactions is listed in table 1.

Rxn	Reactants	Products
1	TEA, 2NO ₂ , and 2OH ⁻ (moist air)	TEA N-oxide, H ₂ O, and 2NO ₂ ⁻
2	TEA, N ₂ O ₄ , and 2NO ₂ (dry air)	NDELA, TEA-nitrate, and TEA-nitrite
3	TEA in water solution and 2NO ₂	Dissociated TEA, NO ₃ ⁻ and NO ₂ ⁻ in water solution
4	TEA in other solvent and NO ₂ (at < -5 °C)	Nitroso-ammonium salt

Table 1: List of possible reactions between TEA and NO₂.

In this study, the goal is to have a sensor which can detect NO₂ electrochemically as well as be deployed in an urban environment. Most urban environments in the United States will be somewhat humid, and it is most likely that reaction 1 will occur. Because the presence of water vapor has been demonstrated to have considerable influence on the TEA-NO₂ reaction products, it becomes necessary to see if water vapor interferes with the electrical response to NO₂.

3.3: Metal Oxide Nanostructure Sensors for NO₂

In recent years, vapor phase sensing of chemicals using various nanostructures has attracted much attention, and many materials and devices have been adapted for high sensitivity to NO₂ gas. Some of these materials are sensitive to other vapor phase analytes, making them less desirable as a standalone NO₂ sensor. Sensors with an active layer made of metals or metal oxides have shown good sensitivity, as well as limits of detection down to the ppb level. NO₂ sensors based on other carbon nanocomposites and carbon nanotubes have shown NO₂ sensitivity as well.

Gas sensors for NO₂ have been developed based on a wide array of metal oxides, however a large amount of attention has been paid to research into the potential of using

metal oxide nanowires as an active sensing layer due to the large surface area to volume ratio of these structures. Most research into metal oxide nanowire/nanobelt sensors has been confined to ZnO, V_2O_5 , and SnO_2 nanosensors, with ZnO receiving much of the attention. [25] Because of the high electronegativity of the nitrogen atom in the NO_2 molecule, NO_2 is an oxidizing gas, and is expected to accept electrons from the active layer as the gas adsorbs on the surface. In general, if the active layer is an n-type material, the conductance should decrease on exposure to NO_2 , and conductance should increase for a p-type material. The reverse should happen upon exposure to a reducing gas, provided that a gas molecule of that species has the capability to adsorb on the surface. [8] However, depending on the material, there may be other interactions simultaneously taking place within the sensing layer, and the expected change in conductance may not always take place.

Non-stoichiometric tungsten oxide ($W_{18}O_{49}$, n-type semiconductor) nanowires have demonstrated good sensitivity to high concentrations of NO_2 . These sensors were deposited on a Si wafer substrate which was fabricated by using a microelectromechanical system (MEMS). Exposure of these nanowires to 3 ppm NO_2 gas in dry air and nitrogen atmospheres at room temperature resulted in a resistance increase of 12.6% and 14.0% respectively. Although these sensors have good sensitivity to NO_2 , they have no specific selectivity and only exhibit good sensitivity at high concentrations, making them an unattractive choice for a standalone sensor for environmental monitoring. At room temperature, resistance increases were also observed when the sensor was exposed to 1000 ppm ethanol and 10 ppm NH_3 vapor. At temperatures of 150-250 °C, a resistance decrease was observed over time when exposed to NH_3 . [26]

Tin dioxide (SnO_2 , n-type semiconductor) nanowires have been adapted as the active layer in sensors for detecting a number of gases, including NO_2 . SnO_2 nanowires in field effect transistors have also been shown to act as oxygen sensors, and they exhibited a dramatic increase in sensitivity to oxygen and hydrogen when doped with Pd nanoparticles. [25] Measurement of NO_2 concentrations can be carried out using a photochemical method at room temperature for high NO_2 levels. Individual single-crystalline SnO_2 nanowires were developed into a photochemical NO_2 sensors that could operate at room temperature, and it has been calculated from first principles that SnO_2 nanowires with exposed (1 0 -1) and (0 1 0) surfaces would be the most effective. [27] These sensors can detect ppm-level concentrations of NO_2 at room temperature under UV illumination (365 nm light) with resolution of 3 ppm. The SnO_2 layer is bombarded with UV light and emits a luminescence spectrum. The intensity of photoluminescence is reduced with increasing NO_2 concentration. [28]

At high temperatures, many metal oxide thin films and nanostructures exhibit a conductivity change when exposed to either oxidizing or reducing gases, with materials showing much better sensitivity than others. Both SnO_2 and ZnO (both n-type semiconductors) nanowire films have been shown to reduce their conductance on exposure to NO_2 . [25] SnO_2 nanowire films showed a 900% resistance increase when exposed to 200 ppb NO_2 at 300 °C. [29] ZnO nanowire films were not as sensitive, showing only 14% increase in resistance when exposed to concentrations as high as 5 ppm NO_2 at 300 °C. [30] ZnO nanowires have also been incorporated into field effect transistors which are sensitive to both NO_2 and NH_3 at room temperature, although at ppm concentrations (40-1000 ppm for NH_3). [31]

Single and multiple indium(III) oxide (In_2O_3 , n-type semiconductor) nanowires have been demonstrated to change their conductivities when exposed to NO_2 gas down to the ppb level. In_2O_3 nanowires were deposited onto a Si/ SiO_2 substrate and gold electrical contacts were patterned and deposited using photolithography. Single nanowire sensors have detection limit of 20 ppb, while devices using multiple wire arrays have detection limits down to 5 ppb. [14] The sensing response of these sensors was accurately described using the Langmuir adsorption model. These sensors are at a distinct advantage to other metal oxide sensors in that they can operate at room temperature. [14]

Sensing material	Detection range NO_2	Operating temperature	Interference sources	Refs.
$\text{W}_{18}\text{O}_{49}$ nanowires	>3 ppm	Room temp.	O_2 , ethanol, NH_3	[26]
SnO_2 nanowire arrays	>200 ppb	300 °C	CO , H_2 , water vapor, H_2S , ethanol, NH_3	[25, 29, 32, 33]
ZnO nanowire arrays	10-5000 ppm	300 °C	NH_3 , ethanol, water vapor, O_2	[25, 30, 31]
ZnO nanowire FETs	1-20 ppm	Room temp.	NH_3 , O_2	[25, 31]
In_2O_3 nanowires	>5 ppb	Room temp.	H_2S , ethanol	[8, 14]

Table 2: Summary of solid-state NO_2 sensors based on metal oxide nanostructures.

CHAPTER 4

EXPERIMENTAL METHODS AND RESULTS

4.1: Sensor Construction

A stock solution of 10% TEA (98%, Sigma-Aldrich, St. Louis, MO), 1% CNPs (99% graphene, Sigma-Aldrich, St. Louis, MO), and 0.0001% Brij-35 surfactant (Sigma-Aldrich, St. Louis, MO) was prepared (in water). The CNP diameter measured ~ 50 nm average, determined by TEM analysis. The surfactant was added to improve nanoparticle and TEA dispersion. It creates a wetting layer on the substrate, resulting in a more viscous film. [6, 34] A circuit board with an interdigitated microelectrode array containing 20 fingers functioned as the electrode array. It was printed on an insulating nanocomposite substrate. The array was fabricated using standard manufacturing techniques with electrodes fashioned from a copper-aluminum alloy. The interdigitated electrodes measured 200 microns across with 420 microns in between each finger. This printed circuit board array is a standard design which allows for the continuous measurement of the resistance of a variety of thin films.

A small amount of solution was drop coated onto the substrate while the substrate lay on a hot plate; the hot plate temperature was maintained at ~ 100 °C. The film was allowed to dry on the hot plate for no longer than 10 minutes. Following the drop coat, the sensor was placed in a vacuum desiccator for ~ 24 hours to ensure that all of the water solvent has been evaporated. The average film thickness was calculated based on the amount of solution deposited onto the substrate; our sensors used films between 2 and 4

microns. Our sensors typically had resistance in the high kilo- Ω to mega- Ω range when first fabricated. A schematic of the sensor prototype can be seen in figure 3.

Figure 3: a) Picture of printed circuit board substrate with interdigitated electrode array. b) Schematic diagram showing the configuration of TEA and CNPs in between electrode fingers. [6]

4.2: Experimental Setup

Sensor prototypes were analyzed in a spherical 200 L glass environmental chamber where NO_x concentration, temperature, pressure, and relative humidity could be carefully controlled and monitored. NO_x concentration was measured using the standard air quality monitoring equipment (Thermo Scientific, Model 42C Trace Level NO- NO_2 - NO_x Analyzer, Waltham, MA). Temperature and relative humidity data were collected with a temperature/relative humidity (RH) combination probe. The NO_x analyzer sample rate was maintained internally at ~ 1 litre per minute. A Keithley 195A digital multi-meter was used to measure the resistance of the sensor; the device restricts current in the sensor during resistance measurements to be between 2 and 4 μA DC. All resistance, concentration, and environmental measurements were connected to an analog to digital converter (ADC), which was connected to a PC.

The sensor is placed in the environmental chamber which can be filled with a variety of gases. All air and gas inlet flow rates were maintained using a set of Tylan FC 280 mass flow controllers (MFC). Clean air was produced from compressed ambient air passed through a laboratory-constructed Purafil/Activated Charcoal/Molecular Sieve filtration pack, and the resulting mix was free of hydrocarbons and oxidizing gases. The pure air could be humidified by running it through a sealed Erlenmeyer flask containing pure water, or this step could be bypassed for experiments involving dry air.

Figure 4: This figure shows the experimental setup. The test bed consists of a glass chamber where the samples are tested, a chemiluminescence trace gas analyzer for verifying gas concentration, and a DMM for monitoring sensor resistance. Modified with permission from Meka et. al. [6]

Experiments were performed where we attempt to detect ppm levels of NO_2 diluted with nitrogen while the sensor was held at low current levels. In order to prevent resistance changes in the sensing film due to current flow through the film, experiments were performed with the current in the sensor regulated at the nano-amps level. In these experiments, we use a different experimental setup with a smaller gas chamber and different NO_2 source. Sensor prototypes were analyzed in a 2 liter glass chamber while

NO_x concentration was measured using the standard air quality monitoring equipment (Thermo Scientific, Model 42C Trace Level NO - NO_2 - NO_x Analyzer, Waltham, MA). The NO_x analyzer sample rate was maintained internally at ~ 1 litre per minute. Current in the sensor was maintained at 10 nA using a Keithley Model 220 programmable current source. Sensor resistance was determined by measuring the voltage drop across the sample, and the resistance was then calculated using Ohm's Law; voltage drop measurements were taken with a Keithley 196 digital multi-meter. The calculated resistance and gas concentration measurements were gathered on a PC using LabVIEW software. The NO_2 source used in these experiments was a gas permeation tube device purchased from Dynacal. A permeation tube device is an inert capsule containing a pure chemical compound in two phase equilibrium between its gas phase and its liquid or solid phase. At a constant temperature, the device emits the compound through a permeable window at a constant rate. The device needs to be above room temperature to begin emitting NO_2 gas, and the temperature of the device was controlled with an oven and a thermostat. The oven was modified with gas inlet and exhaust lines going into the oven; inside the oven these lines are connected to a metal housing containing the NO_2 capsule. The entire apparatus is then heated in the oven to establish high enough temperature for NO_2 gas to begin emitting from the capsule. Our capsule had a listed operating temperature of 50°C . The NO_2 gas can then be diluted to the desired concentration by flowing nitrogen through the metal housing containing the NO_2 source.

Figure 5: Experimental setup used for low current experiments. A regulated current source supplies current to the sample located inside the test chamber, and the voltage drop across the sample is measured with a voltmeter.

4.3: Experimental Procedures

These sensors were exposed to a variety of environments; all sensors that were used in this study were desiccated for 24 hours and immediately connected to the test circuit for experiment. Pressure was monitored and kept near ambient by keeping an open exhaust valve connected to the chamber, and the ambient temperature during all experiments was measured to be between 18 and 20 °C. For introduction of NO₂, gas of 19.9 ppm concentration (nitrogen balance) was diluted with either the dry or humidified air, and the concentration of the inlet gas mix was controlled by maintaining the respective gas flow rates and analyzer sampling flow rate.

It was found early on that water vapor in the air can greatly affect the resistance of the sensor by adsorbing/desorbing from the TEA film. Experiments were performed where a sensor was transferred between lab air (at 40% RH) to higher or lower humidity

environments in the test chamber, and the sensing response was monitored. Response/recovery times were calculated.

Since we know that the sensor exhibits resistance changes when humidity changes, we need to determine if NO_2 can be detected in the presence of water, and how the presence of NO_2 interferes with water vapor. The following experiments were devised to see if NO_2 can be detected by measuring changes in resistance and the H_2O adsorption equilibrium constant, and to see if these changes correlate with NO_2 levels. Before placing a sensor in the chamber, the environment in the chamber was created. NO_2 levels were maintained inside the chamber under low humidity by pumping NO_2 diluted with dry air before a sample was placed in the chamber. Samples spend a small amount of time in lab air ($\sim 40\%$ RH, ~ 40 ppb NO_2) as they travel between the desiccator and the test chamber. When the sample is placed in the chamber, we begin monitoring the sensor response and wait as the sample is allowed to reach equilibrium with the atmosphere in the chamber. Once equilibrium is reached between the sensor and the environment, NO_2 diluted with humid air is pumped into the chamber instead and the humidity begins to increase. As the humidity increases, the sensing response is monitored. These experiments typically take 3 to 5 hours. Measured resistance values in these experiments were normalized by the resistance value at 40% humidity. This method allowed us to produce normalized resistance versus RH% curves at various concentrations, and these curves are easily reproduced at low NO_2 concentrations (~ 20 ppb). Sensitivity data from these experiments were also plotted linearly according to Langmuir isotherm using equation 6, and the equilibrium constant between water vapor and the TEA/CNP films

determined. From these experiments, we wish to see if the presence of NO_2 interferes with the adsorption of water vapor, and if the interference correlates with NO_2 levels.

Another set of experiments were performed for determining whether or not the sensing film exhibits a consistent resistance change from exposure to NO_2 in humid air. Sensors were allowed to age undisturbed (with resistance measurements off) in the gas chamber under various environmental conditions. A new desiccated sensor was taken and placed in the environmental chamber and left there for 24 hours. During this time, the atmosphere in the chamber was maintained at 40% RH with fixed NO_2 levels. After 24 hours, NO_2 and water vapor were pumped out of the chamber down to background NO_2 levels (~ 5 ppb). Next, humid air was pumped into the chamber and the sensor response was monitored as the humidity level was allowed to rise. Resistance versus humidity curves for un-aged samples were compared to samples aged at various NO_2 levels.

Experiments to detect NO_2 in nearly dry air were also performed. First, clean dry air was pumped through the chamber for a day to remove NO_2 , NO , and water vapor from the environment. The sensor was placed in the chamber and the sensor was monitored in the environment while dry air was pumped through the chamber. After some time, NO_2 gas was pumped into the chamber and the concentration was allowed to rise to the intended level while the sensing response was monitored. In these experiments, NDELA should form in the TEA film when exposed to NO_2 . We expect to see results similar to those reported by Meka et. al.: on exposure to NO_2 we expect to see a resistance.

Experiments were also performed where we attempt to detect NO_2 diluted in nitrogen while the current in the sensor was held at nano-amp levels. The setup in figure

5 was used and the current was maintained with the Keithley 220 current source as described above. In preparation for these experiments, any gases present in the environmental chamber are evacuated and replaced with nitrogen three times. The test sensor is placed in the chamber before evacuation and is allowed to come to equilibrium with the environment. After evacuation, the current source is switched on and the sensor resistance is allowed to come to a plateau. Once the resistance reaches a plateau, the sensor is exposed to NO_2 from the permeation tube device and the sensing response is monitored. Similar to the previous experiments with dry air, NDELA should form in the TEA film when exposed to NO_2 and we should see a resistance decrease on exposure to NO_2 .

4.4: Sensitivity to Humidity Changes and Aging

Changing the humidity in the sensor environment from 13% to 41% relative humidity resulted in a resistance decrease of 44.7%. The resistance change was observed to be reversible; increase in humidity resulted in decrease in resistance, and vice versa. The NO_2 concentration in both environments was measured to be 40 ± 5 ppb. Response/recovery times for this experiment were measured to be 59 ± 9 seconds.

Figure 6: Graph showing change in sensor resistance with humidity changes.

On much longer time scales, the sensor exhibits a continuous resistance increase when placed in a dry environment with low NO_2 concentration. The sensor resistance was measured while the environment in the chamber was supplied with nearly dry air. NO_2 concentration in the chamber was measured to be 18 ± 5 ppb. The sensor resistance and relative humidity in the chamber versus time are shown in the figure below:

Figure 7: Graph showing resistance change over large time scales due to a currently unidentified chemical process. NO_2 concentration in the chamber was 18 ppb.

After 48420 seconds (13.5 hours), the resistance was found to have increased from 2.9 MΩ to 20 MΩ. When the sensor is initially inserted into the environmental chamber, some humid air from the lab flows into the chamber through the open bulkhead, which is why the graph starts with a higher humidity level near $t = 0$. As time progresses, the humidity decreases and eventually stabilizes near 1.75 % at ~25000 seconds (7 hours), during which time we see a resistance increase. However, after 7 hours the humidity is nearly constant, and a resistance increase is still observed over time. The resistance continues increasing from 12.2 MΩ and eventually the resistance exceeds the maximum DMM output of 20 MΩ; the average rate of change was calculated to be 333 Ω/second.

The continuous resistance increase of the sensing film under nearly constant humidity is evidence of another chemical process occurring between the sensing film and the environment, possibly photo- or thermally induced degradation. [16]

An experiment was performed attempting to determine if resistance changes were also induced by ultra-violet illumination. A prototype sensor was placed in a Dentlite ultraviolet light chamber with UV-A range bulbs and the sample was allowed to come to equilibrium. UV light was pulsed for 30, 60, and 120 second durations while the resistance was monitored in-situ. Sensor response to the application of UV light is shown in the figure below.

Figure 8: Resistance vs. time as UV-A range bulbs illuminate a prototype sensor. Green arrows mark the time when the light is switched on, and red arrows mark the time when the light is switched off.

In the above graph a resistance increase over time can be seen when the UV lamp is turned on (denoted by the green arrows in the above figure), and rate of change falls close to zero (and can even become negative) when the lamp is switched off (denoted by red arrows). The resistance increase in this case is thought to occur because the incident high

energy photons have the ability to cause bond alterations, probably scission, in polymers.

[16]

Table 3 shows a summary of these results. Sensors that are connected to the DMM and are in operation exhibit a continuous resistance increase over time; after 24 hours of continuous operation causes the resistance increases by a factor of 2.7. Sensors left connected to an open circuit do not see such resistance changes, and illumination with visible range light does not seem to have an effect on the sensor resistance. Illumination of the sensor with UV light while it is operational causes an even larger resistance change (factor 45 increase), as can be seen in the figure above and in table 3.

Operating Conditions	R(0)	R(24 hours)
Darkness, open circuit	595 kOhms	608 kOhms
Visible light, open circuit	370 kOhms	318 kOhms
Visible light, operated at 25 nA	947 kOhms	842 kOhms
Visible light, operated at 110 nA	605 kOhms	987 kOhms
Visible light, operated at 2 to 4 μ A	460 kOhms	1240 kOhms
UV light, operated at 3.5 μ A	223 kOhms	10110 kOhms

Table 3: Summary of long-term sensor behavior for various operating conditions.

4.5: Attempts to Detect NO₂ in Humid Air

Experiments were conducted according to the procedures outlined in section 4.3 to attempt to detect NO₂ electrochemically in the presence of humid air on time scales of 3 to 5 hours. Initially, the film resistance and relative humidity appeared to have an exponential relationship:

$$R \sim R_0 e^{-A(RH \%)}$$

For this reason, we chose to plot the natural logarithm of R versus $RH\%$. The figure below shows a logarithmic plot of normalized resistance measurements versus $RH\%$; each curve is a resistance vs. $RH\%$ plot which was gathered for different amounts of background NO_x . These data have been normalized by the sensor's resistance value at 40% RH . Curves gathered at low NO_2 levels tend to coincide with those gathered at higher NO_2 levels when relative humidity is greater than 25%. From these curves, we initially conclude that the resistance changes do not correlate with background NO_2 levels.

Figure 9: Normalized resistance versus RH (%) on with resistance on a logarithmic scale. Curves were gathered for various concentrations of NO_2 .

Using equation 6, the sensing response data was used to graph changes in sensitivity versus relative humidity (percent) according to Langmuir isotherm. Isotherms

were gathered under different background NO_2 concentrations and are presented in figure 10:

Figure 10: Langmuir adsorption isotherms gathered at various background levels of NO_2 . A linear best fit is shown for the 6 ppb data.

In the above figure we can see a change in the position of the line isotherm when the sensor is exposed to different environments. However, the change in the slope does not correlate with changes in NO_2 concentration. When the isotherms are gathered at NO_2 levels higher than 6 ppb, we see a more negative slope on the 20 ppb line. When the concentration is increased to 165 ppb, the slope is now less negative than the 6 ppb line. When gathering an isotherm in an environment of 623 ppb NO_2 , the slope of the line is now about equal to the sensor tested at 6 ppb. This back-and-forth type of behavior is unpredictable as well as unwanted in a sensor intended for detecting NO_2 in humid air. Adsorption equilibrium constants for water vapor gathered at various NO_2 levels are shown in the table below:

Isotherm gathered at:	Equilibrium constant K_{eq} (RH%)⁻¹
6 ppb	$5.58 * 10^{-2}$
18 ppb	$5.52 * 10^{-2}$
20 ppb	$3.83 * 10^{-2}$
165 ppb	$1.14 * 10^{-1}$
623 ppb	$5.50 * 10^{-2}$

Table 4: Equilibrium constants for un-aged samples, which were determined for the curves in figure 10. K_{eq} has units of (RH%)⁻¹, or equivalently, the units are (concentration)⁻¹.

Except for the equilibrium constant for the isotherm gathered in an environment of 165 ppb NO₂, the equilibrium constant is of the same order of magnitude regardless of the amount of NO₂ in the environment. We can initially conclude that NO₂ does not interfere with adsorption of water vapor in a consistent manner. The sensitivity to humidity appears to be so large that it masks any electrical response due to reaction of TEA with NO₂.

To investigate if the observed resistance increase over time was due to some reaction with NO₂ over longer time scales (>24 hours), a group of sensors were allowed to age under various NO₂ levels at high humidity to see how the resistance vs. RH% curves change over time. We also wish to see if any resistance changes are consistent with the amount of NO₂ in the aging environment. If the resistance increase over time were due to reaction with NO₂, we would expect a greater resistance change when the samples are aged at higher NO₂ concentrations. Sensors were aged at 5 ppb, 40 ppb (in lab air), or 1 ppm NO₂ respectively for a period of 24 hours, with RH maintained at 40% during this time. Following the aging process, the sensors were exposed to background NO₂ (5 ppb) and varying RH% and the resistance was measured. The following figure

shows resistance (normalized by the resistance value at 40% RH) versus RH% on a logarithmic-linear plot:

Figure 11: Normalized resistance versus humidity curves for samples aged in environments with different NO_2 concentrations and 40% RH.

In figure 11, the three curves gathered at 6 ppb, 18 ppb, and 20 ppb with no aging time lie almost on top of each other. When aged samples are tested at 40% RH, the resistance of the samples stays nearly the same, as expected. When aged samples are tested at lower humidity levels, we now see a resistance change in samples aged in NO_2 environments. However, we expect samples aged at higher NO_2 concentrations to have a greater resistance change than samples aged at low NO_2 concentrations. In the above figure we see the sample aged in lab air has a greater resistance change than the sample aged in a 1 ppm NO_2 environment. Also, the sample aged at 5 ppb environment has almost the same resistance vs. humidity profile as the sample aged at 1 ppm. The resistance of aged

samples at 40% RH is nearly unchanged from the un-aged samples, however at lower humidity levels (<30%) the curves begin to diverge. The aged samples all have a slightly steeper slope at lower humidity levels, which suggests an increase in humidity sensitivity at low humidity levels. We initially conclude from these experiments that it is not possible to reliably detect NO₂ in moist air due to high humidity sensitivity.

Langmuir isotherms were also plotted for the sensors which were aged for 1 day at 5 ppb, 40 ppb, and 1 ppm NO₂ and 40% RH respectively; the plot is shown in figure 12.

Figure 12: Langmuir adsorption isotherms for samples aged in environments with different NO₂ concentrations and 40% RH. Table 4 shows the equilibrium constants for each isotherm, which were calculated using equation 6.

Sample	Equilibrium constant $K_{eq} (RH\%)^{-1}$
Un-aged, isotherm gathered at 6 ppb	$5.58 * 10^{-2}$
1 day aged in 40% RH, gathered at 5 ppb	$1.98 * 10^{-2}$
1 day aged in 40% RH, gathered at 40 ppb	$3.61 * 10^{-1}$
1 day aged in 40% RH, gathered at 1 ppm	$1.84 * 10^{-1}$

Table 5: Equilibrium constants for 1 day aged samples, which were determined for the curves in figure 12. K_{eq} has units of $(RH\%)^{-1}$, or equivalently, the units are $(\text{concentration})^{-1}$.

All three of the curves in figure 11 corresponding to the aged samples show a less negative slope than the un-aged sample; this behavior reflects a resistance increase over time, which has already been observed. From the data in table 4, we see that as the amount of NO_2 in the aging environment increases, so does the equilibrium constant, however the change in equilibrium constant is not consistent with the NO_2 concentration in the aging environment.

4.6: Attempts to Detect NO_2 in Nearly Dry Air at Micro-Amp Current Levels

Sensors were exposed to an environment of high NO_2 concentration and low background relative humidity, between 1% and 3%. These humidity levels are much lower than what can be encountered in hospitable environments on earth, however it is still necessary to see if the sensor would exhibit the resistance decrease predicted by Meka et. al. [6] Sensor resistance was measured with the Keithley DMM mentioned above, with nominal current maintained between 2 and 4 μA DC. After a low-humidity environment was established in the chamber, NO_2 gas diluted to 1 ppm was pumped into the chamber and concentration was maintained at a high level. After some time, the NO_2 gas was pumped out of the chamber until a low concentration was reached; the process was then repeated to check for reproducibility. The results of this experiment can be found in figure 13.

Figure 13: Sensor resistance over time with the corresponding graph of NO₂ concentration over time. Red arrows point out time intervals where the resistance decreases over time.

Meka et. al. reported that exposing a TEA-CNP based sensor to NO₂ resulted in a steep resistance decrease of the sample over a time scale of ~1 minute, followed by a smaller continuous resistance decrease over time. [6] From the above figure, we do not see this predicted change in resistance, and any resistance decrease that does occur does not correlate with exposure of the sample to NO₂. In figure 13, the sample is exposed to NO₂ at ~22 hours, and yet we do not see any resistance decrease until ~33 hours; similar behavior occurs when the sensor is exposed at ~55 hours. This behavior is inconsistent with the response time scale of ~1 minute reported previously. Therefore, we still cannot conclude that the resistance fluctuations are due to exposure to NO₂.

From the data on the 6 ppb isotherm in figure 10, we calculate that a humidity fluctuation between 1% and 3% could produce a resistance change of approximately 9.5%. From the data in figure 13, we calculate that the resistance fluctuates by up to 1.5 M Ω , or about 15%, whether or not the sensor is exposed to NO₂. Therefore, we can conclude that it is more likely that the observed resistance fluctuation is due to adsorption/desorption of water vapor, as humidity sensitivity of these sensors has been demonstrated earlier. We conclude that the sensitivity to humidity fluctuations is so great that it renders undetectable any electrical response due to reactions between TEA and NO₂ in humid air.

4.7: Attempts to Detect NO₂ in Nitrogen at Nano-Amp Current Levels

In these experiments, we attempt to detect ppm levels of NO₂ (diluted with nitrogen) while the current in the sensor is maintained at 10 nA using the experimental setup shown in figure 5. Current was maintained using the Keithley 220 programmable current source mentioned above and the voltage drop across the sample was measured; the sensor resistance was calculated using Ohm's law. Prototype sensors were prepared using standard procedures and placed in the test chamber. Prior to exposure to NO₂, all gases initially present in the chamber are replaced with nitrogen. The gas chamber and all connected lines were evacuated down to vacuum levels and nitrogen gas was pumped in until atmospheric pressure is reached; this process was performed three times. The current source is then activated and the sensor resistance is monitored until it reaches a baseline level while nitrogen flows through the apparatus. After evacuation of the gas chamber, the oven containing the NO₂ source and all connected gas lines are evacuated

and replaced with nitrogen three times. During evacuation, the oven is maintained at 30 °C in order to remove any water vapor adsorbed on any surfaces. Once the sensor resistance reaches a plateau, the oven is turned on to 50 °C and the nitrogen flow is diverted into the oven containing the NO₂ source. The emitted gas is diluted with nitrogen to the desired concentration and is allowed to flow into the gas chamber. Because the gas mixture needs to travel through ~30 feet of tygon tubing held at room temperature, we assume that the gas has cooled to room temperature by the time it reaches the chamber. As the gas mixture flows through the chamber, the sensor response and the concentration of NO₂ inside the chamber are monitored.

Figure 14: Graphs showing sensor resistance over time with the corresponding graph of NO₂ concentration over time for two different samples. Green arrows point out when the NO₂/nitrogen mixture begins flowing into the chamber, and red arrows point out when only nitrogen is pumped into the chamber.

From the above figure we see that upon exposure to NO₂/nitrogen a resistance decrease is observed. After the response is monitored for some time, the oven is switched off and the NO₂ concentration falls below the previously reported LOD of 200 ppb. As the environment in the chamber is exchanged, the sensor resistance begins increasing until it plateaus. Similar results are observed upon repeated exposures. In all cases, the resistance changes occur over a timescale of minutes. The largest change in resistance observed was a decrease of 20%. Because the resistance changes are so much larger than expected, it is more likely that an increase in humidity is responsible for these resistance changes, rather than NO₂. In the following table we calculated the change in humidity necessary to cause the observed resistance changes during the five exposures shown in figure 14. These small calculated RH changes are compatible with the idea that the observed resistance changes are induced by humidity changes, primarily because the resistance changes are so much larger than the expected resistance change due to changes in NO₂ concentration.

Percent change in resistance	ΔRH (in percentage points)
-19.046 %	4.167
-19.792 %	4.350
-15.430 %	3.306
-2.234 %	0.446
-16.180 %	3.481

Table 6: Calculated changes in humidity required to cause the resistance changes shown in figure 14. Humidity changes are given in percentage points; for example, a change of 4.167 percentage points would mean humidity changes from 1% to 5.167%.

The experimental setup was modified a final time; in an attempt to remove any water vapor from the gas flow, all test gases were run through a moisture trap containing CaSO₄ desiccant before entering the test chamber. One sensor was exposed to high concentration NO₂ in nitrogen which was emitted from the heated permeation tube

device. A second sensor was exposed only to nitrogen which was flowed through the oven setup while temperature was maintained at 50 °C, but with the NO₂ source absent from the oven. Before the diluted NO₂ is pumped into the chamber, nitrogen is allowed to flow over the NO₂ permeation device for at least 1 hour while the temperature was held at 50 °C, and the gas mixture was exhausted into a fume hood. Doing this allows any water vapor adsorbed on the device to be removed from the permeation device, and the NO₂/nitrogen gas mixture can come to high concentration prior to exposing the samples.

The sensor exposed to the NO₂/nitrogen mix exhibits behavior similar to the sensor exposed only to nitrogen. When exposed to the test gases, we see the resistance increase rather than decrease. The fact that the resistance increases in this case indicates the removal of some amount of water vapor from the chamber; either there is some minute amount of water vapor remaining in the chamber upon exposure or there is some adsorbed water vapor in the sensing film which begins desorbing upon exposure. These results are shown in the figures below:

Figure 15: Sensor exposed to NO₂/nitrogen mix. Green arrows point out when the NO₂/nitrogen mixture begins flowing into the chamber, and red arrows point out when only nitrogen is pumped into the chamber.

Figure 16: Sensor exposed only to nitrogen. Green arrows point out when the nitrogen begins flowing through our apparatus and into the test chamber, and red arrows point out when only nitrogen from a cylinder is pumped into the chamber.

Previous work claimed to detect a bridge voltage decrease of 0.5% on exposure to 1.8 ppm NO_2 over a period of ~ 5 minutes. [6] For such small changes in a bridge voltage circuit, we can approximate the bridge voltage dependence on resistance to be linear, and we should also expect a 0.5% decrease in resistance. We observe resistance decreases as high as 20% when exposed to NO_2 from our permeation tube device, a factor 40 larger than expected. A 0.5% resistance decrease would correspond to a humidity change of 0.1 percentage points (i.e. humidity changes from 1% to 1.1%). The large magnitude, as well as the reversibility of the resistance changes, is more like due to humidity changes in the gas chamber than a reaction with NO_2 . The only potential source of water vapor in the experimental setup would be water vapor adsorbed onto surfaces in the experimental setup. As the heat is applied to the NO_2 source, any adsorbed water vapor present in the system will begin desorbing, causing an increase in humidity and decrease in resistance. This is what we see when the sensor is exposed to NO_2 (denoted by green arrows in figure 14). When the heat is turned off, adsorbed water vapor stops desorbing and the resistance begins increasing as nitrogen flows into the chamber.

In the experiments where test gases flow through a moisture trap, the resistance goes up when exposed to test gases. An increase in resistance corresponds to a decrease in water vapor interacting with the sensing film. This would mean some water vapor is removed from the chamber on exposure, or it indicates that water vapor is desorbing from the sensing film as dry nitrogen flows into the chamber. The fact that we observe the same results whether or not NO_2 is present in the chamber means the observed response is most likely due to humidity fluctuations in the chamber. All this is consistent with the

conclusion that the sensing response due to humidity changes is so large that it can effectively mask any resistance changes that are due to reactions between TEA and NO₂. We can therefore not conclude that at nano-amp current levels, NO₂ can reliably be detected in this experimental setup. This is primarily due to the sensor's overwhelming sensitivity to humidity.

CHAPTER 5

SEM ANALYSIS

SEM imaging was conducted on two samples of TEA/CNP nanocomposite on our usual PCB substrates. Both samples studied here had been fabricated using the standard method mentioned in section 4.1. One of the samples was allowed to operate for 1 day while connected to an active DMM in lab air prior to analysis. All imaging was conducted on a Sirion FEG SEM; accelerating voltage used was 20 kV, and the microscope was operated using working distance between 4 and 5 mm with a through-lens detector used to gather images.

5.1: Unused Sensor

A low magnification image (72x) of an unused sensor is shown below:

Figure 17: 72x magnification image of nanocomposite film covering PCB substrate and interdigitated electrodes.

The electrodes are not easily distinguishable from the polymer-covered substrate, therefore they have been labeled. We can see some carbon nanoparticle agglomerations in the film, however the film appears almost uniform at such low magnification. At higher magnification some variations can be seen in the surface morphology; the surface does not appear to be as uniform. Figure 18 shows a high magnification image of the polymer film; the image was taken from an area between the electrodes. The inset image shows a higher magnification image of the polymer film. [35]

Figure 18: a: High magnification (4609x) image of the nanocomposite film showing variations in thickness. b: Higher magnification of the film.

5.2: Used Sensor

The next set of images presented show images of the sensor which was monitored for 1 day prior to SEM analysis (see figure 19 below).

In the above image, the electrodes can easily be distinguished from the rest of the features in the image. The polymer layer is not as visible as it was in the images showing the unused sensor; some structural or chemical changes have evidently taken place. On some of the electrode walls, we can see that black crystallites have formed; notice that the crystallites have not formed on the electrode B. These crystallites are absent in the images of the unused sensor. This may be evidence of electrodeposition of carbon on the electrode that occurs during the sensor's operation. Namba [36] has shown that carbon films can be grown on conductive and semiconductive substrates by electrochemical processes by holding the substrate at negative potential. Figure 20 below shows an SEM image of these crystallites, along with a zoomed in area showing some of the surface characteristics. The image was gathered from the top-middle area of the image in figure

19. The image in figure 20b shows that the surfaces of these crystals appear to have nearly homogeneous composition with small cracks.

Figure 20: a: Zoomed in SEM image of crystal growth on an electrode and substrate. b: surface morphology.

An SEM image was taken from the region between the two electrodes in the lower right hand corner of the image in figure 19 and is shown below in figure 21. We can see bright spots in the image with bright edges (indicative of charging). Dark areas can also be seen throughout the image as well. These may be the result of variations in the substrate thickness in between the electrodes.

Figure 21: SEM micrograph of nanocomposite coated substrates in between electrodes. The blue box denotes the area selected for high magnification imaging.

Images of the lighter surface features in figure 21 were gathered at high magnification (the area in the blue box above). The darker areas of the film are caused by variations in the film thickness due to valleys that exist on the substrate surface. These images show that these films have a definite amorphous morphology. Individual nanoparticles could not be distinguished in the image, although the outlines and borders of nanoparticle agglomerations can be clearly seen. At high magnification, we see a bright intensity profile for these films as well as the definite border of a solid particle. Because of the ratio of volume of TEA to volume of CNP used in sensor fabrication is 10:1 and from these SEM images, we can conclude that the polymer films completely

covers the nanoparticle agglomerations. The film also contains numerous small holes with average size ~ 800 nm. These images are shown below.

Figure 22: A) Hole in TEA/CNP film. B) CNP agglomerations covered in TEA polymer.

When the images in figure 17 and figure 19 are compared, a marked difference can be seen. First, black crystallites can be seen on every other electrode in used sensor (those labeled “electrode A” in figure 19). These crystallites are either absent in the unused sensor (figure 17), or they simply cannot be seen through the polymer layer because it is too thick. It is possible that the polymer has degraded so much in the used sensor that these crystallites become visible. While electrodeposition of carbon is possible, more research needs to be done to determine the composition and formation process of these crystals. [36]

CHAPTER 6

CONCLUSIONS

In this study we have demonstrated that the sensitivity to water vapor that can mask the electrical response of the sensor to NO₂. Meka et. al. [6] reported observing a resistance decrease over time of a TEA-CNP sensor when it was exposed to NO₂ in dry air; the reaction was reported to proceed on a time scale of ~5 minutes. During the course of this research, multiple attempts to reproduce these results were unsuccessful: exposure of the sensor to NO₂ in a low humidity environment does not produce the predicted resistance change. Fluctuations in humidity also caused a resistance change in the sensor. The results shown in figure 6 show sensitivity to humidity changes: transferring the sensor from an environment at 13% to 41% relative humidity resulted in a resistance decrease of 44.7% with response/recovery times of 59 ± 9 seconds. The resistance change was found to be reversible and can be approximately described in terms of Langmuir adsorption. We have been able to demonstrate the sensor's sensitivity to humidity in both the presence and absence of NO₂.

Resistance changes of the sensor during operation with DC current have also been established. During operation of the sensor over long time scales (~days), we observed a gradual resistance increase of the sensor while driven with 2 to 4 μ A DC. The resistance increase was observed when the sensor was left in an environment kept at low NO₂ concentration and constant relative humidity. Sensors that are left in an open circuit for the same amount of time do not exhibit these resistance changes. We found that the optimal current at which to operate the sensor was at the nano-amps level; a sensor

operated for 24 hours at 25 nA does not exhibit resistance changes as current flows through the sensing film. We conclude that driving the sensor with a high DC current causes a gradual resistance increase during operation for which water vapor and NO₂ are not responsible.

Illumination with light also causes resistance changes in sensing layer. When a TEA based sensor is exposed to UV light, a resistance increase over time can be observed while the sensor is illuminated. The resistance increase stops when the UV light is switched off. This behavior is expected, owing to the fact that most polymers degrade when illuminated with UV light. [16] We do not see this occur when the sensor is illuminated with visible range light.

When we compare SEM images from new sensors and sensors operated at micro-amps level for a day, we can see evidence of degradation; unused sensors have a much more fluid polymer-CNP layer than used sensors. Black crystallites can be seen on the electrodes of the used sensor; these deposits are not present (or they are not visible) on the unused sensor. Although electrodeposition of carbon films is possible [36], further research should look into the process governing the formation of these crystallites. Driving the sensor with AC current could possibly help prevent the growth of these crystallites.

With these results in mind, we attempted to see if NO₂ interferes with the adsorption of water vapor in a manner that is consistent. Resistance vs. concentration curves and Langmuir isotherms were gathered at varying NO₂ concentrations. Upon comparison of the Langmuir isotherms and the equilibrium constants, isotherms gathered at low NO₂ concentrations (<20 ppb) are almost unchanged when compared to isotherms

gathered at high NO_2 concentrations. The water vapor adsorption equilibrium constants for these isotherms do not correlate with the background NO_2 concentration. We initially conclude that the TEA based chemresistor cannot be used to reliably detect NO_2 at typical humidity levels on shorter time scales. This is because the sensing response to changes in humidity is so great that it masks any sensing response due to reactions with NO_2 .

Because the sensor has high sensitivity to humidity and lacks any NO_2 sensitivity on short time scales, we also measured the resistance change in the sensing layer by exposing a sensor to NO_2 gas at 40% RH for one day. Normalized resistance versus humidity curves show a resistance increase over the one day aging period when resistance is measured at low humidity and little to no change in resistance when the resistance is measured at 40% humidity. However, the amount of resistance increase for a sample aged in a 1 ppm environment has the same amount of resistance increase for a sensor aged in lab air (~ 40 ppb NO_2). Langmuir isotherms for these data show similar behavior. We would expect a good NO_2 sensor to have greater resistance increase when aged in an environment with higher NO_2 levels. We can then conclude that the TEA-CNP sensor cannot be used to accurately detect environmental NO_2 in humid air due to overwhelming sensitivity to humidity.

In order to rule out the possibility that resistance changes can be caused by running current through the sensor, we measured the resistance of the sensor while its current was regulated at 10 nA. At these low levels, we have shown that the resistance of the sensing film remains stable. Prior to NO_2 exposure we attempt to remove from the experimental setup any water vapor that may be adsorbed onto surfaces, and the

atmosphere in the test chamber was replaced with nitrogen. Upon exposure to 1.7 ppm NO_2 diluted with nitrogen, the largest observed resistance change was a decrease of 20%, a factor 40 larger than expected. The expected resistance change of -0.5% corresponds to relative humidity increase of 0.1 percentage points (i.e. humidity changes from 1% to 1.1%). Such a large resistance change is more likely due to desorption of water vapor from the metal housing containing the NO_2 source, or desorption from the NO_2 source itself, rather than due to interactions between the sensing film and NO_2 . After modifying our experimental setup and flowing test gases through a moisture trap, we observe a resistance increase. This is indicative of the removal of some water vapor from the system or of desorption of water vapor from the sensing film. The same resistance increase can be seen whether or not NO_2 is present in the chamber. We conclude that even when current is maintained at such low current levels, we cannot see any resistance change that conclusively occurs due to interactions between NO_2 and the sensing film due to the sensor's overwhelming sensitivity to humidity.

REFERENCES

1. Cape, J. N. *Review of the use of passive diffusion tubes for measuring concentrations of nitrogen dioxide in air*. Centre for Ecology and Hydrology (Edinburgh Research Station). December 2005.
2. Navale, S. C.; Ravi, V.; Srinivas, D. *EPR and DRS evidence for NO₂ sensing in Al-doped ZnO*. *Sens. Actuators B Chem.* 2008, 130, 668-673.
3. Liou, W.; Lin, H. *Nanohybrid TiO₂/carbon black sensor for NO₂ gas*. *China Particuology* 5 (2007) 225–229.
4. Palmes, E. D.; Gunnison, A. F.; DiMattio, J. *Personal sampler for nitrogen dioxide*. *Am. Ind. Hyg. Assoc. J.* 1976, 37, 570-577.
5. Glasius, M.; Carlsen M. F.; Hansen T. S.; Lohse C. *Measurements of Nitrogen Dioxide in Funen Using Diffusion Tubes*. Department of Chemistry, Odense University.
6. Meka, et. al. *Triethanolamine Nanocomposite-based Chemiresistive Nitrogen Dioxide Gas Sensor*. *JALA* April 2009: 69-75.
7. Bai, H., and Gaoquan, S. *Gas Sensors Based on Conducting Polymers*. *Sensors* 2007, 7, 267-307.
8. Huang, J.; Wan, Q. *Gas Sensors Based on Semiconducting Metal Oxide One-Dimensional Nanostructures*. *Sensors* 2009, 9, 9903-9924.
9. Ibach, H. *Physics of Surfaces and Interfaces*. Springer-Verlag Berlin Heidelberg, 2006. pgs. 245-258.

10. Ahn, M.W.; Park, K.S.; Heo, J.H.; Park, J.G.; Kim, D.W.; Choi, K.J.; Lee, J.H.; Hong, S.H. *Gas sensing properties of defect-controlled ZnO-nanowire gas sensor*. Appl. Phys. Lett. 2008, 93, 263103.
11. Gardner, J.W.; Bartlett, P.N. *Design of conducting polymer gas sensors: modeling and experiment*. Synth. Met. 1994, 57, 2665-2670.
12. Bartlett, P.N.; Gardner, J.W. *Diffusion and binding of molecules to sites within homogeneous thin films*. Philosophical Transactions of the Royal Society of London, Series A: Mathematical, Physical and Engineering Sciences 1996, 354, 35-57.
13. Gardner, J.W.; Bartlett, P.N.; Pratt, K.F.E. *Modeling of Gas-Sensitive Conducting Polymer Devices*. IEE Proceedings-Circuits Devices and Systems 1995, 142, 321-333.
14. Zhang, D.; Liu, Z.; Li, C.; Tang, T.; Liu, X.; Han, S.; Lei, B.; Zhou, C. *Detection of NO₂ down to ppb levels using individual and multiple In₂O₃ nanowire devices*. Nano Lett. 2004, 4, 1919-1924.
15. Langmuir, Irving. *Theory of Adsorption*. Physical Review, 1915, Vol. 6, 79.
16. Gijpferich, A. *Mechanisms of polymer degradation and erosion*. Biomaterials 17 (1996) 103-114.
17. Curtin, T. A.; Wahlstrom, D.; McCormick, J. *NO₂/N₂O₄ equilibrium experiment*. Journal of Chemical Education, vol. 68, issue 9, p. 781
18. Groneberg-Kloft, B.; Kraus, T.; Mark, A. V. *Analysing the causes of chronic cough: relation to diesel exhaust, ozone, nitrogen oxides, sulphur oxides and other environmental factors*. J. Occup. Med. Toxicol. 2006, 1, 6.

19. Samet, J.; Krewski, D. *Health effects associated with exposure to ambient air pollution*. J. Toxicol. Environ. Health Part A Curr. Issues 2007, 70, 227-242.
20. Samet, J. M. *Traffic, air pollution, and health*. Inhal. Toxicol. 2007, 19, 1021-1027.
21. Sillman, S. *The relation between ozone, NO(x) and hydrocarbons in urban and polluted rural environments*. Atmos. Environ. 1999, 33, 1821-1845.
22. United States EPA. *Fact Sheet: Final Revisions to the National Ambient Air Quality Standards for Nitrogen Dioxide*. January 22, 2010.
23. Dunlea, E. J.; Herndon, S. C.; Nelson, D. D. *Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment*. Atmos. Chem. Phys. Discuss. 2007, 7, 569e604.
24. Yoshimasa, T.; et. al. *Development and optimization of a lab-on-a-chip device for the measurement of trace nitrogen dioxide gas in the atmosphere*. Analyst, 2006, 131, 573–578.
25. Huang, X. J.; Choi, Y. K. *Chemical sensors based on nanostructured materials*. Sensors and Actuators B 122 (2007) 659–671.
26. Kim et al. *Room-temperature semiconductor gas sensor based on non-stoichiometric tungsten oxide nanorod film*. Appl. Phys. Lett. **86**, 213105, 2005.
27. A. Maiti, J.A. Rodriguez, M. Law, P. Kung, J.R. McKinney, P.D. Yang. *SnO₂ nanoribbons as NO₂ sensors: insights from first principles calculations*. Nano. Lett. 3 (2003) 1025–1028.

28. M. Law, H. Kind, B. Messer, F. Kim, P.D. Yang. *Photochemical sensing of NO₂ with SnO₂ nanoribbon nanosensors at room temperature*. Angew. Chem. Int. Ed. 41 (2002) 2405–2408.
29. E. Comini, G. Faglia, G. Sberveglieri, D. Calestani, L. Zanotti, M. Zha. *Tin oxide nanobelts electrical and sensing properties*. Sens. Actuators B 111–112 (2005) 2–6.
30. Park, J. Y.; Choi, S. W.; Kim, S. S. *Fabrication of a Highly Sensitive Chemical Sensor Based on ZnO Nanorod Arrays*. Nanoscale Res Lett (2010) 5:353–359.
31. Fan, Z. Y.; Lu, J. G. *Gate-refreshable nanowire chemical sensors*. Appl. Phys. Lett. 86 (2005) 123510–123512.
32. Kuang, Q.; Lao, C.; Wang, L.; Xie, Z.; Zheng, L. *High-Sensitivity Humidity Sensor Based on a Single SnO₂ Nanowire*. J. Am. Chem. Soc. Vol. 129, #19, (2007) 6070-6071.
33. Hernandez-Ramirez, F.; Barth, S.; Tarancon, A. Casals, O.; Pellicer, E.; Rodriguez, J.; Rodriguez, A.R.; Morante, J.R. Mathur, S. *Water vapor detection with individual tin oxide nanowires*. Nanotechnology 2007, 18, 424016.
34. Arshak, K.; Moore, E.; Cavanagh, L.; Harris, J.; McConigly, B.; Cunniffe, C.; Lyons, G.; Clifford, S. *Determination of the electrical behavior of surfactant treated polymer/carbon black composite gas sensors*. Compos Appl Sci Manuf 2005, 36, 487-491.
35. Nadarajah, Athavan. *SEM Images of Unused TEA-CNP sensor*. Used with permission.

36. Namba, Y. *Attempt to Grow Diamond Phase Carbon Films from an Organic Solution*. J. Vac. Sci. Technol., A 10 (1992) 3368.