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Ram Ravichandran for the degree of Master of Science in Electrical Engineering presented on September 23, 2009.

Title: Fabrication and Characterization of p-type CuO / n-type ZnO Heterostructure Gas Sensors Prepared by Sol-Gel Processing Techniques

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Thomas K. Plant

Increased interest in the field of sensor technology stems from the availability of an inexpensive and robust sensor to detect and quantify the presence of a specific gas. Bulk p-CuO/n-ZnO heterocontact based gas sensors have been shown to exhibit the necessary sensitivity and selectivity characteristics, however, low interfacial CuO/ZnO contact area and poor CuO/ZnO connectivity limits their effective use as gas sensors.

The phase equilibria between CuO and ZnO exhibits limited solubility. By exploiting this concept, a CuO/ZnO mixed solution is formed by combining CuO and ZnO precursors using wet chemical (sol-gel) techniques. Thin films fabricated using this mixed solution exhibit a unique CuO/ZnO microstructure such that ZnO grains are surrounded by a network of CuO grains. This is highly beneficial in gas sensing applications since the CuO/ZnO heterostructure interfacial area is considerably increased and is expected to enhance sensing characteristics.

This work builds on previous research by Dandeneau et al. (Thin film chemical sensors based on p-CuO/n-ZnO heterocontacts, Thin Solid Films, 2008). CuO/ZnO mixed solution thin films are fabricated using the sol-gel technique and subsequently characterized. X-ray diffraction (XRD) data confirms the phase separation
between ZnO and CuO grains. Scanning electron microscopy (SEM) as well as energy dispersive spectroscopy (EDS) reveal a network of ZnO grains amidst a matrix of CuO grains. Optical and electrical characterization provide material parameters used to construct an energy band diagram for the CuO/ZnO heterostructure. Aluminum interdigitated electrodes (IDEs) are patterned on the thin film and gas sensing characteristics in the presence of oxygen and hydrogen are investigated. Optimization of the electrode geometry is explored with the aim of increasing the sensitivity of the sensor in the presence of hydrogen gas.
Fabrication and Characterization of
p-type CuO / n-type ZnO Heterostructure Gas Sensors
Prepared by Sol-Gel Processing Techniques

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Ram Ravichandran

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APPROVED:

Major Professor, representing Electrical and Computer Engineering

Director of the School of Electrical Engineering and Computer Science

Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Ram Ravichandran, Author
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1 Introduction and Project Objectives

1.1 Introduction

During the past few decades, there has been an increased interest in the development of robust solid-state sensor devices which can perform the role of selectively sensing a target gas and provide quantitative information regarding the concentration of a target gas in the surrounding environment. Many industrial and commercial activities involve the monitoring and control of the surrounding environment, with applications ranging from automobile exhaust control and toxic/flammable gas detectors, to environmental and industrial production control. Siyama et al. in 1962 reported the first zinc oxide (ZnO)-based thin film gas sensor [2] demonstrating the detection of gases such as ethanol and carbon dioxide, and this quickly gave rise to rapid development of a wide variety of semiconducting oxide gas sensors.

ZnO and copper oxide (CuO) are widely studied in gas sensing applications due to the inherent properties of these materials. ZnO is an n-type wide band-gap (≈ 3.3 eV) [3] material, while CuO is a p-type material with a narrower band-gap (1.2 - 1.5 eV) [4]. Bulk ZnO and CuO ceramic disks, pressed together using mechanical contact, were employed by Nakamura et al. [5] in the detection of gases such as propane and carbon monoxide. While this sensor distinguished the presence of the two gases, subsequent work by Choi et al. [6] demonstrated that the act of mechanical pressing caused instability in the device and reliable results were difficult to obtain. Bulk p-CuO/n-ZnO also possess inherent drawbacks restricting their use as gas sensors. The sensing region is limited to the interfacial region formed between the two materials in contact. As a result, the connectivity between CuO and ZnO grains is low, minimizing the sensor response. Also, the target gas
does not have a direct path to the interfacial region and has to travel a long, circuitous path to reach the interfacial region.

Previous work on ZnO and CuO bulk powders by Jensen et al. indicated limited solubility between CuO and ZnO when mixed to form a 1:1 atomic ratio of Cu:Zn [7]. The authors observed that CuO and ZnO grains remain segregated as separate particles with no mixed phases present. Dandeneau provided an optimized process route to fabricate CuO and ZnO thin films possessing a high degree of porosity and crystallinity [8]. Increasing the crystallinity of the thin films increases the conductivity due to reduced scattering events at the grain boundaries. Porosity is an important factor in gas sensing applications since it provides the target gas with a short diffusion path to the heterostructure interface. Dandeneau also outlined a process route to fabricate CuO/ZnO mixed solution thin films using the sol-gel fabrication technique.

1.2 Project Objectives

The objectives of this project can be outlined as follows:

1. Characterize the structural, optical and electrical properties of the mixed-solution thin films.

Characterization of the properties of the mixed-solution thin films will be beneficial in understanding the behavior of the thin films. The crystalline structure and morphology of the films will be explored using x-ray diffraction (XRD) and atomic force microscopy (AFM). Elemental spectroscopy, confirming the existence of segregated grains of CuO and ZnO will be investigated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques. Optical and electrical characterization of the
thin films provide important material parameters such as optical band-gap, carrier concentration and mobility, which can be used to model an energy band diagram of the p-type CuO/n-type ZnO grains in contact.

2. Explore different electrode geometries in an effort to maximize sensitivity of the sensor device in the presence of hydrogen gas.

The effect of varying the interdigitated electrode spacing and width will be explored with the intent of maximizing the sensitivity of the device.

This work begins with a review of different types of gas sensors. Specifically, semiconductor oxide gas sensors will be the focus, and relevant concepts pertaining to semiconductor oxide gas sensors will be presented. An experimental section, outlining the methodology utilized in the study will then be presented. The results section addresses the project objectives listed above. Finally, concluding observations from the results section will be summarized and possible topics for future research will be presented.
2 Literature Review

This chapter provides a brief overview of various types of gas sensing technologies explored in the last few decades.

2.1 Review of Solid-State Gas Sensing Technologies

Broadly speaking, a gas sensor should possess two basic functions - a receptor function to recognize a specific gaseous species and a transducer function to convert the recognition into a quantifiable signal [9]. In many gas sensor technologies the gas recognition is carried out through gas-solid interactions such as adsorption, chemical reactions, and electro-chemical reactions along the surface of a gas-sensitive material. For example, gas recognition in semiconducting oxides is transduced into a sensing signal through a resistance change of the sensing material. Mass sensitive sensors use a piezoelectric crystal acting as the transducer forming a sensitive receptor layer such that any gas adsorbed on the surface results in a change in mass and a measurable frequency change. This section provides a brief and broad overview of the different solid-state gas sensor technologies.

2.1.1 Semiconducting Oxide Gas Sensors

In 1953, Bardeen and Brittain demonstrated a change in the contact potential (difference in surface potential between two materials in contact) of germanium under different conditions such as the presence of oxygen, water vapor, and OH radicals [10]. They demonstrated that the electrical properties of germanium change as a result of gas adsorption on the surface of the material. The first reported ZnO-based thin film gas sensor was by Sieyama et al [2] in 1962 and quickly gave rise to rapid development of a wide variety of semiconducting oxide gas sensors. The
The working principle of the sensor was the variation of the surface and grain boundary resistance due to adsorption of an oxidizing gaseous species [11]. This resulted in a subsequent change in resistance in the presence of a reducing gaseous species.

The interaction mechanisms between the gas phase and sensing material not only involve adsorption mechanisms such as physisorption and chemisorption, but also defect states such as surface and bulk defects. Physisorption, a weaker form of adsorption, is a van der Walls interaction mechanism associated with weak bonding and a low heat of adsorption [12]. This results in a reaction to many different gaseous species and therefore a lack of selectivity to specific gases. Chemisorption, a stronger interaction, relies on transfer of charges from the gaseous species to the bulk material (or vice-versa). In this mechanism, a strong chemical bond is formed between the surface atoms and the adsorbate, varying the electronic structure of both the adsorbate and the surface atom. The nature of this bond can be restricted to certain gaseous species, thereby resulting in the chemisorption process exhibiting higher selectivity.

The first commercial semiconductor gas sensor using partially sintered SnO₂ was patented in Japan by Taguchi in 1962 but was limited in application due to a lack of specificity between gases. Gas sensitivity of this sensor was subsequently improved with the addition of noble metals such as platinum, gold or palladium resulting in a low-cost, sensitive and robust domestic gas sensor [13]. Since then, better understanding of sensor behavior and materials has led to an increase in the commercial applications of semiconductor gas sensors, including environmental monitoring [14] and detection of flammable gases [15].
2.1.2  Electrolytic gas sensors

Gaseous species interacting with solid electrolytic materials, similar to semiconducting oxide gas sensors, can cause a change in conductivity. However, in the case of electrolytic gas sensors, this change is due to mobile ions instead of electrons. Similar to liquid electrolytes in a fuel cell, reactions involving electrolytic materials can only proceed if separate paths are provided for the flow of ions (through the electrolyte) and electrons (through a conducting material). Sensors based on this technology exhibit high ionic conductivity of the electrolyte material in the temperature range of 700 to 1573 K [11] and as a result are commonly used in high temperature applications such as monitoring exhaust gases in automobiles.

For gas sensors, a casing containing the electrolyte sandwiched between a cathode and an anode contains a permeable membrane such that the gaseous analyte can reach the electrolytic material. When a chemically reactive gas passes through the permeable membrane, it can either be oxidized, giving up electrons at the anode, or reduced, accepting electrons at the cathode. As a result, a current is created when the positive ions flow to the cathode and negative ions flow to the anode. Electrochemically reducible gases such as oxygen, nitrogen monoxides and chlorides, are sensed at the cathode while electrochemically oxidizable gases such as carbon monoxide, nitrogen dioxide and hydrogen sulfide are sensed at the anode [9].

The output of these sensors is directly related to the concentration or partial pressure of the gaseous species. Electrolytic gas sensors can be classified as potentiometric or amperometric depending on whether the measured output is a potential difference or an electrical current [16]. Potentiometric measurements are performed under near zero current conditions, such that any measurable potential
difference between the anode and cathode is directly correlated to the influence of a specific gaseous species. Amperometric measurements are diffusion controlled requiring an external voltage sufficiently high to maintain a zero oxygen concentration at the cathode surface.

A prominent solid electrolyte used in sensor applications is yttria (Y$_2$O$_3$) stabilized zirconia (ZrO$_2$) which is an O$^{2-}$ conductor at temperatures greater than 300 °C. These sensors are widely used in the automotive industry where legislation has restricted the permissible emission levels of carbon monoxide, hydrocarbons and nitrogen oxides in exhaust gases [16]. The basic design consists of a yttria-stabilized zirconia ceramic pellet coated with porous platinum electrodes on either side. The sensor is located in the exhaust pipe, so that one side is exposed to the exhaust gases and the other is exposed to a reference, air. A potential difference develops across the electrodes under the presence of exhaust gases which can be subsequently measured. In Fig. 1, a mesh cover provides a porous layer for the gaseous species to come into contact with the sensor ceramic material. The heater coil provides the ability to increase the temperature to the relevant working temperature of the ceramic. Advantages of these sensors include quick and continuous monitoring, low temperature dependence, and the ability of the sensor to perform over a wide range of zirconia compositions.

2.1.3 Field Effect Gas Sensors

The development of planar silicon technology revolutionized the field of electronics and simultaneously led to the emergence of silicon-insulator based-gas sensors. This change was driven by the integration of sensor fabrication processes with existing metal-oxide-semiconductor field effect transistor (MOSFET) processes. These MOSFET-based gas sensors are inherently complex to fabricate and require exten-
sive control and measurement electronics. However, these devices can exhibit high dynamic range for the detection of low levels of specific gases [18].

The working principle behind MOSFET-based gas sensors is similar to conventional CMOS transistors, where the application of a potential bias on the gate material modulates a conducting channel between the source and the drain regions. However, in this case, the gate material is replaced by a suitable chemically sensitive material. In response to an analyte-induced change in morphology, stoichiometry, or local electric field, there is a subsequent modulation of charge density in the conduction channel [19]. The most commonly used Chemical FET (CHEMFET) utilizes a palladium gate as a hydrogen sensitive material on a conventional gate oxide [20]. This technology has attracted a lot of attention in recent years for use in portable applications, since the transduced signal containing information on the analyte does not depend on the sensing area allowing these devices to be miniaturized [21].

The ion-selective FET (IFET), first introduced by Bergveld in 1970 [22], is a subcategory of the CHEMFET family of sensors generally used for pH sensing [12].
Unlike the traditional CHEMFET, the IFET lacks a conductive gate electrode. A polymer membrane or borosilicate glass film acts as an ion-selective layer and is placed on top of the insulating layer of the FET structure [21]. By exposing the ion-selective layer directly to an aqueous solution, a potential difference (compared to a reference electrode) proportional to the concentration of ions in the solution can be measured. These devices suffer from the inherent requirement of a reference electrode as well as successful encapsulation of regions other than the gate region which is exposed to the analyte solution.

2.1.4 Fiber-Optics-Based Gas Sensors

Sensors based on fiber optic technology are attracting tremendous attention due to their importance in applications such as environmental monitoring, biomedical sensing, and industrial process control [23]. These sensors are beneficial due to the unique properties of fiber optic cables such as low attenuation over long distances and lack of signal variation due to electrical noise [24]. Low attenuation is especially attractive as this enables in situ monitoring in hazardous locations, such as groundwater monitoring [25] or monitoring of processes in nuclear fuel reprocessing plants [26].

Fiber optic chemical sensors are generally classified into two categories. Direct spectroscopic sensors are sensors where the fiber functions as a waveguide separating the sensing probe from the monitoring instrumentation. As a result, the fiber functions as a source for direct spectral analysis such as monitoring of fluorescence or absorption. Chudyk et al. demonstrated monitoring of naturally fluorescent groundwater contaminants at sub-ppm levels over distances greater than 50 m [27]. The second category, reagent-mediated sensors or optrodes, are fibers where a chemically sensitive reagent is attached to the end of the fiber. Interaction with
a specific target gas changes the optical properties, such as changes in the fluorescence, reflectivity, or absorption spectra, which can be a direct measure of the gas concentration. Conventional silica fibers have an inherent disadvantage since transmission is restricted to the visible and near-infrared regions.

While the function of fibers in spectroscopic and optrode based sensors is to transmit light to and from the sensing location, fibers can also be used such that the transmitted light is modulated by chemically induced interactions between the fiber cladding and a specific analyte. Differences in the index of refraction between the core and cladding of the fiber confines light to within the core as a result of total internal reflection. However, a fraction of the electro-magnetic field extends out a short distance from the core into the cladding decaying exponentially with radial distance away from the core. This exponentially decaying field, known as an evanescent field, defines a short range sensing region within which interaction with a chemical species causes a change in the transmitted spectrum. Utilizing this principle, the cladding can be thinned and subsequently coated with a chemically sensitive layer, such that any interaction with the gas and the sensitive layer produces a change in the transmitted spectrum [28]. Sensors based on evanescent waves provide enhanced sensitivity as well as the ability to perform quasi-distributed sensing, which enables monitoring of the spatial profile of the analyte concentration over long distances [23].

2.1.5 Surface Acoustic Wave Gas Sensors

The mathematical basis of surface acoustic waves (SAW) was first published by Lord Rayleigh in 1885 and immediately attracted the attention of geologists, since the acoustic energy released by earthquakes propagates as a surface acoustic wave along the earth’s crust [30]. Named after the discoverer, Rayleigh waves possess
longitudinal and vertical shear components which couple with any medium in contact with the surface of the material. This coupling affects the amplitude, velocity or phase of the wave, allowing SAW devices to directly sense mass or mechanical properties. Devices based on this technology had an unprecedented rise after the development of an inter-digitated transducer (IDTs), or inter-digitated electrodes by White et al. in 1965 [31], allowing the generation of Rayleigh surface waves on piezoelectric substrates.

SAW-based devices operate on the following principle: a time varying electric field is applied to one of the transducers causing a synchronous mechanical deformation of the substrate and the subsequent generation of a surface acoustic wave on the substrate [32] with a frequency in the megahertz range. Crystal orientation, piezoelectric material thickness, and geometry of the transducers influence the type of the SAW generated as well as the resonant frequency of the device. The interaction of the SAW with any adsorbate present on the surface alters properties of the wave, and subsequent measurement of these changes can be a sensitive indicator of the nature of the material present on the surface [33]. This principle
can be extended to gas sensors by placing a chemically-sensitive layer on the substrate. As a result, when gas molecules are adsorbed onto the chemically-sensitive layer, they perturb the properties of the propagating SAW and measurement of changes in the SAW characteristics can be used as an indicator of the presence of the specific analyte. Vapor-phase sensors based on this principle can be categorized according to the response mechanism in the transducers - electric potential wave interactions (variations in the dielectric constant, or conductivity) or mechanical wave interactions (variations in mass, density or Young’s modulus) [34].

SAW sensors based on conductivity changes exhibit strong sensitivity and selectivity; however, selection of a substrate with appropriate properties becomes
a tradeoff. Since SAW sensors based on physical effects, such as mass or density changes, are not subject to the same stringent materials selection they are more commonly used for chemical vapor sensing applications. D’Amico et al. [35] demonstrated an increase in H₂ sensing using palladium thin films in 1982.

2.1.6 Nanoscale Gas Sensors

Miniaturization is one of the primary driving forces in the development of gas sensors. Thin film semiconductor oxides, SAW-based devices and CHEMFET’s quickly replaced their bulk counterparts. However, in today’s continuously shrinking world of electronics, development of nanomaterials drove the development of nano-scale gas sensors based on carbon nanotubes (CNTs) [36], nanowires [37] and nanoparticles [38]. One of the biggest advantages of CNT-based gas sensors is the high surface-to-volume ratio and porous structure which is advantageous for gas adsorption and detection.

Figure 4: Diagram of single-walled CNTs between two gold contacts. [39].

Kong et al. in 2000 demonstrated the potential of CNT-based gas sensors, using
FET devices with a single semiconductive CNT as the conduction channel, to gases such as NH$_3$ and NO$_2$ [40]. The sensing mechanism in CNT-based sensors is based on the principle that adsorption of gaseous molecules either donates or withdraws electrons from the CNT resulting in a change in the electrical properties of the CNT [37]. An individual nanotube FET-based sensor has also been demonstrated by Helbing et al.[36]. The selectivity of this sensor design is achieved by adjusting the electrical gate to set the CNT sample in an initial conducting or insulating state. The working mechanism for this kind of sensor remains ambiguous, and different models have been proposed to explain the sensing principle. The first model proposes charge transfer between the nanotube and the adsorbed molecules on the surface. The second relies on molecular gating of the CNT by polar molecules such as NO$_2$, resulting in a shift of the threshold gate voltage of the CNT [36]. A third proposed mechanism is based on the change in the Schottky barriers between the nanotube and the source/drain electrodes [41].

One of the primary advantages of CNT-based sensors is their proven ability to work well at room temperature which reduces power consumption of the device and enables the safer detection of flammable gases [42]. Disadvantages of CNT-based sensors include the potential interference from relative humidity at room temperature [43] as well as low sensing areas. Other drawbacks include slow recovery time and poor selectivity. Nonetheless, the discovery of nanotube based sensors provides an excellent candidate for gas sensors, especially for nanosensors required in specialized areas, such as space-based applications [38].

### 2.2 Properties of Sensor Performance

The key characteristics of gas sensor performance are sensitivity, response time, and selectivity.
Sensitivity characterizes variations in physical or chemical properties of the sensing material under the presence of a target gas. It refers to the lowest detectable level of chemical concentrations in a sensing environment [21]. For resistive gas sensors, sensitivity is defined as the ratio of the change in resistance of the sensing material in the presence of a target gas to the change in resistance measured in air at a constant target gas concentration. For an n-type semiconductor, this can be expressed as:

\[ S_{\text{red}} = \frac{R_{\text{red}} - R_{\text{air}}}{R_{\text{air}}} \]  

(1)

\[ S_{\text{oxy}} = \frac{R_{\text{oxy}} - R_{\text{air}}}{R_{\text{air}}} \]  

(2)

In Eq. (1) and Eq. (2), \( S_{\text{red}} \) (\( R_{\text{red}} \)) refers to the sensitivity (resistivity) of the sensor in the presence of a reducing gas such as hydrogen while \( S_{\text{oxy}} \) (\( R_{\text{oxy}} \)) refers to the sensitivity (resistivity) in an oxidizing environment and \( R_{\text{air}} \) refers to the resistivity in air. Numerous methods have been employed to increase the sensitivity of semiconductor gas sensors. Instead of a bulk ceramic material, sensors based on thick- or thin-films with high porosity display an increase in sensitivity. This is attributed to an increase in the surface area and interaction with more grain boundaries for the adsorbed gaseous atoms [44]. Temperature of the sensor surface and partial pressure of the target gas are additional parameters affecting sensitivity.

Response time is defined as the time required to achieve 90% of the final change in the sensing parameter following a step change in the gas concentration at the surface of the sensor. Measured by plotting the change in measurement parameter in the presence of the target gas as a function of time, it is often expressed as a percentage of the final time since the initial response to a step change in the
concentration occurs quickly, followed by a long, drawn out tail before reaching a final steady state value [45].

Selectivity of a sensor refers to the ability to detect a specific analyte in the presence of other gases [21]. A highly selective sensor responds only to a target gas and not to any other gases in the surrounding environment. Selectivity can be adjusted according to the analyte of interest by incorporating catalysts or dopants [9]. Additional enhancement of selectivity can be accomplished by integrating a filter or membrane which allows only the gas of interest to pass through to the surface of the semiconductor. Fukui et al. demonstrated that the addition of a silica surface layer acting as a filter enhanced the selectivity for hydrogen, since hydrogen passes more freely than larger hydrocarbons through the silica layer [46]. Incorporating a catalyst on the surface of the thin film or a bulk ceramic pellet has also been shown to increase the selectivity. Li et al. [44] demonstrated an increase in selectivity towards hydrogen gas by incorporating palladium on a ZnO pellet.

2.3 Semiconductor Device Theory

2.3.1 Electronic Structure of Semiconductors and Electron Transfer at the Surface

Electronic processes in solids can be best understood by utilizing energy band diagrams. Electrons in isolated atoms possess discrete allowable energy levels. When these individual atoms are brought together in a regular three-dimensional arrangement forming a crystal lattice, interactions between neighboring atoms lead to a range of electron energy levels, otherwise known as a band. For insulators and semiconductors, the highest energy band completely filled with electrons at 0 K is known as the valence band. The energy level of the top of this band is the valence band energy $E_v$. The next excited state above the valence band containing
electrons at temperatures above 0 K is known as the conduction band. The lowest energy level in this band is called the conduction band energy $E_c$. Between these two bands is a forbidden energy range in which allowed states cannot exist. This forbidden range is known as the band gap of a material $E_g = E_c - E_v$.

In common semiconductors, in addition to these ideal crystal energy levels, discrete energy levels corresponding to electrons localized at impurity atoms or defects can also exist. Wagner et al. [47] developed the basic theory of semiconducting crystals possessing deviations from ideal integral stoichiometric compositions. An excess of metal can be present in the form of metal ions in interstitial positions (or as anion vacancies) with a corresponding equal number of quasi-free electrons in the conduction band. Cation vacancies, on the other hand, can result in an equivalent number of positive holes in the valence band [48]. For example, in zinc oxide (ZnO), excess zinc atoms located interstitially in the lattice are neutralized at low temperatures. However at higher temperatures, they can donate thermally excited electrons to the conduction band, becoming $\text{Zn}^{2+}$, increasing the net concentration of electrons and giving rise to the observed $n$-type conductivity in ZnO. Cuprous oxide (CuO) on the other hand, exhibits an excess of oxygen atoms which results in a deficiency of Cu atoms. These vacant Cu ion sites correspond to an increase in the concentration of holes in the valence band, resulting in the observed $p$-type conductivity in CuO [49]. Apart from native donor and acceptor levels within a material, energy levels corresponding to dangling bonds at the surface, known as surface states can also be present. Adsorbed ions are an example of a surface state type. They can behave either as donor states, donating electrons to the material, or acceptor states, withdrawing electrons from the material. Impurity atoms at the surface, which can be introduced during sample preparation or can diffuse from the
interior of the sample during heat treatments are another possible type of surface states.

The energy of electrons in these surface states can be strongly affected by a potential barrier at the surface. As a result, the electrostatic potential at the surface differs from that of the bulk regions. The existence of this surface potential barrier, also known as a space charge layer, or barrier layer was first proposed by Bardeen [10] in 1953 to account for the observed surface properties of germanium and silicon. The formation of this surface barrier can be illustrated by the model in Fig. 5. In the case of n-type semiconductors such as ZnO, electrons can be trapped in surface states due to adsorbed oxidizing gas on the surface. The resulting transfer of electrons from the interstitial zinc atoms near the surface to the adsorbed oxygen leaves behind a positively charged region of zinc ions which compensate the negative surface charge of adsorbed oxygen ions. An electric field develops in this space charge region and results in a voltage drop between the bulk and surface traps such that the potential energy of an electron increases as it approaches the surface. The energy of each allowed surface state increases as the surface becomes more negatively charged with increase in oxygen adsorption. This artifact results in the upward band bending shown in Fig. 5 and the curvature consequently increases with increasing oxygen adsorption. This upward band bending results in a potential barrier for electron transfer between the bulk regions and the surface state which Bardeen termed as the surface potential barrier.

The converse of this behavior occurs for a p-type semiconductor material under the influence of a reducing gas such as hydrogen. Here, the adsorbed hydrogen donates electrons to the material, such that the transfer of electrons from the adsorbed hydrogen on the surface to the copper vacancies results in a negatively
charged bulk region with respect to the surface. This causes a downward band bending and increases the potential barrier for hole transport between the bulk and surface regions.

2.3.2 Electron Transport in p-n Heterojunctions

The energy band model of an ideal abrupt heterojunction can be used to explain fundamental transport processes in a p-n heterojunction. The energy band model of an idealized abrupt heterojunction was first proposed by Anderson in 1962 [50]. An ideal heterojunction model assumes that the density of interface states, which serve as recombination or trapping centers, is negligible and does not contribute
to electron transport. The energy band gap $E_g$, permittivity $\varepsilon_r$, work function $\Phi_m$, and electron affinity $\chi$ of the two semiconducting materials are assumed to be different. The work function, $\Phi_m$, of a semiconductor is defined as the energy required to remove an electron from the Fermi level to an energy level outside the material, generally known as the vacuum level. The work function, being dependent on the Fermi level, varies as a function of the doping level. The electron affinity, $\chi$, is defined as the energy required to remove an electron from the conduction band edge ($E_c$) to the vacuum level. Since $\chi$ is a material property and invariant with doping, it is a more convenient parameter to use in characterizing heterojunctions.

Fig. 6 indicates two isolated $p$- and $n$-type semiconductor materials, where the position of the Fermi level in the $n$-type material, $E_{F_n}$, is higher than the Fermi level of the $p$-type material, $E_{F_p}$, since $\chi_p > \chi_n$. When these two materials are brought into contact, equilibrium occurs when the Fermi level reaches the same energy value by a transfer of electrons (in this case) from the $n$-type material to the $p$-type material. This causes a depletion of electrons near the junction of the $n$-type material resulting in the upward band bending. The transfer of electrons to the $p$-type material increases the concentration of electrons near the surface and therefore causes a downward band bending at the edge. This is shown in Fig. 7 below.
Figure 6: Isolated $p$-$n$ heterojunction. [51]

Figure 7: $p$-$n$ heterojunction after contact. [51]

The primary difference between the energy bands of a conventional $p$-$n$ junction and a $p$-$n$ heterojunction is the presence of a conduction band discontinuity, $\Delta E_c$, and a valence band discontinuity, $\Delta E_v$, at the interface between the two materials. The band bending at the interface can be expressed as the total built-in potential
\( \psi_{bl} \) and is equal to the partial built-in potentials \((\psi_{b1} + \psi_{b2})\) on either side of the interface at equilibrium. This can be expressed from [52] as

\[
\psi_{b1} + \psi_{b2} = E_{F1} - E_{F2} = (\chi_{1} + \chi_{g} - \delta_{p}) - (\chi_{2} + \delta_{n})
\]  

(3)

In Eq. (3), \( \delta_{p} = E_{F} - E_{V} \) and \( \delta_{n} = E_{C} - E_{F} \) for the \( p \)- and \( n \)-type materials, respectively. The built-in potentials and depletion widths can be obtained by solving Poisson’s equation for a step junction on either side of the interface as [52] [51]

\[
\psi_{b1} = \frac{N_{A}W_{D1}^{2}}{2\epsilon_{1}}
\]

(4)

\[
\psi_{b2} = \frac{N_{D}W_{D2}^{2}}{2\epsilon_{2}}
\]

(5)

\[
W_{D1} = \left[ \frac{2N_{A}\epsilon_{1}\epsilon_{2}(\psi_{b1} - V)}{qN_{D}(\epsilon_{1}N_{D} + \epsilon_{2}N_{A})} \right]^{1/2}
\]

(6)

\[
W_{Dn} = \left[ \frac{2N_{D}\epsilon_{1}\epsilon_{2}(\psi_{b2} - V)}{qN_{A}(\epsilon_{1}N_{D} + \epsilon_{2}N_{A})} \right]^{1/2}
\]

(7)

From the energy band diagram in Fig. (7) we can express the valence band discontinuity, \( \Delta E_{v} \) as

\[
\Delta E_{v} = (E_{g_{p}} - E_{g_{n}}) - (\chi_{1} - \chi_{2})
\]

(9)

Using Eq. (3) and Eq. (9), the conduction band discontinuity, \( \Delta E_{c} \) can be expressed as
\[ \Delta E_c + \Delta E_v = E_{g_n} - E_{g_p} \] (10)

2.4 Gas Sensor Theory and Operation

Electronic conduction in solids is based on the principle that charge transfer is only possible in a non-ideal lattice, in that a solid must contain crystallographic defects for conduction \([53]\). As a consequence of the third law of thermodynamics, for temperatures above \(T = 0\) K, there exists a finite concentration of defects within a solid material. Defects in crystals can arise from regions where the microscopic arrangement of particles differs from that of the ideal crystal structure as a whole. Depending on whether the imperfect region is bound to the atomic scale in one, two or three dimensions, defects can be classified as point or line defects. In this work, since surface processes are at play, point defects are primarily considered. A schematic of defects is shown in Fig. 8, and crystallographic point defects in a material can be classified as:

1. Interstitials - atoms or ions which occupy a lattice site where there would usually be no atom present, resulting in a high energy configuration

2. Substitutional defect - foreign atoms (impurities, dopants or ions) which are incorporated into a regular atomic site within the lattice

3. Vacancies - an unoccupied lattice site within the crystal structure

4. Antisite defect - these occur in an ordered alloy or compound, where the periodicity of the compound atoms is altered
Figure 8: Schematic representation of defects in semiconductors. (1) foreign interstitial defect, (2) foreign substitutional defect, (3) vacancy and (4) self interstitial defect are indicated. [54]

Since ionic crystals such as ZnO, SnO$_2$ and CuO are widely used as materials for chemical sensors, the most important crystallographic defects in these systems include

- **Schottky defect** - Any ionic crystal of formula $MX$ contains an equal number of cationic and anionic crystals. In such a crystal, a Schottky defect consists of a paired cation vacancy and an anion vacancy. This is illustrated in Fig. 9.

- **Frenkel defect** - This defect forms when an atom or ion dislodges from its position in the lattice, resulting in a vacancy and thereby becomes an interstitial defect by lodging in a nearby location that is unoccupied by an atom. This is illustrated in Fig. 10.
Figure 9: Schematic diagram of a Schottky defect pair in CuO. The □ represent vacancies in the lattice.

Figure 10: Schematic diagram of a Frenkel defect in ZnO. Zinc interstitials as well as free electrons are indicated.

Bulk electronic conductivity, $\sigma$, in a semiconducting material can be expressed as

$$\sigma = \frac{1}{\rho} = q\mu_n n_b + q\mu_p p_b$$

(11)

where $q$ is the charge on an electron (in Coulombs), $\mu_n$ and $\mu_p$ are the mobilities of electrons and holes (in cm$^2$/V.s) respectively, $n_b$ and $p_b$ refer to the bulk concentrations of electrons and holes (in cm$^{-3}$) and $\rho$ is the resistivity of the sample (in $\Omega$cm). Since the density of electrons or holes dominates depending on the nature of the material, only one of the two terms in Eq. (11) needs to be considered. In
addition to the bulk conductivity, mobile ions in a material can also contribute to conduction due to defect states. This temperature dependent ionic conductivity is strongly affected by the presence of gaseous environments (such as hydrogen and oxygen) and can be expressed as

$$\sigma_i = \sigma_o \exp\left(\frac{-\Delta E_A}{kT}\right)p_{O_2}^{1/n} \quad (12)$$

In Eq. (12), $\sigma_o$ refers to the equilibrium ionic conductivity, $\Delta E_A$ is the activation energy for ion migration across grain boundaries, $p_{O_2}$ is the partial pressure of the adsorbed gas (in this case, oxygen) and $n$ is a value between 4 and 6 [17].

2.4.1 Mechanism of Gas Sensing in Bulk Semiconducting Oxides

Bulk semiconductor oxide gas sensors are usually polycrystalline materials with grain sizes ranging from 10 to 100 nm [55]. Fig. 11 is a schematic of grains of $n$-type polycrystalline powder in contact. The depletion region around the surface of each grain is denoted and each grain is assumed to be covered with a chemisorbed oxygen layer indicating exposure to an oxygen atmosphere. For electronic conduction, electrons must possess sufficient energy to pass from one grain to another. The adsorbed oxygen withdraws electrons from the bulk lattice, resulting in the formation of negatively charged oxygen ions on the surface and positively charged donor ions near the surface. This causes the upward band bending as seen in Fig. 11. An electric field develops between the positive donor ions and the negatively charged adsorbed oxygen ions resulting in the depletion of charge carriers near the surface. As a consequence, a potential barrier forms between the boundaries limiting the transport of charge carriers between neighboring grains.
Figure 11: $n$-type polycrystalline semiconductor powder (above). Adsorbed oxygen results in the formation of a space charge region depleted of electrons. The corresponding band diagram is shown below, indicating the potential barrier for charge transport across neighboring grains. [12]

The interfacial potential barrier $qV_s$ and the thickness $L$ of the depletion layer are given as [56]

$$V_s = \frac{2\pi Q_s^2}{\epsilon N_d} = \frac{2\pi (qN_s)^2}{\epsilon N_d} \quad (13)$$

$$L = L_D \left( \frac{qV_s}{kT} \right)^{1/2} \quad (14)$$

$$L_D = \left( \frac{\epsilon kT}{2\pi q^2 N_d} \right)^{1/2} \quad (15)$$

where $Q_s$ refers to the surface charge density, $\epsilon$ is the dielectric constant of the
material, $N_d$ is the concentration of donor impurities, $q$ is the charge on the surface states, $N_s$ is the density of the charged surface states, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $L_D$ refers to the Debye length. The magnitude of $V_s$ increases with increasing adsorbed oxygen on the surface. The concentration of electrons in a grain, $N_s$ with sufficient energy to surmount the potential barrier and reach a neighboring grain, thus participating in conduction, is given as

$$N_s = N_d \exp \left( -\frac{qV_s}{kT} \right)$$  \hspace{1cm} (16)

Since the conductivity is directly proportional to $N_s$, an increase in the adsorbed oxygen increases $qV_s$, and as a result, a majority of the electrons do not have sufficient energy to surmount the barrier, resulting in fewer electrons contributing to the conductivity. This can be monitored as an increase in the resistivity of the sample in the presence of adsorbed oxygen. Introduction of a reducing gas such as hydrogen, donates electrons to the bulk lattice, effectively reducing the height of the potential barrier $qV_s$ and decreasing the resistivity of the sample.

### 2.4.2 Free Carriers in Semiconducting Oxides During Chemisorption

The role of conductivity modulation by the interchange of electrons during the chemisorption of oxygen on an $n$-type material can be understood by considering the following equation

$$O_2^{(g)} + 2e^- \rightleftharpoons 2O_{\text{chemisorbed}}^-$$  \hspace{1cm} (17)

The low electron affinity of oxygen (1.465 eV [57]) compared to ZnO (4.35 eV [58]) causes a transfer of electrons from the interstitial zinc impurities near the surface to the adsorbed oxygen resulting in the conversion of the chemisorbed
oxygen atoms into oxygen ions on the surface. This increase in net negative charge can be confirmed by a change in the electrical conductivity of the semiconductor material.

At high temperatures, the role of oxygen on the surface of a semiconducting oxide is much different than that at low temperatures. The mobility of ionized impurities $\mu_i$ can be empirically described as [51]

$$\mu_i \propto \frac{T^{3/2}}{N_im_i^{1/2}}$$  \hspace{1cm} (18)

In Eq. (18), $N_i$ refers to the concentration of ionized impurities (in cm$^{-3}$) and $m_i^*$ is the effective mass of the impurities. Due to an increase in the mobility of ions at higher temperatures, these metal ions can diffuse from the bulk regions to the surface in the presence of oxygen and can react with the chemisorbed oxygen increasing the concentration of oxide ions at the surface. As a result, the number of ion and electron defects increases or decreases with increasing oxygen partial pressure, depending on the nature of the semiconducting material. The Kröger and Vink notation can now be introduced [59]. A defect can be characterized by the charge it carries relative to the surrounding lattice. This relative charge can be denoted by a superscript associated with the defect charge. According to this notation, a dot (\textsuperscript{*}) denotes a single positive charge, whereas a prime (\textsuperscript{\prime}) denotes a single negative charge. Neutral charges are expressed with an $x$ (\textsuperscript{x}) or without any superscript associated with the defect charge. The lattice site of the defect is denoted with a subscript, with $i$ (\textsubscript{i}) denoting an interstitial atom and $V$ denoting a vacancy site [8]. Using this notation, reactions involving the chemisorption of oxygen and hydrogen on the surface of ZnO and CuO can be expressed.

For example, in the case of a $p$-type semiconductor such as CuO, the oxygen
chemisorption reaction can be written as [60]

\[ \frac{1}{2} O_2^{(g)} \rightleftharpoons CuO + V_{Cu}'' + 2h^+ \]  \hspace{1cm} (19)

In the presence of the adsorbed oxygen, we see from Eq. (19) that the concentration of copper ion vacancies $V_{Cu}''$ as well as the concentration of holes increases within the semiconducting material.

Semiconducting oxides containing an excess of metal ions, resulting in $n$-type behavior do not behave as their $p$-type counterparts. For example in ZnO, there exists an excess of metal ions in the form of interstitial zinc ions such as $\text{Zn}^\bullet$ or $\text{Zn}^{**}$, with an equivalent number of quasi-free electrons. For high temperatures, the reaction of chemisorbed oxygen on ZnO can be written as [48]

\[ \frac{1}{2} O_2^{(g)} + \text{ZnO}^{**} + 2e^- \rightleftharpoons \text{ZnO} \]  \hspace{1cm} (20)

The above reactions results in the dependence of the electrical conductivity of ZnO and CuO on the partial pressure of oxygen. Similarly, ZnO and CuO can also be used to detect the presence of a reducing gas such as hydrogen. For ZnO, the following reactions can occur [61]

\[ 2e^- + O_2 \rightleftharpoons 2O^-_{\text{chemisorbed}} \]  \hspace{1cm} (21)

\[ 2O^-_{\text{chemisorbed}} + 2H_2 \rightleftharpoons 2H_2O + 2e^- \]  \hspace{1cm} (22)

The reaction of $H_2$ with the chemisorbed oxygen on the surface of ZnO in Eq. (22), results in a reduction in the resistivity of the sample due to an increase in the quasi-free electrons. Similarly, the reaction of $H_2$ gas with the chemisorbed
oxygen on the surface of CuO can cause a decrease in the resistivity [12] of the sample due to an increase in the concentration of quasi-free holes in the sample as shown in Eq. (24)

\[ 2H_2 + 4h^+ \rightleftharpoons 4H^+ \]  

(23)

\[ 2O^{\text{chemisorbed}}_\text{chemisorbed} + 4H^+ \rightleftharpoons 2H_2O + 4h^+ \]  

(24)

2.4.3 Role of Surface States during Chemisorption

An alternate theory on the operation of semiconductor oxide gas sensors is the reaction between the chemisorbed gaseous species and surface states on the semiconductor [62] [44]. Surface states can either be of donor or acceptor type. A donor defect state occupied by an electron is a neutral state. By giving up an electron, the defect is occupied by a hole and can become positively charged. Similarly, an acceptor defect can be either in the neutral state - occupied by a hole or, by accepting an electron, can become negatively charged. The appearance of these surface states introduces charge transfer between the bulk bands and the surface in order to establish thermal equilibrium. This can be illustrated by considering the band diagrams in Fig. 12. The left most figure Fig. 12(a) is an energy band diagram for an undoped, or intrinsic semiconductor with a band of surface states, assumed to be neutral acceptor type, distributed in the band gap. Charge neutrality in an intrinsic semiconductor requires that the Fermi level is in the middle of the band gap, and as a result, the band of surface states is half full and centered close to mid-gap, between the conduction and valence bands. If the sample is doped n-type, the Fermi level shifts towards the conduction band minimum \(E_c\). Since the surface states are at a lower energy level, electrons vacate the higher energy
bulk levels and populate the lower lying surface states, as shown in Fig. 12(b). Charge transfer proceeds until thermodynamic equilibrium is reached between the surface states and the bulk. The Fermi level drops from the equilibrium value and becomes pinned to within a narrow energy range around the surface state and is now independent of the bulk doping density, $N_d$.

This charge transfer causes the acceptor surface state to acquire a negative charge with positively charged donors near the surface, resulting in the formation of a space charge layer.\(^1\). Shown in Fig. 12(c), the space charge layer consists of the uncompensated donor ions and solving Poisson’s equation provides the width $W$ as \[63]\]

$$W = \left[ \frac{2\kappa_o \epsilon_o V_s}{q N_D} \right]^{1/2}$$

(25)

Similarity, the charge density, $N_s$ of the acceptor surface states is given by \[63]\]

$$N_s = WN_d = \left[ \frac{2\kappa_o \epsilon_o V_s N_d}{q} \right]^{1/2}$$

(26)

A consequence of the charge transfer is the resulting band bending close to the surface, as shown in Fig. 12(c), since the carrier density in the vicinity of the surface deviates from that of the equilibrium bulk value. The resulting space charge region can have three different configurations

- **Accumulation** - where the majority carrier concentration at the surface is larger than the bulk value.

\(^1\)The formation of this surface space charge or depletion layer is different from the formation of a depletion layer due to the chemisorption of oxygen on the surface of a semiconducting oxide. The chemisorbed oxygen withdraws electrons from the bulk lattice, whereas, the surface states provide lower energy levels for the electrons to populate.
• Depletion - where the majority carrier concentration at the surface is smaller than the equilibrium, but larger than the minority carrier concentration at the surface.

• Inversion - where the majority carrier concentration at the surface is smaller than the minority carrier concentration at the surface.

An accumulation layer arises when surface states are close to the majority carrier band and majority carriers are injected into the bulk material rather than being extracted. For an $n$-type material, this leads to a build-up of positive charge on the surface and extra electrons near the surface. Conversely for a $p$-type material, since the Fermi level is close to the valence band, electrons flow from the surface state to the bulk bands, resulting in a positive charge near the surface (a hole) and a negatively charged surface. The accumulation layer can be shown to be related to highly reactive adsorbates which seldom occur in gas sensors [12].

![Energy band diagram for surface states. (a) Energy band for an intrinsic semiconductor with surface states located at mid-gap, (b) Energy band for $n$-type semiconductor with arrow indicating flow of electrons, (c) Transfer of electrons leads to a space-charged region due to negatively charged surface state and positively charged ionized donors resulting in band bending.](image)
The formation of an inversion layer at the surface can have dramatic effects, including changing the conductivity type of the surface. This layer can form if strong acceptor surface states extract electrons in an $n$-type material, or donor states inject electrons in a $p$-type material. When chemisorption of an electronegative gas such as $O_2$ occurs on an $n$-type semiconductor in the form of negative ions, there is an increase in the net negative charge on the surface states. To maintain charge balance, this is compensated by a positive space charge in the surface barrier between the surface and bulk of the semiconductor. As the negative surface charge $N_s$ increases, the surface barrier $V_s$ increases in accordance with Eq. (26). Visually, it can be understood by considering Fig. 12(c), wherein increasing $V_s$ shifts the bulk Fermi level $E_{Fb}$ down in the band gap. When $qV_s > E_g/2$, the Fermi level becomes closer to the valence band than the conduction band. As $V_s$ increases further, the concentration of holes in the $n$-type material becomes larger, until the concentration of minority carrier holes exceeds the concentration of majority carrier electrons and the surface becomes inverted [12].

2.5 The Materials - Zinc Oxide and Copper Oxide

2.5.1 Zinc Oxide

Zinc oxide ($ZnO$), an $n$-type semiconductor belonging to the II-VI group of semiconductor materials has an average atomic weight of 40.69. Under equilibrium conditions, $ZnO$ crystallizes into the wurtzite structure with lattice parameters, $a = 3.25$ Å and $c = 5.211$ Å at 298 K and a melting temperature of 2248 K [64]. The crystal structure of wurtzite $ZnO$ is shown in Fig. 13. The $ZnO$ hexagonal lattice is characterized by two interconnecting sublattices of zinc and oxygen atoms such that each $Zn$ atom is surrounded by a tetrahedral arrangement of oxygen atoms and vice versa. This tetrahedral coordination gives rise to polar symmetry along
the hexagonal (c) axis which is responsible for the exotic properties of ZnO such as piezoelectricity and spontaneous polarization along the c-axis [65].

![Wurtzite crystal structure of ZnO.](image)

Figure 13: Wurtzite crystal structure of ZnO. [66]

Bulk ZnO is characterized by a band gap of 3.2 eV at room temperature and 3.44 eV at 4 K [67], while the optical band gap measured on thin films provides a value close to 3.3 eV at 300 K [68]. The electronic band structure of ZnO calculated using a semi-empirical tight-binding model is shown in Fig. 14. The valence band maximum as well as the lowest conduction band minima occur at the Γ point at \( k = 0 \), confirming the direct band gap nature of ZnO. According to Jagadish et al. [65], the six bands from -5 eV to 0 eV correspond to O 2p bonding states. The bands from 5 eV to 10 eV correspond to empty Zn 3s levels and the O 2s bands occur close to -20 eV. The carrier effective mass in ZnO is isotropic and equal to 0.24m_0 and 0.59m_0 for electrons and holes, respectively [67].

The electrical properties of ZnO bulk ceramics and thin films have been widely
investigated by Natsume et al. and Mridha et al. [70] [71] [72]. The equilibrium carrier concentration varies widely according to sample quality but can be assumed to be between $10^{15} - 10^{16}$ cm$^{-3}$ [73] with donor densities as high as $\approx 10^{21}$ cm$^{-3}$ reported by Liu et al. for ZnO nanostructures [74]. The electron Hall mobility at 300 K for $n$-type ZnO is $\mu_n = 200$ cm$^2$/V.s [64]. Using spectroscopic ellipsometry techniques, the static dielectric constant was determined by Sun et al. to be 8.65 with an index of refraction close to 2.01 [75]. Table 1 lists the common properties of ZnO.

ZnO is widely used as a key element in many industrial manufacturing processes including pharmaceuticals, batteries [76], electrical equipment and sunscreen. With recent developments of ZnO nanostructures, epitaxial layers, and nanoparticles, ZnO is proving to be a highly functional material in numerous exotic applications. ZnO-based nanostructures, including nanoparticles and nanowire
arrays, are used in a variety of applications from flat screen displays to chemical and biological sensors. The direct, wide bandgap nature of ZnO creates substantial interest for light emission in the near-UV (≈ 370 nm) range and therefore in the development of blue LEDs. Epitaxial and single crystal ZnO can be of interest as substrates in the development of optoelectronic, piezoelectric and spintronic devices. Transparent ZnO thin films doped with aluminum, gallium or indium possess high electrical conductivity for use as transparent conductive electrodes in solar cells and in display devices.

### 2.5.2 Copper (II) Oxide

Among the II-VI compounds of the periodic table, oxides, sulfides, selenides, and tellurides of copper and silver are of great interest in semiconductor physics. The two main oxides of copper are cuprite (Cu$_2$O) and tenorite (CuO). The dependence of oxygen pressure and temperature on the composition of copper oxide films is shown in Fig. 15. For temperatures above 200 °C and pressures of 1 atm (≈ 1
bar), the CuO phase is the stable, whereas Cu$_2$O is stable under lower pressures and higher temperatures.

![Temperature-pressure plot showing regions of Cu$_2$O and CuO formation for bulk samples.](image)

Figure 15: Temperature-pressure plot showing regions of Cu$_2$O and CuO formation for bulk samples. [79] [80].

Cupric (II) oxide (CuO) is a $p$-type semiconducting material which crystallizes in the monoclinic crystal structure with lattice parameters $a=4.69$ Å, $b=3.43$ Å, and $c=5.13$ Å. The crystal structure for monoclinic CuO is shown in Fig. 16. The atomic arrangement is such that each atom is linked to four neighbors of the opposite kind. In the (100) plane, each copper atom is linked to four coplanar oxygen atoms at the corner of a rectangular parallelogram and each oxygen atom is linked to four copper atoms in the form of a distorted tetrahedron [81].

CuO is a direct band gap material with an optical band gap between 1.2 - 1.5 eV [4]. The electronic band structure of CuO using a self-consistent orthogonalized linear combination of atomic orbitals was calculated by Ching et al. and is shown in Fig. 17. The characteristic $p$-type nature of CuO can be attributed to the existence of intrinsic hole states at the top of the valence band.

Figueiredo et al. investigated the effects of annealing on the properties of CuO
thin films. The authors reported a carrier concentration of $\approx 4 \times 10^{16} \text{ cm}^{-3}$ when annealed at 200 °C which increased to $\approx 7 \times 10^{17} \text{ cm}^{-3}$ when annealed at 450 °C. Bulk CuO samples investigated by Samokhvalov et al. exhibited a mobility of $< 0.1 \text{ cm}^2/(\text{V.s})$ [82]. The properties of CuO are listed in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_o$</td>
<td>4.68 Å</td>
<td>[64]</td>
</tr>
<tr>
<td>$c_o$</td>
<td>5.13 Å</td>
<td>[64]</td>
</tr>
<tr>
<td>Density</td>
<td>6.31 $gm/cm^3$</td>
<td>[73]</td>
</tr>
<tr>
<td>Melting point</td>
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<td>[73]</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
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<tr>
<td>Static dielectric constant</td>
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<td>[73]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.4</td>
<td>[83]</td>
</tr>
<tr>
<td>Band gap</td>
<td>1.21 - 1.55 eV, direct</td>
<td>[4]</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>$0.24 m_o$</td>
<td>[64]</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for p-type conductivity</td>
<td>0.1-10 $cm^2/\text{Vs}$</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Table 2: Properties of CuO

CuO is a key component of a family of high temperature superconductors, yit-
Figure 17: Band structure of monoclinic CuO [81]

Tritium barium copper oxide (YBCO). Among the various commercial applications of YBCO, the largest market share is in the field of tunable microwave devices such as filters, mixers, phase shifters and delay lines. Other applications of YBCO include fault current limiting switches used to protect electric grids against short circuits and over currents [84] [85] as well as in superconducting quantum interference devices (SQUID) [86] and magnetic resonance imaging (MRI) receiver coils [87]. CuO displays high absorption in the visible regions making it an interesting candidate for applications as a selective absorber material for solar cells [88] [89].

2.6 Bulk Heterocontact and Thin Film Heterostructure Gas Sensors

The following section provides a brief review of bulk and thin film heterocontact gas sensors.

2.6.1 Bulk p-n Heterocontact Gas Sensors

The application of heterocontacts in the field of gas detection was first introduced by Namakura et al. in 1986 [5]. Using bulk p-type CuO and n-type ZnO pellets
pressed together to form a mechanical contact, the authors were able to show a change in resistance in the presence of gases such as carbon monoxide (CO), hydrogen (H₂) and propane (C₃H₈). This heterocontact device showed high sensitivity and selectivity towards CO gas, and the sensitivity towards the gas was 2-3 times greater than hydrogen gas or propane. The optimum working temperature for this device for CO gas detection was shown to be around 260 °C which is considerably lower than previously reported values of 500-700 °C for ZnO bulk ceramic gas sensors [90].

While Namakura et al. were able to show a pronounced sensitivity increase for CO compared to the response for H₂, further research indicated that the act of mechanical pressing caused instability in the system and reproducible results were difficult to obtain [91] [6]. As a result, Choi et al. used a layered structure comprised of ZnO+SnO₂ and CuO. The samples were doped with Al₂O₃ as a donor additive to increase the sensor response [92]. The authors demonstrated that the Al-doped ZnO+SnO₂/CuO heterocontact structure had a two-fold increase in the CO sensitivity compared to the bulk ZnO+SnO₂ case or the ZnO+SnO₂/CuO heterocontact case. Since semiconducting oxide gas sensors are sensitive to oxidizing gases, distinguishing between different flammable gases such as CO, H₂ and propane can be difficult [93]. To overcome this limitation, sensing properties of a device can be tuned to distinguish between CO and H₂ gases by using impedance analysis measurements. Selecting a specific measurement frequency and applied dc bias can optimize the response for the target gas [94].

By understanding bulk doping effects in ZnO and CuO, Aygün et al. demonstrated an increase the sensitivity of CuO/ZnO heterocontact sensors to hydrogen gas. Here, polycrystalline samples of ZnO and CuO were doped with different mole
fractions of monovalent and divalent dopants, such as lithium (Li), sodium (Na), strontium (Sr), calcium (Ca) and nickel (Ni). Pellets were subsequently formed by pressing the powders under high pressure. Heterocontacts were formed by mechanically pressing the two pellets using the spring force of a conductivity cell. Along the interface of the heterocontact, porous structures with gaps ≈ 20 μm enabled the adsorption of hydrogen gas on the p- and n-type ceramics [94]. The authors reported that the undoped CuO/ZnO heterocontact exhibit strong rectification characteristics under forward bias conditions, i.e. when a forward bias was applied to CuO and a negative bias to ZnO. The additions of Na and Li were shown to increase the sensor response. The forward current in the presence of H₂ gas compared to air increased with increasing mole fractions of the Li dopant while decreasing the reverse leakage current. While the addition of Ni lowered the forward current, the I-V characteristics in the presence of air was greatly reduced increasing the sensitivity towards H₂ gas. The authors proposed the following reaction occurring near the heterocontact interface [94]

\[ \text{ZnO} : \ O_2 + 2e^- \rightarrow 2O^- \] (27)

\[ \text{CuO} : \ 2H_2 \rightarrow 4H^+ + 4e^- \] (28)

\[ \text{Interface} : \ 4H^+ + 2O^- \rightarrow 2H_2O \] (29)

The porosity dependence on the sensitivity of ZnO/CuO heterocontacts was investigated by Tongpool et al. in 2000. ZnO and CuO powders were compacted together and sintered at high temperatures to study the sensitivity difference between dense and porous heterostructures. While both devices exhibited a change in the I-V characteristics in the presence of hydrogen gas, the magnitude of the re-
sponse in the presence hydrogen gas was much more pronounced in the porous case compared to the dense structures [95]. This can be understood by the fact that the porous sample provides an easier path for the gas to reach the heterostructure interface as opposed to a circuitous path in the dense case reflecting the enhancement of sensor response due to the porous microstructure.

### 2.6.2 Thin Film Heterostructure based Gas Sensors

Thin film CuO/ZnO heterojunctions fabricated via r.f. magnetron sputtering techniques were first investigated by Baek et al. in 1995. Undoped polycrystalline ZnO was used as the substrate and CuO was reactively sputtered to form a thin film layer above the ZnO bulk plate. The rectifying nature of the I-V characteristics under forward bias at room temperature confirmed the formation of a p-n heterojunction between the two materials. The authors demonstrated that the forward bias current increased correspondingly with decreasing oxygen partial pressure which indicated a close correlation between the barrier height formed as a consequence of the adsorbed oxygen at the surface [96]. The authors constructed an energy band diagram for the CuO/ZnO heterojunction using material values previously reported; however, they did not include non-ideal contributions from interface states.

The effect of interface states on the gas sensing properties of a CuO/ZnO heterojunction was first investigated by Yanagida et al.. Using sputtering techniques, the authors fabricated two types of structures. In the first type (type I), a CuO layer was first deposited on a bottom gold contact and was exposed to air before a ZnO layer was sputtered over the CuO. In this case, adsorbates such as oxygen ions are assumed to exist on the surface of the CuO layer affecting the interface properties. The second type (type II) was such that the CuO and ZnO layers
were sputtered continuously. The type I device showed high selectivity towards CO and H₂ at temperatures between 100 °C and 200 °C. The type II junctions on the other hand, displayed no current increase in the presence of gases such as CO and H₂ at any temperature. The authors attributed the difference in behavior to the combination of the CO molecules adsorbed on the CuO surface as well as the oxygen ions close to the interface between the two junctions [97]. By modeling interface states as a single layer between the CuO and ZnO junctions, the authors accounted for the role of interface states in an energy band diagram for the system. They proposed that tunneling or recombination current mechanisms through the interface states, rather than injected carriers under forward bias, would dominate the I-V characteristics.

The low cost of precursor material and easy control of composition quickly spurred a family of gas sensors fabricated using the sol-gel methodology. Mridha et al. fabricated CuO/ZnO heterostructures by depositing CuO on a ZnO layer in 2006 [98]. The x-ray diffraction scans show the presence of wurtzite ZnO peaks and tenorite CuO peaks with no mixed phases or impurity peaks. While the device displayed small current conduction from room temperature to 200 °C, strong rectification characteristics were observed at temperatures between 200 °C and 300 °C. Sensitivity in the presence of H₂ gas at temperatures above 250 °C was 4-5 times that at lower temperatures which the authors attributed to enhanced H₂ adsorption and additional transport mechanisms such as defect-assisted-tunneling and recombination in the space charge regions via interface states [98].

Dandeneau et al. fabricated thin film heterostructure ZnO/CuO thin films to investigate the role of crystallinity and porosity on the sensitivity in the presence of hydrogen gas. The authors focused on optimizing the porosity as well as the
crystallinity of the component oxide films by varying the pyrolysis and annealing temperatures. Optimum porosity and crystallinity of the ZnO and CuO thin films was obtained when the films were pyrolyzed at 250 °C and annealed at 800 °C. The authors fabricated two configurations of planar heterostructure gas sensors - ZnO on CuO and CuO on ZnO. They demonstrated that devices incorporating CuO as the top layer increased the conductivity response since the CuO layer displayed higher porosity which provided an easier path for the target gas to interact with the heterostructure interface [8]. The limited solubility between ZnO and CuO [99] can be exploited to fabricate gas sensors with increased sensitivity. To this effect, Dandeneau et al. reported ZnO/CuO mixed solution thin films displaying a mesh of individual ZnO wurtzite with CuO monoclinic crystal structures and proposed the fabrication of gas sensors based on the mixed solution route. Their work formed the motivation for this study on the construction and fabrication of ZnO/CuO mixed solution hydrogen sensors.

2.7 Sol-Gel Fabrication

The sol-gel method of fabricating thin films is a low-cost wet chemical technique used to prepare inorganic metal oxide thin films. Using lower processing temperatures, the fabricated films result in high homogeneity and purity of the resulting materials [100]. The chemistry of the solution used in the fabrication determines the final film properties. This can be used to design materials with specific mechanical, optical, electric and physiochemical properties [101]. Sol-gel synthesis provides a degree of control of the composition and structure at the molecular level and offers an economical alternative to expensive vapor deposition techniques used in the manufacturing of coatings and fibers. This technique can be used to fabricate ceramic powders, thin films, fibers and coatings making it advantageous
in a variety of applications. A diagram of the sol-gel process is shown in Fig. 18.

![Diagram of the sol-gel process](image)

**Figure 18:** Basic schematic of the sol-gel process [102]

A sol is a stable suspension of solid colloidal particles in a liquid. Colloids can be defined as solid particles with diameters of 1-100 nm [103] that are evenly dispersed within another substance. Milk, for example, is a colloidal suspension with colloidal fat globules dispersed within a water-based fluid [104]. A gel is a porous, interconnected, rigid network of the sol in a liquid phase. The gel forms when the homogeneous dispersion present in the initial sol rigidifies through a process known as gelation. This prevents the development of inhomogeneities within the material [102]. A sol abruptly changes from a viscous liquid state to a solid gel phase at a particular temperature range known as the gel-point. There are six important processes during sol-gel synthesis listed below [105]:

1. **Precursors**
2. **Chemistry**
3. **Solution**
4. **Colloidal Gel**
5. **Drying**
6. **Polymeric Gel**
7. **Sintering**
8. **Ceramic**
• **Hydrolysis:** This process begins with a mixture of a metal alkoxide and water in an alcohol solvent at ambient or slightly elevated temperatures. This mixture forms the precursors which define the final properties of the resulting sol-gel.

• **Polymerization:** This step, taking place at higher temperatures, involves the elimination of organic molecules such as water and alcohols resulting in the condensation of adjacent molecules and forming metal oxide linkages in the liquid sol.

• **Gelation:** In this step, the polymeric networks link together forming a three-dimensional network throughout the liquid sol. Here, solvents are removed from the sol and the resulting film becomes rigid, forming a gel.

• **Drying:** Organics such as water and alcohols are removed at moderate temperatures ($T < 400$ °C), leaving behind a hydroxylated metal oxide with a residual organic component.

• **Dehydration:** This step is carried out at temperatures greater than the drying step, generally between 400 K and 800 K in an effort to drive out any organic residues and chemically bound water.

• **Densification:** This final anneal step is carried out at high temperatures to provide the metal oxide lattice formed during the dehydration step with sufficient thermal energy to crystallize and to promote grain growth.

While these are common processing steps during sol-gel fabrication, based on the necessary application, the last three steps may or may not be strictly followed. For example, the gel formed as a consequence of the gelation step can be processed
by two methods. In a single stage process, the gel is rapidly heated to a crystallization temperature wherein, the rapid elimination of organic molecules as well as the crystallization of the gel take place simultaneously [8]. This process results in the formation of densely packed thin films. During a two-stage process, the first drying step, known as pyrolysis, occurs at temperature ranges between 200 °C - 400 °C [8]. This drying step involves the burning out of organic molecules from the liquid sol leaving behind open pores in the film. The second densification step occurs at temperatures above 500 °C which provides sufficient thermal energy to promote grain growth and crystallize the metal oxide crystal lattice.
3 Experimental

This chapter provides an overview of the materials and techniques used in the fabrication of the mixed solution thin films and gas sensor devices.

3.1 ZnO and CuO Precursor solutions

The ZnO precursor solution is formed by mixing 2.6337 gms of zinc acetate dihydride \([\text{Zn(OOCCH}_3\text{)}_2\cdot\text{2H}_2\text{O}, \text{Alfa Aesar}, 98.0-101.0\%]\) with 19.28 ml of 2-methoxyethanol (MOE: \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}, \text{Alfa Aesar, 99.3}\%\)) and 0.72 ml of monoethanolamine (MEA: \(\text{COCH}_2\text{CH}_2\text{NH}_2, \text{Alfa Aesar, 99+}\%\)). These precursors are stirred at 300 rpm for 60 mins at a constant temperature of 60 °C. In this case, MOE is used as a solvent with zinc acetate dihydride as the metal-oxide solute and MEA acting as a stabilizing agent.

The CuO precursor solution is formed by mixing 0.9982 gms of copper (II) acetate monohydrate \([\text{Cu(OOCCH}_3\text{)}_2\cdot\text{H}_2\text{O, Alfa Aesar, 98.0-102.0}\%]\) with 17.6 ml of 2-Propanol \([\text{(CH}_3\text{)}_2\text{CHOH (IPA): C}_3\text{H}_7\text{OH, Alfa Aesar, 99}\%\)], 1 ml of polyethylene glycol 400 \([\text{H(OCH}_2\text{CH}_2)_n \text{OH (PEG): Alfa Aesar}], 1\text{ml of MEA and 0.4 ml of de-ionized (DI) water. These precursors are stirred at 300 rpm at room temperature for 90 mins. IPA is added as a solvent. MEA is added as a stabilizing agent with DI water serving to facilitate hydrolysis of the solute [8]. PEG is added to the CuO precursor to maintain solution viscosity and, in this case, copper (II) acetate monohydrate is the metal-oxide solute.}

The two precursor solutions are mixed with the molarity held constant at 0.6 M for the ZnO solution and 0.25 M for the CuO solutions. 6 ml of the ZnO precursor solution and 14.4 ml of the CuO precursor solution were mixed together and stirred at 300 rpm at room temperature for 10 mins to obtain the CuO-ZnO
mixed solution. The values used to mix the precursor solutions were such that a 1:1 molar ratio of Cu : Zn atoms in the mixed solution was achieved. The mixed solution was aged overnight prior to the fabrication of thin films.

3.2 Mixed Solution Film Deposition

3 ml syringes (Norm-Ject, Henke Saas Wolf) along with 0.2 μm (Fisherbrand) filters were used to deposit the solutions via a drop-by-drop methodology. 125 mm, <100> p-type silicon wafers (Sumco Corp., USA) were cut using a diamond scribe into 1.5 cm x 2.5 cm rectangles for use as substrates for structural and gas sensing characterization. Optical and electrical characterization was accomplished on quartz substrates cut into dimensions of 1.5 cm x 2.5 cm.

Each substrate was rinsed in individual beakers with acetone in an ultrasonicator and cleaned using standard clean room cleaning procedures. Each substrate was rinsed using acetone, IPA, and DI water (a standard AMD clean) and dried using N₂ gas prior to solution deposition. The deposition of the mixed solution was performed via the spin-coating technique, using a standard spin coater (Laurel Technologies Corporation) and spinning the substrates at 3000 rpm for 30 s. The initial pyrolysis step took place on a hot plate at 300 °C for 5 mins. The substrates were then allowed to cool to room temperature before depositing the following layer. The final annealing step took place in an open furnace at 800 °C for an hour, after which the substrates were cooled down to room temperature. 15 layers were deposited to characterize the structural and gas sensing response while 10 layers were deposited for the optical and electrical characterization. The process flow followed in the fabrication of the mixed solution thin films is shown in Fig. 19.
3.3 Electrode Fabrication

Electrodes used to characterize the electrical and gas sensing properties were fabricated using the *lift-off* technique. This simple method is commonly used to pattern electrodes on thin films. A mask design is initially patterned on a substrate using photolithographic techniques following which a metallic layer is blanket-deposited over the patterned substrate covering the resist as well as the areas in which the resist has been removed. The term *lift-off* comes from the fact that when the resist under the metal film is removed using a solvent, the metal layer above the resist is also removed, leaving behind metal only in the exposed regions of the thin films.

Following an AMD clean, the films were dried using N\textsubscript{2} gas. Shipley 1818 posi-
tive photoresist (Microposit S1818, Rohm & Harris Electronic Materials) was spin coated onto the thin films at 3000 rpm for 30 s using a standard spinner (Headway Research). The films were subject to an initial baking step at 85 °C for two minutes. Mylar masks containing the relevant mask designs were patterned onto the photoresist using an aligner (KSM Karl Suss MJB 3 Aligner) and exposed to UV light for eight seconds. Following the exposure step, the films were baked at 85 °C for three minutes and subsequently developed in a premixed 4:1 mixture of developer (Microposit 351 developer, Rhom & Harris Electronic Materials) solution: DI water for 15 s. The films were immediately rinsed with DI water to remove excess developer solution and dried using N₂ gas. The films were observed under a conventional microscope to ensure well developed features. 200 nm of aluminum metal was subsequently evaporated on the patterned films using a thermal evaporator source (Polaron thermal evaporator) at a pressure of 3 × 10⁻⁵ torr. The aluminum coated samples were placed in individual beakers using acetone as a solvent to perform the metal lift-off in an ultrasonicator.

Three different planar interdigitated electrode masks were designed each with electrode finger length of 4 mm. The finger widths of the three electrode designs were 150 μm, 200 μm and 250 μm with spacing between each fingers kept constant at 150 μm, 200 μm and 250 μm, respectively. The mask designs for the 150 μm, 200 μm and 250 μm finger width/spacing is shown in Fig. 20, Fig. 21 and Fig. 22. An optimized structure was then designed keeping the finger length at 4 mm and finger widths constant at 500 μm, and the spacing between fingers was sequentially increased from 500 μm to 750 μm, 1000 μm, 1250 μm and 1500 μm. This is shown in Fig. 23. To further increase the sensor response, three different interdigitated electrodes with finger lengths of 4 mm and finger widths and spacing of 250 μm,
500 µm and 750 µm, were designed to be fabricated on platinized-silicon (Pt-Si) silicon substrates with 150 nm of sputtered platinum. The Pt-Si layer serves as a bottom metal contact in this configuration. An example of this design is shown in Fig. 24. To measure mobility and resistivity of the thin films, a Van der Pauw cross structure was fabricated on fused-silica substrates. This design is shown in Fig. 25.

![Figure 20: Mask design for 150 µm finger width/spacing electrode.](image1)

![Figure 21: Mask design for 200 µm finger width/spacing electrode.](image2)
3.4 Mixed Solution Film Characterization

Structural characterization of the component oxide films as well as the mixed solution thin films was performed via $\theta$-$2\theta$ scans using a Bruker D8 Discover X-ray diffractometer (XRD) with Cu-K$_\alpha$ (1.54 Å) as the radiation wavelength source. The morphology of the films was characterized using an FEI Quanta 200 environ-
mental scanning electron microscope (SEM), and atomic force microscopy (AFM) images were obtained on a Digital Instruments Nanoscope IIIa using silicon nitride tips (Veeco). Optical parameters of the films were investigated using an Ocean Optics HR4000 spectrometer equipped with a Mikropak DH-2000-BAL deuterium tungsten halogen light source. Transmission and reflection spectra of the films were measured in the UV-visible spectral range and the absorption coefficient, $\alpha$ was calculated using [70]
\[ \alpha = -\frac{1}{d} \ln \left( \frac{\sqrt{(1 - R)^4 + 4T^2R^2} - (1 - R)^2}{2TR^2} \right) \]  

where \( T \) and \( R \) are the measured transmission and reflection coefficients and \( d \) refers to the film thickness. The index of refraction and thickness were measured using a variable angle spectroscopic ellipsometer. The electrical characteristics of the films such as mobility, carrier concentration and sheet resistance, were measured using the Van der Pauw technique (Lakeshore 7504).

3.5 Gas Sensor Characterization

The gas sensing characteristics of the mixed solution films were investigated via current-voltage (I-V) measurements in a NorECs Probostat high temperature conductivity cell. The schematic of the test structure is shown in Fig. 26.

Following electrode deposition, the thin films were fixed to alumina plates using silver conductive epoxy (Duralco 124). Platinum wires were subsequently fixed to the electrodes using the conductive epoxy to measure the I-V characteristics in the presence of the target gas. The silver epoxy was cured in a box furnace (Protherm PLF 120/7) for four hours at 121 °C and then at 176 °C for an additional four hours. Sensor characteristics were measured in the tube furnace at room temperatures as well as 250 °C in the presence of dry air (\( N_2:O_2 = 4:1 \), Airgas-Nor Pac Inc.,) and 4000 ppm of hydrogen (Airgas-Nor Pac Inc.,) as the target gas. The flow rate and concentrations of the gases were controlled using mass flow controllers (Omega, FMA 5400/5500) with a constant flow rate maintained at 200 sccm. The outlet of the gases was directed under a fume hood so as to not affect the sensor measurements. The films were heated from room temperature to the measurement temperature at a rate of 5 °C/min and were allowed to equilibrate.
for 30 mins before measurements were taken. Once the measurement temperature was reached and the system equilibrated, dry air (oxygen) was introduced into the conductivity cell for 30 mins following which I-V measurement were obtained in an oxygen environment. The dry air supply was then closed and the system was allowed to equilibrate for 30 mins. Hydrogen gas was then introduced into the conductivity cell for 30 mins and I-V measurements in a hydrogen environment was noted. A voltage source measurement unit (Keithley 237) was used to apply a bias to measure the current value.

![Experimental setup](image)

Figure 26: Experimental setup used to measure the I-V characteristics of the mixed- solution gas sensors. Adapted from [1]
4 Results and Discussion

4.1 Structural Characterization

In this section, the crystal structure of the component films and the mixed solution thin film is investigated. The morphology as well as the elemental composition of the films are studied.

4.1.1 X-ray Diffraction (XRD) Analysis

The x-ray diffractograms for a 10 layer ZnO, CuO and the mixed solution thin film pyrolyzed at 300 °C and annealed at 800 °C are shown in Fig. 27, Fig. 28, and Fig. 29. ZnO crystallizes in the hexagonal wurtzite structure with a characteristic (002) peak intensity which occurs at approximately $2\theta = 34.4^\circ$. This can be confirmed in Fig. 27, where a strong peak is observed at $2\theta$ value of $34.5^\circ$. The (002) peak is characteristic of a strong c-axis orientation of the ZnO grains, where the grains are oriented perpendicular to the substrate and is an indication of a highly crystalline thin film. Such a thin film is beneficial for gas sensing applications since it results in less scattering interactions with grain boundaries as an electron travels through the material and results in an increase in the electron mobility and enhances sensor response.

The XRD scan for a CuO thin film is shown in Fig. 28 and indicates the presence of a single tenorite phase (CuO) with no cuprite (Cu$_2$O) phase present. High intensity reflection peaks in the x-ray diffratogram occur close to $35.5^\circ$ and $38.7^\circ$ is in good agreement with previously reported values on CuO [8]. The CuO XRD scan (Fig. 28) has fewer counts and is nosier when compared to the ZnO XRD scan (Fig. 27). As mentioned earlier, the (002) peak is characteristic of a strong c-axis orientation of the ZnO grains and can dwarf the presence of other
Figure 27: XRD scan for a ZnO thin film. A high c-axis orientation corresponding to a 2θ value of 34.4° indicates the formation of a highly crystalline thin film.

Figure 28: XRD scan for a CuO thin film. The plot indicates that the CuO is the only phase present.
phases. CuO on the other hand, does not exhibit a strong preferential orientation and as a result exhibits an increased number of phases.

Fig. 29 is an XRD scan of a mixed-solution thin film. The phase separation between ZnO and CuO is visible in Fig. 29 confirming the existence of segregated ZnO and CuO grains. ZnO peak intensities occur at 2θ values of 31.6°, 34.4° and 36.4°, while those for CuO occur at 2θ values of 35.5°, 38.75° and 61.8°. While not present in Fig. 29, certain samples also exhibited reaction phases. These reflections were not quantified; however, Dandeneau suggested that these peaks could be attributed to silicon dioxide (SiO₂), zinc silicate (Zn₂SiO₄) [8] or copper reaction phases. To aid the eye, all three scans are shown in Fig. 30. Here, peak intensities from the individual ZnO and CuO thin films occur at the same 2θ values as the peaks in the mixed-solution thin film confirming the phase separation between the CuO and ZnO grains.

![XRD scan](image)

Figure 29: XRD scan for a mixed-solution thin film. The occurrence of the 2θ peaks matches the values of ZnO and CuO.
Figure 30: XRD scans for all three films. The plot compares the $2\theta$ values of ZnO and CuO and shows that they match the $2\theta$ values of the mixed-solution peaks.

4.1.2 Atomic Force Microscopy (AFM) Analysis

The morphology of the mixed-solution thin films was subsequently examined using AFM analysis. Fig. 31 is an AFM scan of the mixed solution thin film. Corresponding to the phase separation shown in the XRD scans, an interconnected network of ZnO and CuO grains is visible. Fig. 31(left) indicates the presence of a network of two dissimilar grains illustrating the existence of a coherent network of ZnO and CuO grains. Fig. 31(right) is a magnified image in the same area indicating the presence of ZnO surrounded by a matrix of CuO.

The topography of the film is not uniformly dense as seen in a three-dimensional AFM scan in Fig. 32. It can be noted in Fig. 31 and Fig. 32 that the larger
hexagonal shaped grains corresponding to ZnO are oriented with the $c$-axis which is perpendicular to the surface of the substrate and surrounded by a network of CuO grains. These figures also indicate the high interfacial contact area between the ZnO and CuO grains which is beneficial in gas sensing applications. This can be compared to the bulk heterocontact case wherein the majority of the gas sensing takes place in regions close to the interface between the two materials. Since these films exhibit a high degree of interfacial contact between ZnO and CuO grains, the space-charge region in this case extends throughout the film. This indicates an increase in the available interfacial regions to react with adsorbed oxygen and hydrogen, thus enhancing sensor response.

4.1.3 Scanning Electron Microscopy (SEM) analysis

The AFM images presented in the previous section as well as the XRD data presented indicate that the thin film comprises of a interconnected network of ZnO.
and CuO grains. In this section, scanning electron microscopy (SEM) as well as elemental analysis in the form of electron dispersive spectroscopy (EDS) confirms the existence of a porous network along with individual ZnO grains surrounded by a mesh of CuO (or vice-versa). The SEM image shown in Fig. 33 is a scan of the mixed solution thin film confirming the presence of hexagonal shaped ZnO grains surrounded in a matrix of almost circularly shaped CuO grains. The darker areas in Fig. 33 indicate gaps on the surface that are approximately 50-100 nm in length and indicate the presence of porous structures on the film. Dandeneau showed an SEM cross-section of the mixed solution thin film and demonstrated that these open pores do not necessarily extend throughout the sample as a single pore [8] but, can be connected via different pores to form a network extending throughout the thickness of the sample. The anneal step during the fabrication of the films is performed not only to provide the disorganized sol-gel network sufficient thermal energy to crystallize but to also promote grain growth. This is evident in Fig. 33 where smaller grains can be observed growing on larger grains. A magnified SEM
scan indicating the grain structure of ZnO and CuO along with the open pores is shown in Fig. 34.

Figure 33: 1 μm SEM scan of the mixed-solution thin film indicating the presence of hexagonal shaped ZnO grains surrounded by a matrix of circularly shaped CuO grains as well as open pores on the surface.

Figure 34: 200 nm SEM scan of the mixed-solution thin film indicating the presence of hexagonal shaped ZnO grains surrounded by a matrix of circularly shaped CuO grains.
4.1.4 Energy Dispersive Spectroscopy (EDS) Analysis

In order to quantify the elemental nature of the grains shown in Fig. 33 and Fig. 34 to visually confirm the phase separation between CuO and ZnO grains seen in the previous sections, elemental spectroscopy was performed via EDS measurements. Fig. 35 is an EDS scan where green, purple and yellow regions indicate the presence of silicon-rich, copper-rich and zinc-rich areas. Comparing the pores, or the darker regions in the raw SEM image with the silicon-rich areas, indicate that the open pores could extend through the depth of the sample to the silicon substrate. The bottom two figures in Fig. 35 confirm the presence of segregated grains of ZnO and CuO indicating the presence of a high interfacial area between the two grains. Fig. 35 also indicates the presence of ZnO and CuO grains in areas that are predominantly CuO or ZnO rich. This confirms the assertion that the grains are not columnar structures extending through the substrate, but instead are layered grains of CuO and ZnO. An overlay of the elemental plots of Cu and Zn is shown in Fig. 36b), with the SEM image taken prior to the EDS scan shown on the left. This figure, shown to aid the eye, indicates the presence of segregated grains of Cu and Zn. An EDS profile on a different area is shown in Fig. 37. While the morphology of the grains are different when compared to Fig. 35, the EDS profile once again indicates the presence of segregated Cu and Zn grains. An overlay of the elemental plots of Cu and Zn is shown in Fig. 38.

4.2 Optical Characterization

In this section, optical characterization of ZnO, CuO and the mixed solution thin film is presented.
Figure 35: EDS profile of mixed-solution film. (a) SEM scan of region prior to EDS scan, (b) elemental profile of silicon substrate, (c) elemental profile of copper, (d) elemental profile of zinc.

Figure 36: EDS overlay of Cu and Zn elemental plots. (a) SEM scan of region prior to EDS scan, (b) Overlay of Cu and Zn elemental plots. This figure indicates the segregation of phases between Cu and Zn.
Figure 37: EDS profile of mixed-solution film at a different location. (a) SEM scan of region prior to EDS scan, (b) elemental profile of silicon substrate, (c) elemental profile of copper, (d) elemental profile of zinc.

Figure 38: EDS overlay of Cu and Zn elemental plots. (a) SEM scan of region prior to EDS scan. b) Overlay of Cu and Zn elemental plots.

4.2.1 ZnO Thin Film Characterization

The optical transmission and reflection spectrum for a 10 layer ZnO film is shown in Fig. 39. The measured film was highly transparent (85-95%) in the visible region.
(300-800 nm) with a sharp fundamental absorption edge close to 370 nm. A Tauc plot used to extract the optical band gap value of ZnO is shown in Fig. 40. For a direct band gap material such as ZnO, the square of the absorption coefficient, $\alpha^2$ is plotted against the photon energy ($h\nu$) and the optical band gap can be determined from the extrapolated $x$-intercept [54]. From this plot, the optical band gap value can be determined as 3.28 eV which is consistent with previously reported values of ZnO thin films based on the sol-gel technique. Srikant et al. reported band gap values between 3.2 - 3.32 eV [3].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{transmission_reflection_spectra.png}
\caption{Transmission and reflection spectra of a 10 layer ZnO thin film. The film is highly transparent in the visible region and a sharp fundamental absorption edge can be seen close to 370 nm.}
\end{figure}

4.2.2 CuO Thin Film Characterization

The transmission and reflection spectra of a 10 layer CuO thin film is shown in Fig. 41. Consistent with the opaque nature of CuO thin films, the measured film
Figure 40: Tauc plot of a 10-layer ZnO thin film. The x-intercept provides an optical band gap of 3.25 eV.

has low transmission in the visible spectrum, reaching 50% at 780 nm and a peak transmission (70%) at 830 nm. The reflection spectrum in the same wavelength range ranged between 10 - 20% with a dip occurring at maximum transmission. Fig. 42 is a Tauc plot for the same film. Since CuO is a direct band gap material, the square of the absorption coefficient, $\alpha^2$ is plotted against the photon energy ($h\nu$) to extract the optical band gap value as 1.52 eV. Serin et al. have reported the band gap of CuO to range between 1.21 - 1.55 eV depending on the processing conditions [106].

4.2.3 Mixed-Solution Thin Film Characterization

The optical transmission and reflectance spectra for a 10 layer mixed-solution thin film is shown in Fig. 43. The mixed solution thin film, similar to the CuO film is opaque with a low transmission (10%), with the reflection spectrum reaching
Figure 41: Transmission and reflection spectra of a 10-layer CuO thin film. Peak transmission (70%) occurs at 830 nm.

Figure 42: Tauc plot of a 10-layer CuO thin film. The x-intercept provides an optical band gap of 1.52 eV.
60% at 800 nm and a maximum value occurring close to 800 nm. Since both ZnO and CuO are direct band gap materials, the square of the absorption coefficient, $\alpha^2$ is plotted against photon energy to extract the effective band gap of the mixed solution thin film. From this figure, the band gap value for the mixed solution film is 1.65 eV, a value closer to the band gap of CuO than ZnO.

![Graph](image)

Figure 43: Transmission and reflection spectra of a mixed-solution thin film. The film is opaque through the visible region, reaching peak transmission at wavelengths beyond 1000 nm.

### 4.3 Electrical Characterization

The electrical properties of the ZnO, CuO and mixed-solution thin film as measured using the Van der Pauw method are tabulated in Table. 3. The measured carrier concentration of the ZnO film is in good agreement with previously reported values of ZnO [71] [73] where carrier concentrations on the order of $10^{15} - 10^{17}$ cm$^{-3}$ have been observed. The carrier concentration values for CuO are not as widely reported
as ZnO, but the measured value of $3 \times 10^{16}$ cm$^{-3}$ is reasonably consistent with Baek et al. where the authors reported a carrier concentration of $2.1 \times 10^{17}$ cm$^{-3}$ [96]. The average carrier concentration and the Hall mobility for the mixed-solution thin film are on the order of both the ZnO and CuO values. The conductivity nature of the mixed solution thin film could not be accurately quantified. For a given sample, the carrier type varied between repeated Van der Pauw measurements while the sheet resistivity, carrier concentration and average Hall mobility values remained reasonably constant. To further investigate the conductivity nature of the mixed-solution films, Van der Pauw measurements as a function of film thickness could be performed to observe any trend with increasing number of mixed-solution layers. Since a 1:1 molar ratio of Zn:Cu atoms was used to fabricate the thin films, it would imply that there are an equal number of ZnO and CuO atoms and hence the properties of these film would be an average value of the individual properties.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>$n$-ZnO</th>
<th>$p$-CuO</th>
<th>Mixed Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet Resistivity, $\Omega/\square$</td>
<td>$5.6 \times 10^{-2}$</td>
<td>$7.74 \times 10^{-2}$</td>
<td>$4.58 \times 10^{-2}$</td>
</tr>
<tr>
<td>Carrier Concentration, cm$^{-3}$</td>
<td>$2.8 \times 10^{16}$</td>
<td>$6 \times 10^{17}$</td>
<td>$3.25 \times 10^{17}$</td>
</tr>
<tr>
<td>Hall Mobility, cm$^2$/V.s</td>
<td>165</td>
<td>0.96</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 3: Electrical properties of ZnO, CuO and mixed-solution thin films

This however is not the case for the measured carrier concentration, mobility and optical band gap values. The $n$-type nature of ZnO arises from an oxygen deficiency due to zinc interstitials or oxygen vacancies. The $p$-type nature of CuO, on the other hand, is attributed to a deficiency of Cu atoms resulting in an oxygen-rich stoichiometry. Since, in individual ZnO and CuO thin films, the oxygen deficiency or excess oxygen atoms was not quantified, it is difficult to predict how the role of oxygen atoms would alter the properties of the mixed solution thin films.

4.3.1 Energy Band Diagram Analysis

The energy band diagram for a $p$-type CuO and $n$-type ZnO heterojunction is modeled in this section. Fig. 45 shows isolated energy bands of $p$-type CuO and $n$-type ZnO. The parameters used to model the energy band diagram are shown in Table 4. The electron affinity ($\chi$) of ZnO is greater than CuO. As a result, the conduction band of ZnO is positioned lower in energy than the conduction band of CuO. The Fermi level of ZnO is higher than that of CuO, so when the two materials are brought together, charge transfer occurs from ZnO to CuO such that the Fermi level energies are equal. The energy band diagram of the two materials once they are brought into contact, separated by an interface, is shown in Fig. 46. Available interface states are shown as dashes in this figure.

Consistent with Fig. 11, the energy bands for the $p$- and $n$-type materials are
<table>
<thead>
<tr>
<th>Parameters</th>
<th>$p$-CuO</th>
<th>$n$-ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$</td>
<td>4.07</td>
<td>4.2</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>18.1$\epsilon_o$</td>
<td>8.65$\epsilon_o$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>1.5</td>
<td>3.2</td>
</tr>
<tr>
<td>$m_{de}^*$</td>
<td>0.93$m_o$</td>
<td>0.24$m_o$</td>
</tr>
<tr>
<td>$m_{dh}^*$</td>
<td>0.56$m_o$</td>
<td>0.59$m_o$</td>
</tr>
<tr>
<td>Carrier Conc.</td>
<td>$N_A = 6 \times 10^{17}$</td>
<td>$N_D = 2.8 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Table 4: Parameters to calculate CuO-ZnO heterostructure band diagram

separated by an interface layer which allows for the incorporation of adsorbed gases in the model. Based on the measured carrier concentrations for individual CuO and ZnO thin films, the equilibrium conduction and valence band discontinuities were calculated as $\Delta E_C = 0.13$ eV and $\Delta E_V = 1.57$ eV respectively. The built-in voltage was calculated as 1.23 V. Transfer of electrons between the Fermi levels of the two materials is known as Fermi-level-mediated charge transfer and is a first order effect in modeling the energy band diagram for heterojunctions. To include the effects of an adsorbed gas on the interface, an additional parameter at the interface can be included for charge transfer known as the charge neutral level. The position of this level plays a crucial role in the current-voltage relationship of a heterojunction and can also determine if transport properties are dominated by thermionic emission (thermally driven process) or by drift-diffusion (diffusion of carriers in the depletion region promoted by an electric field) processes. The position of the charge neutral level can be explored using electron spectroscopic techniques and would provide a complete energy band diagram to fully understand transport properties of a CuO-ZnO heterojunction.

The mechanism of gas adsorption from the energy band diagram model can be explained in the following manner. Adsorbed gas molecules such as oxygen
and hydrogen alter the shape of the potential barrier, and electronic transport can occur over the potential barrier via thermionic emission. At the same time, the thickness and energy levels of the interfacial layer change. If the interfacial layer thickness becomes thin enough, tunneling between the grains can occur, promoting electronic conduction. The change in the potential barrier during gas adsorption can be understood by considering the two materials as separate bulk entities. Since
adsorption of oxygen withdraws electrons from ZnO, an upward band bending for the n-type ZnO occurs. Conversely, hydrogen donates electrons when adsorbed on CuO, and as a result causes a downward band bending on the CuO side.

4.4 Gas Sensing Characterization

4.4.1 Planar interdigitated electrodes (IDEs)

The current-voltage (I-V) characteristics of planar IDEs with finger widths/spacing of 150 μm, 200 μm and 250 μm are presented in this section. Murphy et al. [107] demonstrated that aluminum electrodes on ZnO thin films produce ohmic contacts. It can be expected that an ohmic I-V relationship could be observed for the mixed-solution thin films. However, while not presented in this study, aluminum electrodes could be patterned on individual ZnO and CuO thin films to ensure ohmic behavior. Fig. 47 is an I-V plot of the room temperature, DC characteristics of a 250 μm finger spacing device exposed to air. A linear I-V characteristic, indicating the presence of an ohmic contact can be observed.

Figure 47: Room temperature DC I-V characteristics of a 250 μm electrode spacing device. The linear I-V behavior is consistent with an ohmic contact.
This ohmic I-V relationship is not maintained after the device is exposed to oxygen and subsequently to hydrogen. Since the resistance value of the device changes in the presence of both oxygen and hydrogen, it does not approach the room temperature DC value originally measured before exposing the device to either gas. This behavior can also be explained by the fact that the adsorbed gas has not been fully desorbed, and there might exist a small concentration of adsorbed oxygen or hydrogen which can affect the room temperature DC I-V characteristics of the device. Fig. 48 is an I-V plot of a 250 μm finger width/spacing device measured in air and at room temperature after exposing it to 200 sccm of oxygen initially and subsequently to 200 sccm of hydrogen. The measurements were obtained after the sample was exposed to air for 30 mins.

![Graph](image)

Figure 48: Room temperature DC I-V characteristics of a 250 μm spacing device after initially exposed to oxygen and then subsequently to hydrogen. I-V characteristics are obtained after the sample is exposed to air for 30 mins. The ohmic, linear I-V relationship is no longer maintained.

Fig. 49 is an I-V plot measured in air comparing the I-V characteristics of the device at room temperature (T = 25 °C) and at temperature of T = 250 °C. Since
the peak sensitivity of bulk ZnO gas sensors occurs between 200 - 300 °C [108], a nominal temperature of 250 °C is chosen to perform the sensing measurements. It can be observed in Fig. 49 that the resistance of the device decreases with increase in temperature. The mobility of majority carriers in a semiconducting material increases with increase in temperature. An increase in the mobility of the carriers increases the conductivity of the material as in Eq. 11 and, conversely, decreases the resistance of the device.

Figure 49: The resistance of the device decreases with an increase in temperature. The device is only exposed to air in these measurements.

The change in resistance as a function of temperature for devices exposed to oxygen and subsequently exposed to hydrogen was measured. Fig. 50 is an I-V plot of a device measured at room temperature as well the sensing temperature after exposure to oxygen and hydrogen.

To confirm the change in resistance of the devices in the presence of oxygen and hydrogen, devices were heated from room temperature to 250 °C. I-V measurements were taken in the presence of air before the introduction of oxygen and hydrogen gases. 200 sccm of oxygen was introduced and was allowed to equilibrate for 30
Figure 50: A change in resistance of the device at higher temperatures when exposed to oxygen and subsequently to hydrogen is observed. The device is exposed to air for 30 mins before I-V measurements are performed.

mins, after which I-V measurements were taken in the presence of oxygen gas. The device sat idle for 30 mins after exposure to oxygen, following which 4000 ppm of hydrogen gas was introduced for 30 mins maintained at a constant flow rate of 200 scem. I-V data in the presence of hydrogen gas was measured in order to compare the characteristics to that of oxygen gas. Fig. 51 and Fig. 52 are I-V plots of the device comparing the response in air to the presence of oxygen and hydrogen gases. An increase in the resistance of the device in the presence of oxygen can be observed as shown in Fig. 51. This is consistent with the behavior of a resistive semiconducting gas sensor in the presence of oxygen. Conversely, a decrease in the resistance, corresponding to an increase in the conductance of the device is observed when comparing the device response in the presence of hydrogen gas to that of air as shown in Fig. 52. This behavior is consistent with the reducing nature of hydrogen gas, wherein hydrogen donates electrons to the material resulting in an increase in the conductivity of the material.
Figure 51: Comparison of the I-V characteristics in the presence of oxygen gas and air at $T = 250 \, ^\circ C$. An increase in resistance can be observed compared to the response in air, corresponding to a decrease in the conductivity.

Figure 52: Comparison of the I-V characteristics in the presence of hydrogen gas and air at $T = 250 \, ^\circ C$. A decrease in resistance compared to the response in air, corresponding to an increase in the conductivity can be observed.

Hydrogen and oxygen sensing characteristics at $T = 250 \, ^\circ C$ for devices fabricated with 150 $\mu m$, 200 $\mu m$ and 250 $\mu m$ finger width/spacings are shown in Fig. 53,
Fig. 54 and Fig. 55. It can be observed that the I-V characteristics of the sensor in the presence of hydrogen gas increases with increase in electrode spacing. To observe a trend in the I-V characteristics as a function of increasing electrode spacing, the three plots are shown with the same voltage and current axis. The 150 µm finger width/spacing device exhibited virtually no difference in the I-V characteristics in the presence of either gases. The 200 µm finger width/spacing device exhibited slight deviations between the I-V characteristics at voltages V < ± 2V. The 250 µm finger width/spacing device exhibited the largest difference between the I-V characteristics in the presence of oxygen compared to that of hydrogen. The 200 µm finger/width spacing device approached a current limited value of 100 mA at ± 8V with slight differences in I-V characteristics in the presence of either gas. The 250 µm finger/width case on the other hand, could be driven with ± 8V before reaching the current limited value of 100 mA and displayed a larger difference in the I-V characteristics in the presence of oxygen and hydrogen. A plot of the 250 µm finger width/spacing comparing the response of oxygen to that of hydrogen while driving the device with higher biases is shown in Fig. 56. An increased response at V > ±5 V can be observed.
Figure 53: Comparison of the I-V characteristics in the presence of oxygen gas and hydrogen gas for a device with 150 µm electrode spacing. Virtually no sensing behavior is observed.

Figure 54: Comparison of the I-V characteristics in the presence of oxygen gas and hydrogen gas for a device with 200 µm electrode spacing. Improved sensing characteristics compared to the 150/µm electrode spacing case can be observed.
Figure 55: Comparison of the I-V characteristics in the presence of oxygen gas and hydrogen gas for a device with 250 μm electrode spacing. The sensing characteristics in the presence of hydrogen gas shows an improvement compared to the previous two cases.

Figure 56: Comparison of the I-V characteristics in the presence of oxygen gas and hydrogen gas for a device with 250 μm electrode spacing at higher biases.
Ansoft’s Maxwell SV electromagnetic simulator was used to simulate the electromagnetic field generated by the application of a bias on this electrode geometry. Fig. 57 is a plot of the electric field variation in a simulated device with finger/widths and spacing as 250 μm. The white blocks represent aluminum electrodes over a mixed-solution thin film deposited over a silicon substrate. The mixed-solution thin film layer was modeled using average values for the dielectric constant and the conductivity values of ZnO and CuO. Dielectric values of CuO and ZnO used in the simulation are listed in Table 1 and Table 2. Conductivity values used were $7.26 \times 10^{-7}$ S/cm [109] and $5 \times 10^{-4}$ S/cm [110] for ZnO and CuO, respectively. The applied bias on the electrodes was alternated between ±4 V, simulating a similar applied bias on the fabricated IDEs.

![Electric field simulation](image)

Figure 57: Electric field simulation of a constant spacing electrode. The maximum electric field occurs at the edges of the electrodes, and the electric field does not extend throughout the mixed solution layer.

In this section, gas sensing characteristics of planar IDEs with constant finger widths and finger spacing was explored. The device with 150 μm finger width/spacing displayed poor sensing characteristics in discerning the presence of oxygen and hydrogen gas. The trend in the I-V characteristics observed by
increasing the finger width and spacing can be explained as follows - the 250 µm finger spacing and width sense more grains under the fingers since the finger width is the widest amongst the three electrodes. Also, devices with the 250 µm finger width and spacing had maximum spacing (compared to the other two devices) between the electrode fingers, which allowed for an increase in the concentration of oxygen (or hydrogen) atoms adsorbed at the CuO/ZnO interfaces, enhancing the I-V characteristics shown in Fig. 55 and Fig. 56. While this electrode configuration displayed an enhancement in current characteristics, the electric field simulation shown in Fig. 57 provides additional information towards improving the sensor characteristics. It can be seen in the figure that the peak electric field (25 V/cm) occurs under the edges of the electrodes, while the electric field under the electrodes is on the order of 5 V/cm. This simulation indicates that only the CuO/ZnO grains close to the surface of the film participate in electronic conduction.

To enhance the I-V characteristics in the presence of hydrogen gas, two techniques are explored. First, keeping the finger width constant, spacing between fingers is increased to improve the sensor characteristics. Increasing the spacing between electrode fingers provides an increase in the effective area available for gas adsorption, which contributes to an increase in the I-V characteristics. Secondly, incorporation of a platinized-silicon substrate as a bottom electrode is expected to increase the sensitivity of the sensor. The electric-field lines in such a device, originating from a positive bias on the top electrode and a negative bias on the bottom electrode is such that the field lines penetrate through the thickness of the thin film. This increases the number of CuO/ZnO grain participating in electronic conduction and can lead to an improvement in the sensing characteristics.
4.4.2 Chirped IDEs

The next set of sensor devices were fabricated such that the finger width was held constant at 200 \( \mu m \) and spacing between subsequent fingers was increased in increments of 250 \( \mu m \) from 500 \( \mu m \) to 1500 \( \mu m \). Fig. 58 is a plot comparing the DC characteristics of the device at room temperature and at \( T = 250 \) °C. Consistent with the constant electrode width/spacing case, the device exhibits an increase in conductance (or a decrease in resistance) with increase in temperature.

![Graph showing current vs voltage for different temperatures](image)

Figure 58: Change in resistance of the chirped electrode at higher temperatures. Consistent with the planar electrode case, the resistance of the device decreases with an increase in temperature.

Hydrogen and oxygen sensing characteristics of the chirped electrode device at \( T = 250 \) °C is shown in Fig. 59. The form of the I-V characteristics is similar to the measured I-V characteristics for the 250 \( \mu m \) constant spacing electrode device shown in Fig. 55.

Using Ansoft, a device with a chirped electrode spacing was simulated with finger width as 200 \( \mu m \) and spacing between fingers increased in increments of 250
μm from 500 μm to 1500 μm, similar to the fabricated case. Fig. 60 is a plot of the electric field variation in the simulated device. The position of the electrodes was correspondingly increased to simulate the increase in spacing of the staggered electrodes. Similar to the constant spacing electrode case, the mixed-solution thin film layer was simulated using average values used in the planar electrode case. An bias of ±4 V was applied to the alternating electrodes.

The chirped electrode design displays an enhancement in sensing characteristics compared to the 250 μm electrode spacing characteristics shown in Fig. 55. The I-V characteristics in the presence of oxygen and hydrogen shown in Fig. 59 follows a similar form as the 250 μm constant electrode spacing characteristics. However, the chirped electrode case displays an slight current response increase in the presence of hydrogen gas. This behavior can be expected, since an increase in the spacing between electrodes results in an increased oxygen adsorption in the mixed-solution thin film. This increase in resistance due to the oxygen adsorption
Figure 60: Electric field simulation of the chirped interdigitated electrode device. The maximum electric field occurs at the edges of the electrodes. However, the electric field extend further into the the mixed solution layer compared to the 250 µm electrode simulation results.

is compensated by the reaction of hydrogen gas with the adsorbed oxygen in the thin film, increasing the conductivity and thus enhancing the sensing capabilities of the sensor device compared to the 250 µm constant finger/width spacing case shown in Fig. 55. The electric field simulation is presented in Fig. 60, and it can observed that there is a slight increase in the electric field under the surface of the thin film as compared to the 250 µm constant electrode spacing simulation case presented in Fig. 57. The electric field has a maximum value of approximately 15 V/cm under the surface of the film and extends further into the thin film as compared to that shown in Fig. 57 and has an electric field of 5 V/cm in the middle of the thin film. It can also be observed that electrodes closer to each other display an increased electric field under the electrodes as compared to when the electrodes are further apart. While this design displays an increase in the sensing characteristics of the device, the electric field simulation suggests that once again,
CuO/ZnO grains close to the surface contribute most to the I-V characteristics of the sensor.

To improve the I-V characteristics of the sensor, a mixed-solution thin film with one set of interdigitated electrodes was fabricated on a platinized-silicon substrate to investigate the I-V characteristics in the presence of oxygen and hydrogen. In this configuration, a positive bias is applied to the top electrode and a negative bias is applied on the platinized-silicon substrate, which serves the purpose of a bottom electrode. Since the electric field lines penetrate through the thin film, this configuration can be expected to increase the sensing characteristics of the device.

4.4.3 Platinized-Silicon with a Top Electrode

The methodology of fabricating the mixed-solution thin film was designed such that the final thin film was porous in nature. This can be confirmed in the AFM, SEM and EDS measurements presented earlier. Porosity plays an important role in gas sensors since it reduces the diffusion path and allows for an increase in the adsorption sites for the target gas. However, as seen in the EDS scan shown in Fig. 35, these pores, in certain cases, can extent through the film to the substrate.

This feature hindered the optimization of the sensor by fabricating devices on a platinized-silicon substrate. Initial devices were fabricated by spin-coating 15 layers of the mixed solution following the same methodology shown in Fig. 19. A corner of the film, prior to the anneal step was etched using hydrofluoric acid (HF, Alfa Aesar, 99.99%, 40% concentration) so as to use the platinized-silicon as a bottom electrode. One set of interdigitated electrodes with finger widths and spacings of 500 μm was fabricated on top of the films. However, this procedure resulted in the electrodes shorting since the open pores provided a path of least
resistance between the top aluminum electrode as well as the platinized-silicon bottom electrode.

Dandenau described that ZnO thin films pyrolyzed at 300 °C displayed a dense microstructure as compared to thin films pyrolyzed at 250 °C [8]. As a result, 5 layers of ZnO pyrolyzed at 300 °C was first deposited, before 15 layers of the mixed solution were deposited to form the final sensor devices. Similar to the previous case, a corner of the film was etched using HF and the top electrode was fabricated. However, this methodology was not successful and the two electrodes were still shorted.

While fabricating the device yielded poor results, Ansoft was used to simulate the theoretical behavior of the devices based on a platinized-silicon bottom electrode. The result of the simulation is shown in Fig. 61. To simulate the platinized-silicon bottom electrode, a layer of platinum was added in between the silicon substrate and the mixed-solution thin film. ±4 V was applied to the top electrode as well as the platinum layer, respectively. Consistent with the previous simulation cases, the maximum electric field (60 V/cm) occurs at the edge of the electrodes. However, in Fig. 61, the electric field (34 V/cm) extends from under the electrode through the mixed-solution thin film layer. As a result, sensor devices incorporating a platinized-silicon bottom electrode as well as a top inter-digitated electrode can be expected to show a dramatic enhancement in sensing characteristics.
Figure 61: Electric field simulation of the device incorporating a platinized-bottom electrode. The maximum electric field occurs at the edges of the electrodes. However, the electric field extend through the the mixed-solution layer and is expected to enhance sensitivity characteristics.
5 Conclusions

5.1 Structural, Optical and Electrical Characterization

The existence of separated CuO and ZnO phases is evident in the XRD data presented. The CuO and ZnO peaks occur at the same 2θ value in the XRD plot for the mixed-solution thin films. SEM images display a network of ZnO grains surrounded by a matrix of CuO grains and this is validated in the elemental scan provided by EDS measurements. It can be observed that the CuO and ZnO grains are not columnar in nature, but instead are layered randomly such that a Cu-rich region could be present under a Zn-rich region. This can be beneficial for gas sensing since this could result in an enhancement in the available p-n heterocontact interfacial regions.

Optical characterization of the thin films provided optical band-gap values of 3.25 eV, 1.52 eV and 1.65 eV for ZnO, CuO and the mixed-solution thin films, respectively. The values measured for ZnO and CuO are in agreement with films fabricated using the sol-gel fabrication technique.

The Van der Pauw measurements provided mobility and carrier concentration values for the thin films. Characterizing the conductivity type of the mixed-solution thin films yielded inconclusive results. The thin films used in this study were fabricated by depositing 15 layers of the mixed solution. Measuring the conductivity type on subsequent layers would provide information regarding the variation of conductivity type as a function of film thickness. The average carrier mobility as well as the average carrier concentration of the mixed solution thin was measured as 76 cm²/(V.s) and $3.25 \times 10^{17}$ cm⁻³ respectively. These values are between the measured mobility and carrier concentration for CuO and ZnO thin films. Since the precursors used in the fabrication of the thin films were mixed to maintain a
1:1 molar ratio of Cu:Zn atoms, one would expect the material properties to be an average value of the properties of CuO and ZnO. However, this is not the case for the measured values of band-gap, mobility and carrier concentration. This can be attributed to the role of oxygen atoms in the material and the porous nature of the thin films. ZnO is an $n$-type semiconductor predominantly due to zinc interstitials or oxygen vacancies while CuO is a $p$-type material with an oxygen rich stoichiometry. Since the oxygen deficiency or excess oxygen was not quantified in individual ZnO and CuO thin films, it is difficult to predict how the role of oxygen atoms alters the properties of the mixed-solution thin films. The porous nature of the film would affect the mobility of the charge carriers in the material since the carriers would have to travel around the open pores, resulting in increased scattering at the grain boundaries and decreasing the overall conductivity.

5.2 Gas Sensing Characterization

Planar interdigitated electrodes were fabricated on the mixed-solution thin films and gas sensing properties were investigated. All the devices displayed a linear I-V relationship in an air environment, ensuring ohmic contact at room temperature. However, after exposure to oxygen and hydrogen, the devices exhibited a non-ohmic behavior. Choi et al. suggested that this behavior could originate from a leaky reverse current or due to voltage dependent gas adsorption [6]. Another possible theory is the formation of a Schottky barrier between the aluminum metal and CuO. The I-V characteristics of the sensor devices fabricated with finger widths and spacings of 150 $\mu$m, 200 $\mu$m and 250 $\mu$m are presented. There is a negligible change in the sensor characteristics of the 150 $\mu$m electrode geometry as compared to the 250 $\mu$m finger width and spacing geometry. This can be attributed to enhanced gas adsorption in the 250 $\mu$m finger width and spacing case. Since the finger widths
were wider, this allowed for more grains to be sampled under the electrodes, and the electrode fingers were spaced apart wider than the 150 µm electrode case allowing for an increase in the availability of CuO/ZnO heterocontact interfaces which serve as adsorption centers.

While a significant improvement of sensor characteristics was observed when comparing the 150 µm electrode case to the 250 µm electrode case, a simulation of the electric field under the electrodes indicated that only grains close to the surface of the thin film participate in electronic conduction. To improve sensor characteristics, a set of electrodes with varying electrode spacing (chirped electrode) was designed to maximize the available interfacial area, increasing the number of adsorption centers. The I-V characteristics of this device exhibited a similar behavior to the 250 µm finger width and spacing case. However, this device displayed an enhancement in the I-V characteristics, displaying an increased current value at lower voltages. An electric field simulation suggests that electrode fingers closer to each other display an enhanced electric field under the electrodes as compared to when the electrodes are further apart. While this design displays an increase in the sensing characteristics, it suggests that only CuO/ZnO grains close to the surface contribute to the I-V characteristics of the sensor.

To further improve the sensing characteristics, one set of interdigitated electrodes were fabricated on a platinized-silicon bottom substrate. The porous nature of the mixed solution thin film was detrimental to this design since it provided a path for the top electrode to connect to the bottom platinized-silicon substrate, shorting the device. 5 layers of ZnO, pyrolyzed at 300 °C which produces dense ZnO films, was first deposited on Pt-Si substrates before 15 layers of the mixed solution thin film was fabricated. These devices were found to be shorted as well.
An electric field simulation confirms the assertion that devices fabricated using this electrode geometry will display an enhancement in the sensing characteristics since the electric field extends through the thickness of the sample. As a result, an increased concentration of CuO/ZnO grains participate in the electronic conduction, enhancing the overall sensitivity of the device.

5.3 Future Areas of Research

5.3.1 Incorporating Dopants to the Mixed Solution Precursor

Aygün et al. demonstrated an increase in the hydrogen sensing characteristics of bulk CuO/ZnO heterocontact gas sensors when doped with metals such as lithium, sodium, strontium, calcium and nickel [94]. These metals serve to increase the majority carrier concentrations in the thin films and can play a role in enhancing the sensor characteristics. They can also play a crucial role, behaving as catalysts and facilitate an enhancement in the chemical reaction occurring at the CuO/ZnO heterocontact interface.

5.3.2 Adding a Buffer Layer to the Platinized-Silicon Substrate

The final sensor configuration did not yield positive results due to the porous nature of the mixed-solution thin films. To avoid shorting of the electrodes, a buffer layer can be deposited prior to the mixed solution layers. Dandeneau et al. demonstrated that ZnO films pyrolyzed at 300 °C displayed a dense microstructure compared to the 250 °C case, however, open pores were still visible in SEM scans. Fabricating thin films with an increased ZnO molarity in the precursor solution would provide a denser microstructure. This can be verified via SEM scans to ensure the absence of open pores extending through the thin film. Upon optimization of the precursor for the buffer layer, 5 layers can be spun at 6000 rpm for 30 s to ensure that this
layer is very thin. The samples can be pyrolyzed at 300 °C and annealed at 800 °C. 15 layers of the mixed-solution thin film can be subsequently deposited. A corner of the film can be etched, such that the Pt-Si substrate serves as a bottom electrode. This configuration will ensure that the top and bottom electrodes do not short.

The shorts could have also occurred since the samples were placed directly above aluminum source during the thermal evaporation process. Angling the substrates during the metal evaporation so that the evaporation occurs at an angle would ensure that only the surface is coated. Since only the surface is coated with the metal layer, this method would ensure that the top and bottom electrodes do not short.

5.3.3 Including a Resistive Heating Element to the Sensor Device

In this study, devices were placed in a furnace and heated to elevated temperatures. Including a resistive heating element at the bottom of the sensor can be expected to enhance sensitivity in the presence of hydrogen gas, since mobility of the charge carrier increases with increase in temperature. This can result in faster response times, significantly improving the sensor characteristics. Optimizing the substrate temperature would contribute to an enhancement in the sensing characteristics.
BIBLIOGRAPHY


[95] R. Tongpool, C. Leach, and R. Freer. Temperature and microstructural
dependence of the sensitivity of heterocontacts between zinc oxide and copper

[96] Kwang-Ki Baek and Harry L. Tuller. Atmosphere sensitive CuO/ZnO junc-

[97] Yoshihiro Ushio, Masaru Miyayama, and Hiroaki Yanagida. Effects of inter-
face states on gas-sensing properties of a CuO/ZnO thin-film heterojunction.

[98] S. Mridha and D. Basak. Investigation of a p-CuO/n-ZnO thin film hetero-

[99] Seok-Taek Jun and Gyeong Man Choi. Composition dependence of the elec-
trical conductivity of ZnO(n)-CuO(p) ceramic composite. Journal of the


