Characterization of Conductive Tin Oxide for MEMS Chemical Gas Sensors

Alycia N. Roux

Abstract— **Conductive tin oxide films were deposited through reactive sputtering on glass substrates under different preparation conditions such as substrate temperature, substrate type, and total chamber pressure. The films were characterized via X-ray diffraction (XRD), thickness, and sheet resistance. The thicknesses of the films were found to be around 0.5 microns for the oxide films which is half the thickness of the metal control films. The thickness of the heated oxide film was measured to be 0.4 microns. The sheet resistances of the oxide films ranged from values of 98 Ω/sq. to an unreadable value due to the entire film being oxidized for a room temperature deposition. In the 300 °C temperature deposition, the sheet resistance was determined to be 12 Ω/sq. The XRD results showed that the film deposited at 300 °C show some crystallinity while the films deposited at room temperature are primarily amorphous.**

Index Terms—**metal oxide; X-ray diffraction; sheet resistance; reactive sputtering**

I. Introduction

CURRENTLY, the most widely investigated groups of chemical gas sensors are those that include the use of a conductive oxide film as the sensing material. They have attracted a significant amount of attention when considering gas sensing under atmospheric conditions due to the fact that they are flexible in production and are a low cost option. These conductive oxide films are also able to detect various gases simultaneously, adding to the range of use. In addition to the conductivity of these semiconducting materials, there are a range of other available testing methods to determine the presence of a gas. Some of these methods include (i) change in capacitance, (ii) change in work function, and (iii) optical characteristics. In this case, the focus will be on the change in resistance of the material.

Another characteristic of conductive oxide gas sensors is the reversible interaction of the gasses with the surface of the film. This interaction can be caused by a number of factors, all of which contribute to a gas sensor's sensitivity. This sensitivity currently is unable to be uniformly defined due to the number of factors that affect it, such as the base material's natural properties, the microstructure of the film, temperature, and humidity. As of yet, there is no special review relating to the factors that influence the sensitivity of a given gas sensor with a conductive oxide as the sensing material.

Alycia N. Roux is with the Rochester Institute of Technology, Rochester, NY 14623 USA (e-mail: anr9501@rit.edu).

Taking these factors into account, it is important to characterize the sensing mechanism of the metal oxide gas sensor. Currently, the mechanism is mostly theoretical, meaning the exact fundamentals that result in a conductive oxide responding to a gas are controversial. The agreed upon theory is that band bending caused by the trapping of electrons at adsorbed molecules causes the change in conductivity. When the film is in contact with Oxygen gas (O_2), some of these molecules adsorb to the surface of the film, extracting electrons from the film's conduction band. This causes the adsorbed molecules to ionize, creating an electron depleted region, or space charge layer which decreases the conductivity (increasing the resistance). This effect is reversed when the gas sensor then is exposed to a reducing gas or a gas that contains competitive adsorbing and replacing molecules (such as CO), increasing the conductivity (decreasing the resistance). This effect seems to be maximized at an operating temperature of between 300-450 °C. Fig. 1 is a diagram of the structural and band models of the conductive mechanism of these films [1].

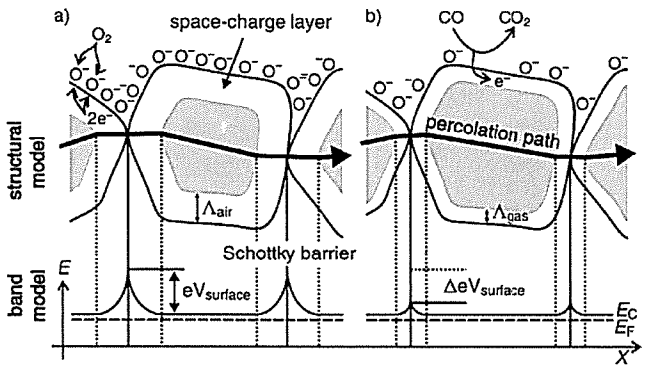

Figure 1: Structural and band model of the conducting mechanism of the metal oxide films upon exposure to a gas (a) containing CO and (b) without CO [1]

II. Experimental

A. Tin Oxide Screening

Due to its physical properties and performance in detecting reducing gases and taking into account the available tools and materials, tin oxide was chosen as the conductive oxide film. A sputtering system, in this case the CVC 601, with reactive capabilities was used to deposit the tin oxide films on 2 inch by 3 inch glass slides in order to determine whether obtaining a conductive oxide was able to be done. The system was

pumped down for one hour until the system reached a stable pressure in the 10^{-5}-10^{-6} Torr range. Two deposition runs were completed each with four glass slides. Two slides in each run were deposited with unreacted tin as a control, one slide at a total chamber pressure of 6 mTorr and one slide with a total pressure of 12 mTorr. The remaining slides in both runs were reactively sputtered with an Argon to Oxygen ratio of 3:1. The reactively sputtered samples in the first run were completed at two different chamber pressures (6 mTorr and 12 mTorr), one for each slide. For the second run, all the slides were deposited at a total chamber pressure of 6 mTorr, but the first two slides were completed at room temperature. The first was reactively sputtered, while the second two were deposited at a substrate temperature of 300 °Cvia reactive sputtering. The system completed both runs at a power of 100 Watts and a time of 5 minutes. The thickness and sheet resistance of the films were determined using a stylus profilometer and a manual 4-point probe respectively.

B. Tin Oxide Repeatability

After the screening, more depositions were run in order to obtain films with consistent values of sheet resistance and thickness. Three additional deposition runs were completed, one at the same process conditions as the first screening run. The second run was an alteration of the first screening run slightly by using only a total pressure of 6 mTorr. The third run used these conditions, and altered the power to 75 Watts for the final two slides. Thickness measurements were taken of the third and fourth runs and sheet resistance measurements were taken of all three runs.

C. X-ray Diffraction (XRD) and Film Gas Sensing

Since the physical properties of the metal oxide film have a large impact on its sensing capability, X-ray diffraction (XRD) was used to determine the composition of the film and its structure. It has been determined that films deposited at a temperature of about 300 °C appear to have a higher conductance than those deposited at room temperature. These films deposited at the elevated temperature showed some crystallinity compared to the films deposited at room temperature [2]. Therefore, if the films deposited via reactive sputter are crystalline in nature, there is a higher likelihood that they will be able to sense gases.

III. Results and Discussion

A. Thickness and Sheet Resistance

The tin oxide screening showed mixed results after deposition. The tin films that were deposited showed a slight variation in thickness, but showed relatively consistent results. The reactively sputtered films on the other hand showed significant variations in the sheet resistance. The thickness values between the two samples with the same process conditions had similar thickness but drastically different sheet resistance values. Figs. 2 and 3 show the deposited films on the glass slides for the first screening run and the deposited films for the second run and Table 1 displays the resulting thickness and sheet resistance values.

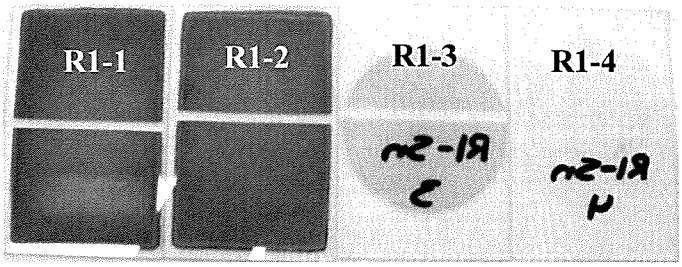

Figure 2: First Screening Run Deposited Films (left two slides are tin only, right two slides are tin oxde)

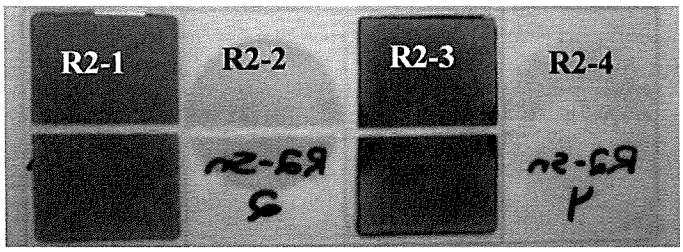

Figure 3: Second Screening Run Deposited Films (left two slides at room temperature, right two slides at 300 °C)

Table 1: Sheet Resistance and Thickness Measurements of the Screening Runs

Slide #	Substrate Heating (°C)	$Ar:O_2$ / Total Pressure (mT)	Sheet Resistance (Ω/sq)	Average Thickness (angstroms)
R1-1	--	1:0 / 6	0.79	10,600
R1-2	--	1:0 / 12	0.63	9,780
R1-3	--	3:1 / 6	978	6,780
R1-4	--	3:1 / 12	22×10^6	3,980
R2-1	--	1:0 / 6	0.56	14,100
R2-2	--	3:1 / 6	510	5,720
R2-3	300	1:0 / 6	52×10^4	8,630
R2-4	300	3:1 / 6	12	4,070

In Table 1, the grayed sections correspond to those depositions that were tin only while the white sections correspond to those depositions that were tin oxide. The samples that were deposited using the same process conditions were R1-1 and R2-1 for tin only and R1-3 and R2-2 for tin oxide. Comparing R1-1 and R2-1, the sheet resistances differ by 0.22 Ω/sq. and the average thickness is off by 3,500 Å.The thickness difference seen between the runs is acceptable within . Overall, these values can be considered to be consistent with one another. In contrast, the sheet resistances for R1-3 and R2-2 differ significantly. The sheet resistance for R2-2 is greater than R1-3 by about 400 Ω/sq. In addition, there was a concerned as to whether or not the glass slide was interfering with the film and causing additional changes. Therefore, in the hopes of producing more reliable repeatable results, three more runs were completed, two of which included wafers coated with Nitride (SiN_4).

Comparing the remaining results, the depositions performed at an overall pressure of 12 mTorr were decided against due to the significant decrease in the thickness and the increase in the

sheet resistance. Thicker films are better when performing XRD. In addition, the thicker the film, the more likely the film will have crystalline qualities, meaning a better conductive oxide. The heated sample R2-4 appears promising as a film even though the sheet resistance appears to be low. However, heated films are more likely to have a crystalline structure when compared to films deposited at room temperature which is a desirable feature.

The remaining runs performed for the repeatability experiment resulted in inconclusive results. The films that were deposited at the same process conditions as the screening runs produced a range of differing sheet resistance values even though the thickness values appeared to stabilize. Figs. 5-7show the first, second, and third repeatability depositions and the tabulated thickness and sheet resistance results are shown in Table 2.

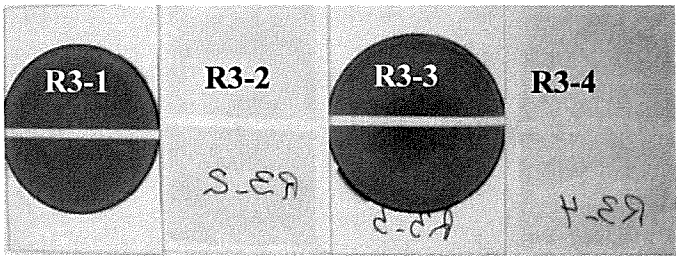

Figure 5: Third Overall Deposited Film (left two total pressure of 6 mTorr, right two total pressure of 12 mTorr)

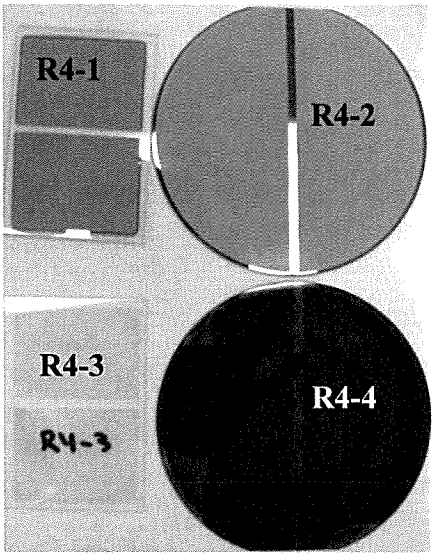

Figure 6: Fourth Overall Deposited Film (top two tin only, bottom two tin oxide)

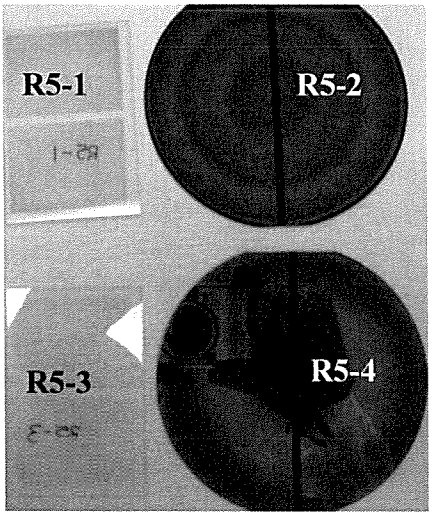

Figure 7: Fifth Overall Deposited Film (top two 100 Watts power, bottom two 75 Watts power)

Table 2 : Sheet Resistance and Thickness Measurements for Runs 3-5 (repeatability runs) (samples R5-3 and R5-4 deposited at a power of 75 Watts)

Slide/Wafer #	Substrate Type	$Ar:O_2$ / Total Pressure (mT)	Sheet Resistance (Ω/sq)	Average Thickness (angstroms)
R3-1	Slide	1:0 / 6	0.63	12,300
R3-2	Slide	3:1 / 6	68×10^6	5,640
R3-3	Slide	1:0 / 12	1.0	9,550
R3-4	Slide	3:1 / 12	no reading	3,060
R4-1	Slide	1:0 / 6	0.50	11,800
R4-2	Wafer	1:0 / 6	0.32	10,000
R4-3	Slide	3:1 / 6	6,600	4,990
R4-4	Wafer	3:1 / 6	190	5,700
R5-1	Slide	3:1 / 6	190	NA
R5-2	Wafer	3:1 / 6	180×10^4	NA
R5-3	Slide	3:1 / 6	no reading	NA
R5-4	Wafer	3:1 / 6	2.2×10^4	NA

From these results, it is seen that although the thicknesses of the oxide films with the same process conditions are all around a thickness of 5000 angstroms, the sheet resistance changes drastically between the films. Even when comparing the films deposited on the wafers, the sheet resistance did not improve in consistency, ranging from 190 Ω/sq. to 180×10^4 Ω/sq. Therefore, repeatability was not achieved. The reason for the discrepancies is a topic for future work. Regardless, a conductive oxide was achieved. Therefore, in order to determine the most appropriate film for future gas sensing, XRD measurements were taken of two of the films to determine the composition and the structure of the films. The chosen slides were R1-3 and R2-4 to determine the difference between the room temperature deposition and the heated deposition.

B. XRD Results

Since it is known that crystalline films will have a better conductivity and therefore will be able to sense chemical gases

more efficiently, it is important to note which of the deposited films exhibit this structure. XRD works by measuring the difference between two waves reflected from the surface of the film. If the film is crystalline in nature, there will be clear peaks due to its structure. If the film is amorphous, there will not be peaks since the film is completely oxidized. Fig. 8 and 9 are the XRD results from measuring R1-3 and R2-4.

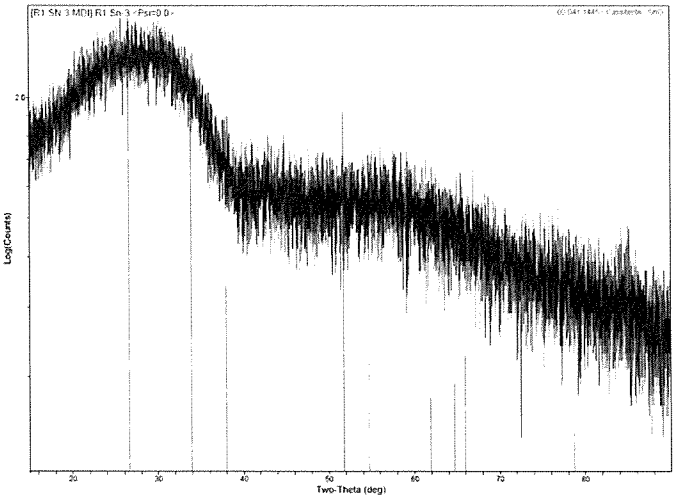

Figure 8: XRD results of R1-3, room temperature deposition

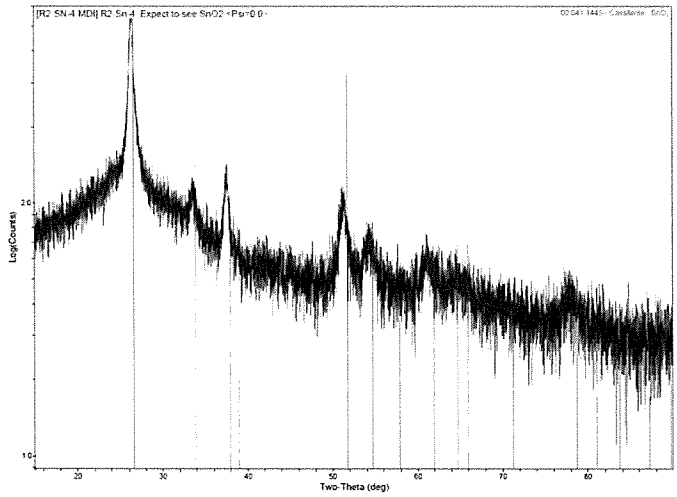

Figure 9: XRD results of R2-4, 300 °C deposition

Clear differences between slides R1-3 and R2-4 can be seen in the XRD results. A common stoichiometry of tin oxide was chosen to compare the films to in order to determine the films crystallinity. It is seen in Fig. 9 that the film deposited at 300 °C shows crystallinity and matches a composition of SnO_2. In contrast, Fig. 8 shows one very rounded peak but the remainder of the film appears to be very smooth. This indicates an amorphous film. Therefore, in order to create a gas sensing film, a heated deposition is needed to obtain the proper film quality.

IV. Conclusion

Although obtaining repeatable results was not able to be done, the XRD measurements taken have shown that in order to create the required gas sensing film, a heated deposition is required. This experiment has shown that room temperature depositions are not worth exploring due to the amorphous structure of the film. In future work, determining repeatable results using a heated deposition is worth exploring as well as testing the gas sensing capability of the film.

Acknowledgment

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References

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Alycia N. Roux was born in Omaha, Nebraska and grew up in Amsterdam, NY. She is expecting to receive a Bachelor of Science in Microelectronic Engineering in May of 2014 from Rochester Institute of Technology in Rochester, NY. She has held an internship position at the University of Rochester's Laboratory for Laser Energetics where she co-authored a paper published in Applied Optics concerning the chemical cleaning of multi-layer dielectric diffraction gratings for high energy laser systems. She will be joining the Global Foundries team in June of 2014.