Effects of Annealing Aluminum Doped Zinc Oxide (AZO) in the Form of a Transparent Conductive Oxide

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Abstract

TCOs can be improved by decreasing the sheet resistivity; dopant concentration and annealing alters the microstructures of AZO films.[11] This experiment was done to look at using annealing in order to decrease the resistivity of AZO postdeposition.[12] The samples were done with DC magnetron sputtering and the heat treatment was done in a kiln. The resulting characterization data are in the form of four-point probe readings and UV-vis transmittance spectrums. The data gathered in this experiment reports that the resistance is on average two orders of magnitude less in the annealed samples than in the unannealed samples. There were changes in the UV-vis transmittance spectrum pre- and post-anneal for the sample sputtered at room temperature but once annealed both samples had similar band gaps. It would also be of interest to see how much of a decrease of resistivity could be reached with annealing with cooler temperatures to work toward better efficiencies.

Introduction

Transparent conductive oxides (TCOs) are utilized in many of the world's quickly advancing technologies. The attributes of TCOs, high conductivity and transparency, allow them to be used for a plethora of applications: transparent electrodes for liquid crystal[1], solar cells[1-3, 6], low emissivity architectural windows[4], electro-optical devices, thin film photovoltaics,[4] transistors,[3] handheld smart devices and other flat panel displays (FPD). The most common TCO used in FPDs is indium tin oxide (ITO)[4, 5, 7] but indium is a scarce element in the earth's crust, driving up the production cost, and has unfavorable chemical attributes. The chemical instability of indium in a reduced ambient can lead to the ITO diffusing into organic material which degrades LEDs.[5] Indium is also toxic,[5] leading to dangers to humans in manufacturing and pollution.

The TCO zinc oxide (ZnO) is being explored further as an alternative to ITO because zinc is a more abundant element, making production cheaper,[8] and is nontoxic.[1] ZnO films with dopants are already used across industries for purposes like photoconductors in electrography, varistors in ceramic technology, sensors in sensing combustible gases, etc.[1]

There are many methods of deposition for TCOs, the one this experiment will utilize is sputtering with DC magnetron. Magnetron sputtering is a scalable process that allows for deposition at lower temperatures[9, 10] with good optical and electronic properties.[9] TCO semiconductors are classified as wide band gap semiconductors[6, 9], undoped ZnO show a n-type conductivity.[2] The lowest resistivities for undoped ZnO are independent of deposition method and in the range of 1.4 to $2x10^{-4}\Omega$.

TCOs can be improved by increasing the conductivity of the films or by decreasing resistivity which is important for use in making better portable technologies with faster graphics.[4] To increase conductivity ZnO can be doped with group III elements (boron, aluminum, gallium, or indium);[3] the TCO aluminum doped zinc oxide (AZO) has a high transmittance with low resistivity.[7] Dopant concentration and annealing alters the microstructures of AZO films.[11] This experiment is looking at using annealing in order to decrease the resistivity of AZO postdeposition.[12]

Materials and Methods

An aluminum doped zinc oxide (AZO), with 98% ZnO 2% Al, plate was used as provided by SCI Engineered Materials Inc. in a DC Magnetron sputter deposition. The sputter deposited the AZO onto a glass slide made of soda lime borosilicate glass, having its own band gap[13]. The preparation of the glass slides before being placed into the sputter-coater required the slides to be scored so one slide would break into three samples, washed with Alconox, rinsed with water, rinsed with isopropyl alcohol, and then dried with nitrogen gas. The parameters of the sputtering of the two samples are listed in tables 1 and 2.

Table 1

Sample 1	
Pressure	7 mTorr
Temperature	200 °C
Power	30 W
Pre-sputter	5 min
Sputter	30 min

Table 2

Sample 2	
Pressure	7 mTorr
Temperature	23 °C
Power	30 W
Pre-sputter	5 min
Sputter	30 min

Past literature annealed TCOs at a wide variety of temperatures, from 150°C[14] to 850°C.[11] For this experiment each sample was divided and put in a Sentro Tech Corp. kiln and heat treated for 3 hours in regular atmosphere conditions, one set at 300°C and the other at 900°C.

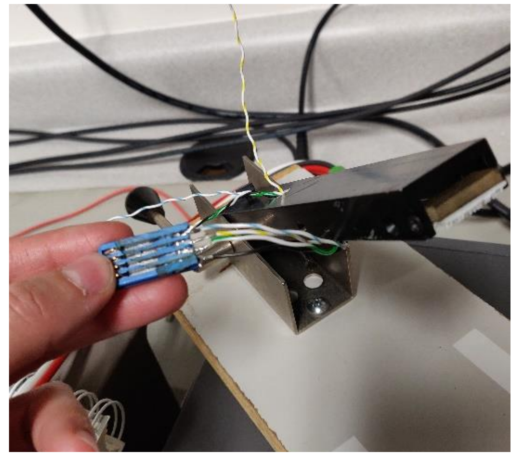
Figure 1 Print cartridge sensor for the four-point probe.

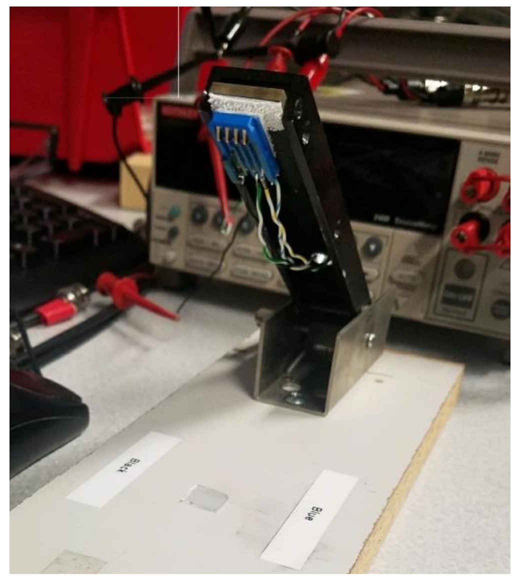
Figure 2: The four-point probe assembled.

Characterization of the sample was done before and after the postdeposition heat treatment using Ultraviolet–visible spectroscopy (UV-vis), done on a PerkinElmer Lambda 950 UV/VIS/NIR Spectrometer, to test transmittance and a four-point probe to record resistivity. A Scanning Electron Microscope (SEM), model Hitachi TM3030Plus tabletop microscope, was also used to analyze the topography of the thin film surface. For the SEM section of characterization an acid etch was attempted to give a better image of the film for 60 seconds using 0.37 M HCl, used as provided by Sigma Aldrich.

The four-point probe was created using the sensor detached from a printer cartridge and connected, via solder and alligator clips, to a Keithley 2400 that could run a current (I) through the outside points of the probe and read a voltage (V) through the inside.[15] Using Ohm's law $\frac{V}{I} = R$ a resistance could be found and converted to a resistivity $R = \frac{\rho d}{A}$ where Area $A = dt$ d being distance between prongs and t being thickness of the film. This would result in resistivity being $\rho = Rt$. Readings were taken of the samples in three different locations in a portrait orientation: top, middle, bottom.

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Results

Outlying points of note would be that the samples that were annealed using 900°C melted so those data points are not included in these results. Also, the sample on which the acid etch was attempted to get better SEM images left the sample with a UV-vis spectrum that mimics that of a blank slide, as seen in figure 3. Figure 3 also shows that though the sputtering conditions were different for sample 1 and sample 2, the transmittance spectrums for the post-annealed samples are similar in their band gap hitting around 380 nm.

Sample 1 was sputtered at a higher heat than sample 2, 200°C, and little difference can be seen in the transmittance of the UV-vis pre-annealed and post-annealed treatments in figure 4. Sample 2 was sputtered at 23°C and shows a difference between the pre-anneal and post-anneal in the treatments, as seen in figure 5,

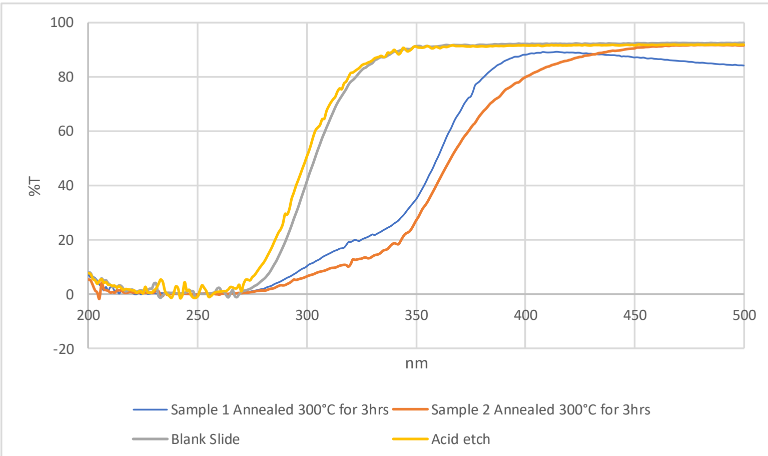

Figure 3: After annealing, sample 1 and sample 2 have a similar transmittance. The transmittance of the acid etched sample is nearly identical to that of the blank glass slide.

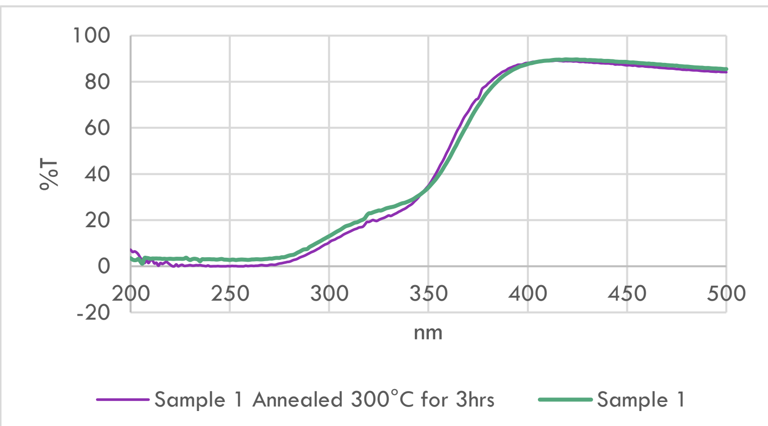

Figure 4: Sample1, sputtered at 200°C, doesn't show much of a difference in transmittance from pre- to post-annealing

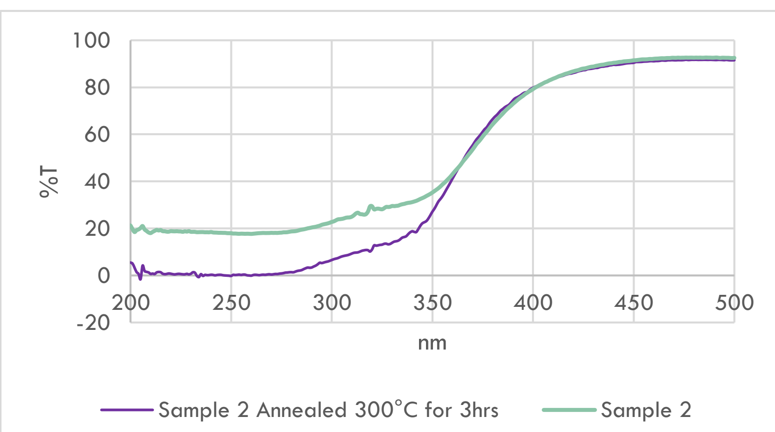

Figure 5: Sample 2, sputtered at 23°C, shows a marked difference in transmittance with the pre-annealed sample having a higher base line.

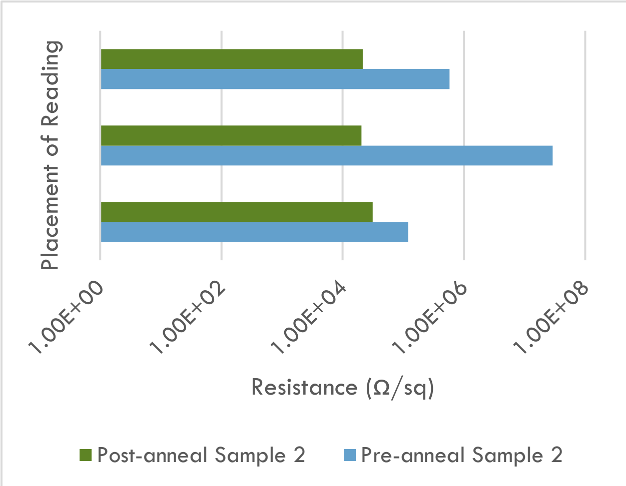

Figure 6: The resistance of sample 2 was greater prior to annealing

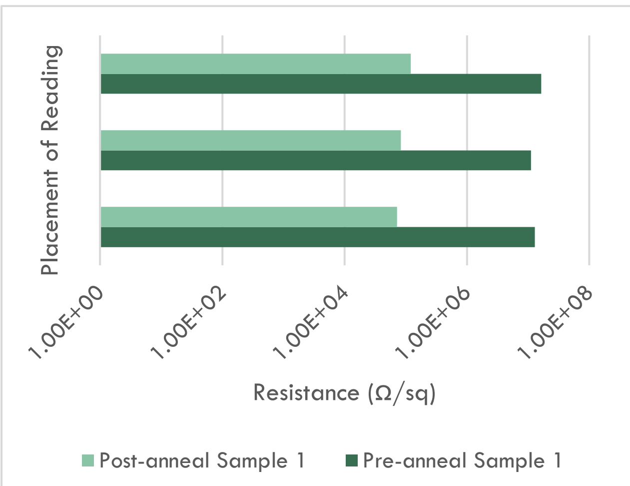

Figure 7: The resistance of sample 1 was greater prior to annealing

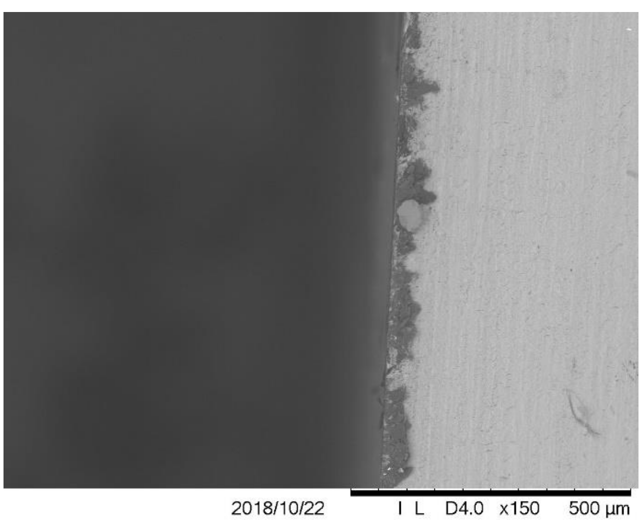

Figure 8: SEM image of the top of the slide.

with the pre-annealed sample having a higher transmittance base line than the annealed sample.

In order to get resistivity, the thickness of the TCO would have needed to have been obtained to multiply against the resistance, in absence of the film thickness measurements this paper will address the trends of resistance of the TCO under annealing and will not state specific measurements of resistivity. Across all surviving samples there can be seen a decrease in resistance after annealing, as seen in figures 6 and 7.

A profile of the TCO via scanning electron microscope (SEM) can be seen in figure 8. SEM photos of the TCO straight on did not show any topography.

Discussion

Literature is consistent that annealing TCOs result in a reduction of resistivity. The data gathered in this experiment reports that the resistance, and therefore in resistivity since resistivity is $\rho = Rt$, is on average two orders of magnitude less in the annealed samples than in the unannealed samples which keeps with past findings, as seen in figures 6 and 7.[12] Since this was the expected result the new data that this experiment yielded would be the specifics of the annealing choices since that is unique to the past literature. Most of the literature listed annealing temperatures that were higher than the 300°C used in this experiment and annealed for much less time, one hour compared to this project's three hours. Future work on this project would be to measure the thickness of the film so actual sheet resistivity numbers could be calculated. It would also be of interest to see how much of a decrease of resistivity could be reached with annealing with cooler temperatures as a way to work toward better efficiencies in production.

Sample 2 was sputtered at 23°C and shows a marked difference between the pre-anneal and post-anneal treatments, as seen in figure 5, with the pre-annealed sample having a higher transmittance base line, which could have been caused by impurities that were allowing more transmittance in the TCO because the transmittance of the sample decreased after annealing. Sample 1 was sputtered at a higher heat than sample 2, 200°C, and the transmittance of the UV-vis pre-annealed and post-annealed treatments in figure 4 do not show any marked difference. Figure 3 also shows that though the sputtering conditions were different for sample 1 and sample 2, the transmittance spectrums for the post-annealed samples are similar in their band gap hitting around 380 nm.

When looking at the UV-vis transmittance of the acid etched sample compared to that of the blank slide, as seen in figure 3, it looks as if the acid etch removed the TCO which is an occurrence not backed up by past literature.

Conclusion

Transparent conductive oxides (TCOs) are utilized in many of the world's quickly advancing technologies. A common TCO used is indium tin oxide (ITO)[4, 5, 7] but indium is costly and has unfavorable chemical attributes. The TCO zinc oxide (ZnO) is being explored further as an alternative to ITO because zinc is cheaper[8] and nontoxic.[1]

TCOs can be improved by increasing the conductivity of the films or by decreasing resistivity. Dopant concentration and annealing alters the microstructures of AZO films.[11] This experiment was done to look at using annealing in order to decrease the resistivity of AZO postdeposition.[12]

The sputter for the samples was done with a DC magnetron. The postdeposition heat treatment was done in a kiln. The resulting characterization data are in the form of four-point probe readings and UV-vis transmittance spectrums.

In conclusion, the data gathered in this experiment reports that the resistance is on average two orders of magnitude less in the annealed samples than in the unannealed samples. The sample that was sputter at room temperature had a large transmittance spectrum change between the pre-anneal and post-anneal treatments, as seen in figure 5, with the pre-annealed sample having a higher transmittance. The sample sputtered at a higher heat, 200°C, had transmittance spectrums that look nearly identical pre-annealed and post-annealed, as seen in figure 4. Though the sputtering conditions were different for the samples, the transmittance spectrums for the post-annealed samples are similar in their band gap hitting around 380 nm.

Future work on this project would be to measure the thickness of the film so sheet resistivity measurements could be calculated. It would also be of interest to see how much of a decrease of resistivity could be reached with annealing with cooler temperatures to work toward better efficiencies in production.

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