

Electrical Characterization of Hydrogen-Treated ZnO Thin Films

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Primary Sources of 2019 NNCI iREU Funding: National Science Foundation via awards ECCS-1626153 (NNCI Coordinating Office at Georgia Tech) and NNCI-1542081 (Cornell NanoScale Facility)

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Abstract:

Zinc oxide (ZnO) thin films have been used commercially and are gaining traction as a reliable transparent oxide semiconductor material. Recent research has suggested that ZnO thin films are unique semiconducting oxides in that the hydrogen defects counteract the prevailing conductivity [1]. It is important to understand the effects of hydrogen impurities within the crystal lattice. This includes the effects that different deposition conditions have on hydrogen impurity formation as well as the effects that the impurities have on the electrical characteristics of the thin films. This project aims to explore the nature of hydrogen impurities in ZnO thin films by introducing a controlled hydrogen treatment. Varied deposition conditions were studied, and the resulting thin films were characterized physically and chemically. The deposition conditions tested in this project were temperature and substrate type; either glass, sapphire plane-A, or sapphire plane-C. Electrical characteristics were measured before and after a controlled hydrogen plasma treatment. The deposition was performed by magnetron sputtering. Electrical characterization was performed by Hall Effect measurement and 4-Point Probe. Elemental data and crystal lattice data were obtained by X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Diffraction (XRD), respectively.

Summary of Research:

The first step of the project was deposition of zinc oxide (ZnO) thin films by magnetron sputtering. A total of nine samples were prepared for measurements. Deposition was performed at room temperature, 150°C, and 500°C on glass, sapphire A-plane orientation, and sapphire C-plane orientation. Immediately after deposition, each sample was analyzed with (XPS) to verify successful deposition by elemental composition. Each sample was then analyzed using (XRD) to determine crystal structure and quality of the ZnO films as well as determine junction quality. After XRD, the samples were cut in half.

One half of each of the samples were subjected to 30-minute hydrogen-plasma treatment. The treatment was performed at room temperature and a partial hydrogen pressure of 3.5E-5 Torr, with a radio-frequency power of 150 Watts and hydrogen flow of 3.0 sccm. All samples had their Hall Effect characteristics measured with a ResiTest 8400, including resistivity, carrier concentration, and electron density. These

quantities were measured over a range of temperatures to see how hydrogen treatment affected the values as well as temperature dependence.

In the last step of the process, silver nodes were deposited by evaporative deposition on the surface of the samples and a four-point probe was used to measure the current-voltage (IV) and capacitance-voltage (CV) characteristics of the films. The data obtained through this process was used to show how hydrogen-concentration in ZnO thin films affects the electrical characteristics.

Results and Conclusions:

According to XPS measurements in Figure 1, the depositions were performed successfully. Expected binding energy peaks for Zn2p orbitals at 1022 eV and O1s orbitals at 531 eV were evident. Negligible offset in some of the data was likely the result of surface charge effects. According to XRD results in Figure 2, all the ZnO

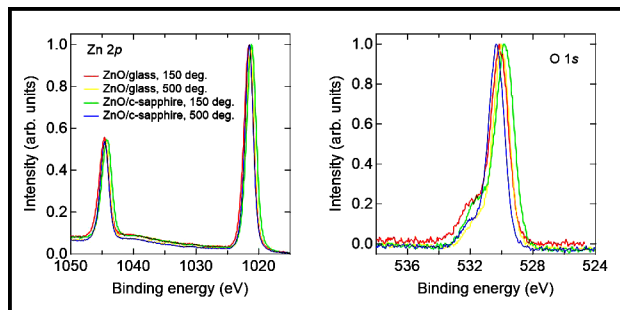


Figure 1: XPS measurements of ZnO deposited films.

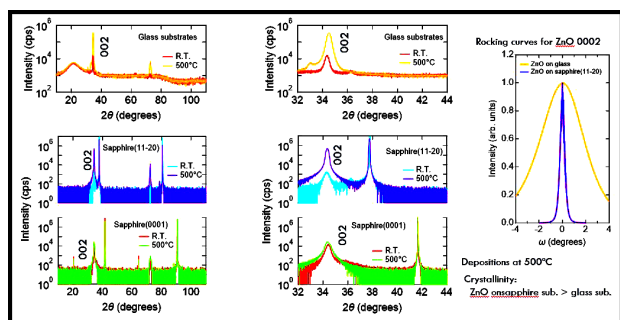


Figure 2: XRD data of ZnO deposited films.

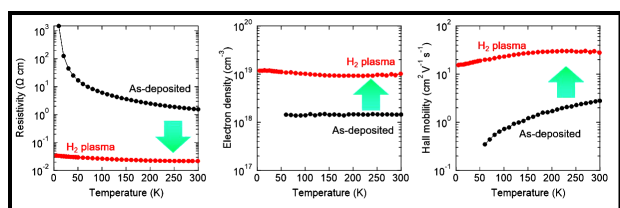


Figure 3: Hall Effect measurements obtained before (as-deposited) and after (H_2 plasma) hydrogen treatment from 0 to 300 K.

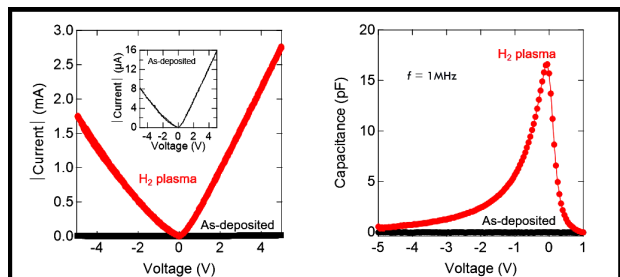


Figure 4: IV and CV curves before (as-deposited) and after (H_2 plasma) hydrogen treatment.

thin film crystal structures were oriented around the C-axis, as expected. The best crystallinity was achieved with the 500°C, C-plane sapphire substrate. Samples deposited under higher temperature exhibited more consistent crystal orientation throughout the film. Based on XRD rocking curves, sapphire is a much better choice for ZnO thin film epitaxy.

For electrical measurements, the thin films deposited at room temperature failed to produce reliable results. The same was true for most of the 150°C samples. This is believed to be because the films were too thin

and inconsistent in presence of ZnO to have sufficient conductivity for measurement. However, the films deposited at 500°C showed massive changes in electrical characteristics after hydrogen-treatment.

Hall measurements shown in Figure 3, obtained with the ResiTest 8400, indicated a rise in electron density, and a fall in resistivity, and a rise in resistivity. The results also show a decrease in temperature dependence.

The IV and CV characteristics obtained using the four-point probe can be found in Figure 4. After hydrogen doping, conductivity increased dramatically. Asymmetry was present on hydrogen-treated and non-hydrogen-treated samples and did not seem to significantly change after treatment. The CV curves show characteristics similar to those of a typical Schottky junction, indicating that there might be potential for using hydrogen-doped ZnO films for use in resistive switching devices.

Future Experimentation:

Further characterization of hydrogen-treated ZnO films is necessary to truly understand the mechanisms and limitations of the doping method. More experiments should be performed to obtain a much larger dataset, including more deposition temperatures, different types of substrates, different deposition pressures, and longer and shorter deposition times. Also, changes in the properties of the hydrogen treatment should be tested. Longer hydrogen treatment or higher hydrogen pressure during treatment might provide higher levels of doping. More electrical measurements should be taken, and over a wider range of voltage values, in order to test for hysteresis and electrical property fatigue. As previously mentioned, the treated ZnO thin films have potential for use in resistive switching devices based on the Schottky-like characteristics of their CV curves.

Acknowledgements:

Special thanks to the NNCI and the NSF for funding the research conducted via awards ECCS-1626153 (NNCI Coordinating Office at Georgia Tech) and ECCS-154208 (Cornell NanoScale Facility). Thank you to NIMs for providing mentorship under Naoki Ohashi and Takeo Ohsawa during this process. Additional thanks to Lynn Rathbun and Quinn Spadola for coordinating the iREU. Finally, thank you to Cornell University for allowing this program to be a part of the NNCI Convocation in Ithaca, New York.

References:

- [1] Miyase T., Watanabe K., Sakaguchi I., et al. Roles of Hydrogen in Amorphous Oxide Semiconductor In-Ga-Zn-O: Comparison of Conventional and Ultra-High Vacuum Sputtering. ECS Journal of Solid State Science and Technology, 3 (9) Q3085-Q3090 (2014).