Volume 3 | Issue 1 Article 6

2014

Characterization of Electrical Performance of Aluminum-Doped Zinc Oxide Pellets

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ABSTRACT Recently, the electronic industry has been shifting towards devices that can be controlled by touching the screen with one or more fingers. This technology makes use of transparent conducting oxides (TCOs). Zinc oxide (ZnO) is a potential replacement for the most currently used TCO (indium-tin oxide) due to its comparable optical properties. However, the doping mechanisms of zinc oxide need to be understood and improved. In this research, the optimum concentration of aluminum dopant in ZnO at 1400 ^{o}C was investigated. The aluminum doping concentrations studied were 0 %, 1 %, 2 %, 2.5 %, and 4 % by weight. The electrical conductivity for all doping levels improved compared to undoped ZnO. The highest conductivity was obtained for the 2 % and 2.5 % aluminum concentrations, indicating that this is the maximum solubility limit of Al in ZnO at this temperature.

INTRODUCTION

Transparent conducting oxides (TCO) have become very popular in the past decade, and are used in the fields of electronics, optoelectronics, and spintronic devices [1]. The TCO field is expanding amazingly fast due to the potential applications of materials that are both conductive and transparent. ZnO is cheaper than many other TCOs and is safer, making it a viable candidate to research for future applications [2].

Some of the applications of ZnO include ultraviolet light emitters; spin functional devices, gas and other molecular sensors, and transparent electronics, among others [1]. Although ZnO is naturally an insulator, it can be doped with substitutional impurities to defect the lattice structure. Appropriate dopants of ZnO can make it an effective *n*- or *p*-type semiconductor by incorporating electrons or holes that easily flow across the lattice. The *n* stands for negative charge carriers (electrons) while the *p* means that the majority carriers are positive charges (holes).

Metals are excellent conductors, but they are highly opaque. Intrinsic semiconductors are normally pure materials with modest conductivities. Extrinsic semiconductors are

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Research Completed in Winter 2014
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doped by controlling the impurity concentrations to improve the material's properties [3]. The defect mechanism responsible for ZnO's semiconducting properties is still not well understood by the scientific community; however atomic point defects and impurities are believed to be responsible for its electrical behavior [1-3].

Currently, the transparent conductor used for flat-panel displays is tin-doped indium oxide (ITO). It has a resistivity of ~ 10^{-4} Ω-cm and a transmittance in the visible spectrum exceeding 80 % [3]. Indium is not an abundant resource on Earth, and its scarcity makes it very expensive [4]. More cost-efficient means of producing a robust material with the same functionality and productivity as ITO are currently being investigated by considering alternative materials and methods.

Aluminum-doped zinc oxide (AZO) is an attractive replacement since zinc and aluminum are inexpensive materials. In this research, micro-sized granules of ZnO powder and Al_2O_3 doping agents were used to study the effects of impurities and heat treatment methods on the electrical characteristics of AZO. High temperature was used to dope ZnO with 1, 2, 2.5 and 4 aluminum weight percentages. The electrical conductivity of the samples was measured with a four-point electrical probe and a current source. With the four-point probe, a small current is applied across two points on the surface of the sample, and a potential difference is measured across the other two probes.

The resistance of the sample is determined by applying Ohm's law:

$$R = \frac{\Delta V}{I} \qquad (1)$$

where R is resistance , ΔV is voltage, and I is the current. The conductivity of the sample is inversely proportional to the resistivity since

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} = \mu n e \qquad (2)$$

where σ is the conductivity, ρ is the resistivity, l is the length of the sample, A is the cross-sectional area of the sample, n is the carrier concentration, μ is the mobility, and e is the charge of an electron [5]. From Equation (2), the conductivity of a material is directly proportional to both the carrier mobility and carrier concentration.

A heat source, gold foils, and thermocouples connected to a power source/digital multimeter were used to record the thermopower coefficient. With this technique the voltage difference experienced by charge carriers due to a temperature gradient between the top and the bottom of the sample is measured. The thermopower or Seebeck coefficient, Q, is given by

$$Q = \frac{\Delta V}{\Delta T} \propto n^{-1/3} \qquad (3)$$

where ΔV is the difference in electric potential, and ΔT is the difference in temperature between the top and bottom of the sample [6]. Negative values for Q indicate that the semiconductor is n-type with surplus of electrons, while positive differences can be explained through the presence of electron holes, which are positive carriers. The magnitude of the thermopower is inversely related to the concentration of carriers, therefore a smaller $|Q|$ corresponds to a sample with high electron populations.

METHODS

The materials used were high-purity ZnO powder (99.9999%, Puratronic from Alfa Aesar, and referred to as B1) with micron-sized grains and nano-grain sized powders of aluminum oxide. The purity of Al_2O_3 was 99.995% (also obtained from Alfa Aesar, and referred to as A2). The ZnO and Al_2O_3 powders were crushed into very fine powders and mixed together with acetone using a mortar and pestle. Four different aluminum compositions were prepared: 1%, 2%, 2.5%, and 4% by weight. For reproducibility purposes, the powders were pressed into eight identical pellets for each composition. The homogenized powder was placed into a 6-mm die, which was then put into a hydraulic press under a pressure of 60 MPa to obtain pellets. This was a delicate process

depending on the amount of Al_2O_3. Acetone helped with the pressing process by preventing flaking of the pellets. A hand-held x-ray fluorescence (XRF) instrument (Tracer III-SD from Bruker) allowed the identification of the elements, including impurities, present in the samples. This gun excites electrons and measures the intensity and energy of the emitted photons. Their energy corresponds to the electronic configuration of specific elements. The purity of the raw powders and the pellets after treatments were determined with the XRF instrument.

Once pressed into compacted disc-shaped pellets, the samples were placed into a box annealing oven to sinter at 1400 °C for a period of 24 hours. This sintering step increases the particle to particle contact and allows for the incorporation of Al into the ZnO structure. The samples were covered with sacrificial powder of the same composition to avoid contamination from the alumina crucibles. After the samples were heated, their conductivity and thermopower were measured. While under the C4S four-point electrical probe, automated measurements for resistance were taken using a connected programmable current source and a digital multimeter. The range of amperage applied to the samples varied depending on the instrument's capabilities to establish an adequate signal through the material. A typical interval ranged from -100 mA to +100 mA with 10 step intervals. The conductivity was calculated using Equations (1) and (2) and applying geometrical corrections [7-8].

Thermopower testing was conducted using an existing setup and procedure [6]. The technique consisted of using a soldering iron to achieve a temperature gradient of 230 °C between the two thermocouples placed on either side of the pellet faces. The sample was then allowed to cool. The thermocouples measured how well heat was transferred throughout the material by exploiting its thermoelectric properties. A digital multimeter measured the voltage drops due to the thermal gradient. The transference of heat and thus the thermopower were determined for each sample using Equation (3). The elemental compositions were measured again using the XRF instrument.

After these tests, the pellets were placed into another boat crucible and bedding to undergo reduction in a tube furnace (Thermo-Fischer). The furnace was attached to a pressurized tank of forming gas (4% hydrogen, 96% nitrogen mixture). The samples were heated to 500 °C and simultaneously exposed to the forming gas for 10 hours. The samples were allowed to interact with forming gas at high temperatures in order for reduction to occur. For samples like indium-tin oxide, the exposure to reducing gases increases the conductivity since some of the oxygen ions in the structure are removed resulting in a higher population of free electrons [6]. The mechanism for zinc oxide is not well understood, but it is hypothesized that either oxygen is removed resulting in oxygen vacancies, zinc interstitials, or complex defects that combine both point defects [1]. The electrical properties were tested again following the same procedure described above.

RESULTS AND DISCUSSION

No impurities were detected in the XRF spectra of the B1-ZnO and A2-Al_2O_3 untreated batches or in any of the pellets used in this study. After the high-temperature synthesis, one side of the pellets reflected light more than the other side that appeared more opaque. XRF measurements showed that the amount of aluminum was different on the opaque side and the surface with sparkles. The reflective side had more Al than the opaque side of the pellet. Figures 1, 2, and 3 show a comparison between five different batches of B1-A2, with 0%, 1%, 2%, 2.5%, and 4% Al doping before and after reduction of both the surfaces. Both sides of the pellet had similar electrical results, within experimental error, even when their surfaces appeared different. This indicates that the conductivity measurements were probing the bulk of the samples, not just the surface. It is clear that aluminum doping had a dramatic effect on the materials. The reducing gas affected the 4% Al-ZnO samples the most (an increase of a factor of ~10), but did not have a significant effect on the other samples. The results for the 4 % sample could be attributed to the formation of defects in the structure.

However, x-ray and neutron structural studies are needed to determine which type of defects is present in the samples. The undoped ZnO samples were about 3000 times less conductive than the AZO doped pellets. The conductivity increased with doping, reached a maximum for the 2% and 2.5% samples, and then decreased. The highest conductivity was approximately 150 S/cm (siemens per centimeter).

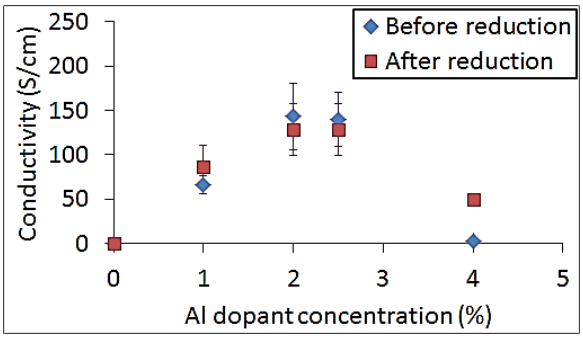

Figure 1: Conductivity of the reflective side before and after reduction.

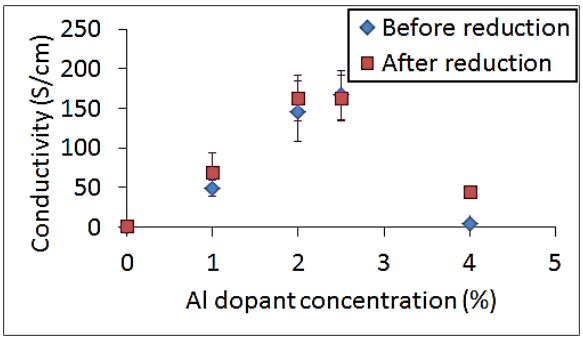

Figure 2: Conductivity of the opaque side before and after reduction.

Thermopower tests were run after the pellets came out of the annealing and reducing ovens. These measurements were performed using a heat source, gold foils, and S-type thermocouples. S-type thermocouples consist of two wires that are joined together at one end. One wire has a composition of 90 weight % Pt/10% Rh while the other wire is pure Pt. The thermocouples allow the measurement of the transference of heat, which directly correlates to the carrier concentration of each pellet. Figure 4 presents the thermopower results of the B1-A2 series, before and after reduction. The magnitude of the thermopower decreased as the doping concentration increased suggesting that larger electron populations are present at lower doping levels. The undoped ZnO samples (not shown in Figure 4) had a thermopower of ~500 μV/K. Therefore doping with aluminum dramatically increased the number of conduction electrons. The reduction treatment did not have an effect on the thermopower, within experimental error, except for the 4 % sample where there is a decrease of about 20 %.

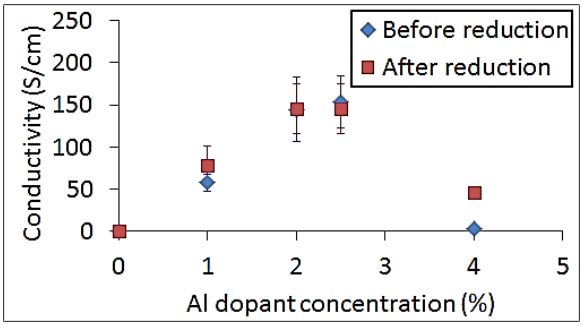

Figure 3: Average of the conductivity of both surfaces before and after reduction

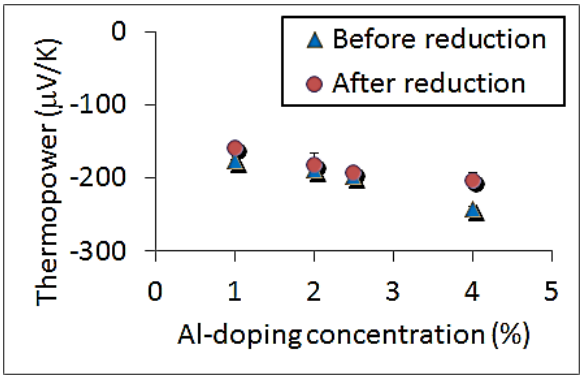

Figure 4: Thermopower before and after reduction

Since as shown in Equation (2), the conductivity is a product of the carrier concentration and the mobility, from the results

it can be concluded that aluminum doping increased both the population of electrons and their mobilities. For the 1% doping level, the mobility was relatively low, but it improved substantially for the 2% and 2.5 % samples. Even when the carrier concentration decreased for these doping levels, the overall conductivity reached a maximum. The 4 % sample can be classified as overdoped, since the electrical properties worsened as more aluminum was introduced.

The conductivity of thin film samples is typically higher than in powders since more desirable defects can be incorporated in the lattice of metastable samples. The preparation of thin films allows for higher doping levels that result in a wide range of electrical properties. For Al-doped ZnO films, the conductivity can reach up to 6500 S/cm [1]. Those values are comparable to the conductivity of indium-tin oxide thin films. For bulk powders, the conductivity can be lower since during the high-temperature synthesis, thermodynamic solubility limits are achieved and less defects can be incorporated. ITO powders exhibit a wide range of electrical properties depending on the synthesis temperature and post-annealing treatments. For example, ITO powders prepared at 1350 ^{o}C, before reduction, had conductivity of 600 S/cm; and after CO/CO_2 reduction at 800 ^{o}C, the conductivity increased to approximately 1700 S/cm [9]. These values are one order of magnitude higher than the aluminum-doped ZnO samples prepared in this study. From previous experiments, the purity and grain size of the starting powders, the sintering temperature, the gas reduction atmospheres, temperatures, and annealing times have major effects on the conductivity [10]. Optimization of the synthesis conditions is needed to further improve the electrical behavior of these samples. However, as mentioned before, the Al-doped samples are 3000 times more conductive compared to undoped ZnO samples.

CONCLUSIONS

The electrical results give conclusive evidence that aluminum doping significantly increases the electrical conductivity, carrier concentration, and mobility of ZnO. The ratios between ZnO and Al_2O_3 also indicate that there is a specific range for optimizing the percentage of doping in ZnO. As more experiments are conducted, a better understanding of ZnO is achieved.

ACKNOWLEDGEMENTS

I would like to thank Dr. Gabriela González Avilés for the opportunity to work on the project and her research. I would also like to thank the previous students who worked on the project, allowing for the research to continue on to the present: Mark Procaccio, Bruce Griffin, Anna Wesolik, Jared Hennen, Thomas McManus, Alexander Slawik, and Leonel Hernandez. The CSH Undergraduate Research Assistantship Program funded my project in the summer and fall of 2013.

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