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DePaul University

The Effect of Grain Size and Forming Gas Reduction on the Electrical Properties of Zinc Oxide

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MASTER OF SCIENCE

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ABSTRACT

Zinc oxide is an n-type transparent conducting oxide (TCO), which is used in solar cells and optoelectronics devices. ZnO has the potential to become the future choice for a wide range of TCO commercial applications replacing the current, more expensive, and toxic indiumbased materials. The isothermal grain growth of ZnO nano-powders with two different initial grain sizes and the effect of forming gas reduction on their electrical properties were studied at 900 °C. The particle size was determined using synchrotron x-ray diffraction data and scanning electron micrographs. The grain size, shape, trace impurities, and synthesis methods had an effect on the electrical performance of crystallites smaller than 300 nm. For grains larger than 300 nm, similar conductivity values were achieved regardless of the initial grain size and impurities. While grain growth modestly increased the electrical performance of ZnO, the exposure to reduction gases dramatically improved the conductivity by five orders of magnitude. Synchrotron x-ray diffraction data collected *in situ* at 500 °C also showed that reducing gases enhanced the grain growth of nanoparticles.

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Life is an interesting journey but where I am in this journey is not just because of what I have done or who I am. I have been very fortunate to have many excellent teachers to show me the way and family and friends to encourage and support me in this path. I am grateful for each and every one of them.

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1. Introduction

1.1 Description of a transparent conducting oxide

A transparent conducting oxide (TCO) is a material with high transparency in the visible region as well as high electrical conductivity. TCOs have been produced from a broad selection of materials including semiconducting oxides of zinc, tin, indium, cadmium [1] [2]. TCOs' properties make them ideal materials for flat-panel displays and smart windows [3] [4]. High transparency and functional conductivity can be obtained in wide band-gap oxides (> 3 eV) [5].

The electrical properties of TCOs are related to the stoichiometry of the material, the nature and quantity of impurities, grain size, and synthesis conditions [6]. Imperfections in the crystal structure, some of which are caused by certain impurities, significantly affect the electrical behavior of semiconductors. A non-stoichiometric semiconductor has deficiencies that can act as electron donors or acceptors. Doping is a calculated and intentional addition of desirable impurities to a semiconductor. In semiconductor facilities, the materials are typically first purified as much as possible and then the impurities are introduced in a controlled manner. When the pure semiconductor behavior is caused by its own inherent properties, the semiconductor is called 'intrinsic'. For zinc oxide, the intrinsic defects depend on how the material was produced. After the impurities are introduced in the semiconductors their innate traits are altered due to the external impurities and thus they are called 'extrinsic'.

Commercial TCO materials are n-type semiconductors; however extensive efforts have been devoted to find and optimize p-type materials. The p-type conductivity of some TCOs fades within days or weeks and is not persistent [7]. P-type semiconductors are doped with acceptor atoms. N-type semiconductors are doped with donor atoms; the *n* stands for negative charge carriers. High n-type conductivity is obtained due to the presence of a high population of electrons and/or electrons having high mobility. Equation 1.1 describes the electrical conductivity in a semiconductor,

$$
\sigma = \left(\frac{e}{m^*} \tau\right) (N_e e) = \mu_e (N_e e)
$$
 1.1

where *e* is the electron charge, *m** is electron effective mass, *σ* is the electrical conductivity, and τ is the collision time. The electrical conductivity depends on charge density or carrier concentration (N_e) and mobility (μ_e) of relevant free carriers [4]. The mobility depends on *τ* and *m*.*

1.2 Zinc oxide as a transparent conducting oxide

Zinc oxide (ZnO) is a wide band-gap semiconductor (*Eg*=3.2 *eV*) that has been investigated as an electronic material since the 1930s. ZnO is an important component in light-emitting devices, as well as high-temperature electronics. ZnO is typically an n-type semiconductor, and p-type doping remains a challenge.

The rare mineral *zincite*, a natural formation of ZnO, crystallizes in the hexagonal wurtzite structure [3]. The unit cell of ZnO contains two molecules within a lattice with constants *a*=*b* =0.325 nm and *c*=0.52066 nm [8].

1.3 Motivation for this study

TCOs are important for technology. They need to be electrically conductive and optically transparent in the visible region. Every day the demands for green energy increase due to the emission of green house gases. In order to reverse the trend of green house gas emissions, renewable source of energy will have to play a bigger role in the supply of the energy demand of the world. Solar energy is one of the most abundant sources of renewable energy and it is therefore important to discover improved methods for using and storing solar energy. ZnO has the potential to become a future choice for TCO commercial applications replacing the current, more expensive, and toxic indium-based materials.

The attempt of this research is to better understand the relationships between grain size, conductivity, thermopower, and impurities in zinc oxide. Two different zinc oxide nanopowders containing different impurities and grain sizes were used to study these relationships.

Literature studies have reported the grain growth and sintering of ZnO in air at various temperatures [[9], [10], [11]]. Other studies have focused on the effect of dopants and

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reducing gases on zinc oxide materials [[1],[2],[4],[5]] and on doped indium oxide, tin oxide, gallium oxide, and cadmium oxide n-type thin films [12], [13], [14]]. However, no systematic studies have investigated directly the effect of grain growth and reducing gases on the conductivity of zinc oxide nano-materials.

2. Experimental procedure

2.1 Characterization of nanopowders

Several batches of ZnO nanopowders were purchased from Alfa Aesar (Ward Hill, MA). Five batches (labeled N5, N6, N7, N8, and N9) were chosen for preliminary studies based on their particle size, impurities, electrical and thermal properties. The size distribution, shape and homogeneity of the nanoparticles were observed using scanning electron microscopy (SEM). The impurities were determined from x-ray fluorescence (XRF) measurements. Four-point DC probe measurements were used to measure the electrical conductivity. Two batches of the ZnO nanopowders, N5 and N6, were selected for further experiments based on their electrical properties.

2.2 Sample preparation

ZnO powders were ground in a mortar using a pestle. Acetone was used to homogenize the powder and reduce the static charge of the nanoparticles. The mass of powder used for each pellet was approximately 0.3 grams. The exact mass for each pellet was measured using a high precision scale (Mettler toledo, ab54/fact, Greifensee, Switzerland). Thereafter, the powder was poured into a 6-mm stainless steel die. The die set was inserted in a hydraulic press (Carver 4350, Wabash, IN) and pressurized to approximately 1000 psi for 90 seconds. This pressure value was experimentally determined to achieve uniform

pellets. The pellet was released from the die set and its mass was measured. Since the next step was to anneal the samples, it was important to record the as-pressed masses and compare them with the post-annealing measurements. A total of ninety 6-mm pellets were prepared using this procedure.

Another set of samples was prepared to study the defect structure of zinc oxide. Sixteen pellets with 13 mm diameter were pressed for N5 and N6. They were heated for 10 hours at 500°C. Neutron diffraction and x-ray diffraction data were collected on these samples to investigate the effect of reducing atmospheres and grain size on the defect structure of ZnO. The analysis of these data and the defect structure results are not discussed since they are not the subject of this thesis.

2.3 Annealing

The samples were annealed using two different environments: air and reducing gas. The air annealing was done in a high-temperature box furnace (Lindberg/Blue M, 1500°C, bf51333c, Asheville, NC). The reduction anneal was performed using a tube furnace (Thermolyne type F79330-33-70, Dubuque, Iowa) with a temperature stability range of ± 0.5 °C.

For reproducibility purposes, four pellets of identical composition were placed in a hightemperature alumina crucible (Coors Tek, Golden, CO). In order to decrease the volatilization and contamination from the crucible, the four pellets were surrounded with sacrificial powder with identical composition to the powder of the pellets. The crucible was then covered with a tight-fitting crucible lid and loaded into a bigger crucible with a sealed cover to minimize evaporation. Thereafter the samples were placed inside the box furnace and fired at 900°C for different lengths of time (1 minute, 30 minutes, 1 hour, 3 hours, 8 hours, 18 hours, 24 hours, 48 hours, and 55 hours for N5; and 1 minute, 30 minutes, 1 hour, 2 hours, 3 hours, 8 hours, 55 hours, and 68 hours for N6) using a heating rate of 3°C/min. Different time intervals were chosen to study the relationship between grain growth and the heat exposure. After the heat treatment, the pellets were immediately pulled from the furnace and were quenched in air to room temperature. This was achieved by removing the crucible from the oven and uncovering it, then pouring the material on an alumina rectangular tray to quickly expose the pellet to room temperature.

For the reduction treatment two out of the four samples were placed in an alumina combustion boat. Again, in order to minimize contamination, sacrificial powder was used to surround the two pellets. The combustion boat was placed in the middle of the furnace tube. These pellets were exposed to forming gas $(4\% H₂$ and $96\% N₂)$, which was injected from one end of the tube, exhausted from the other end and vented out to a fume hood (Fisher scientific, Two Rivers, WI). Each set of pellets was reduced for 10 hours at 500°C. The heating and cooling rates were 5° C/min under the same flowing forming gas. After reduction, the masses of the pellets were re-measured. The thickness and the diameter of each pellet were determined using a micrometer and a Vernier caliper.

2.4 Conductivity

For every quenched pellet, the conductivity of each side was measured at room temperature using a four-point DC probe (Cascade c4s 44/1s 2381, Beaverton, OR). The four-point head consisted of osmium-tipped probes with a tip radius of $250\mu m/10$ mil, spacing of 1.25 mm, and a pressure of 40-70 grams per tip. The equipment was connected to a constant current source (Keithley, 6220 precision current source, Cleveland, IO) and a digital multimeter (Keithley, 2700 multimeter/data acquisition system, Cleveland, IO). The four-point probe was attached to an adjustable-height stand with a granite base. The data were collected using LabVIEW 8.5. [15].

The sample was placed on a granite base, and then the 4-point probe was lowered to make contact with one side of the sample. Current (*I*) was applied to the two outer pins and the voltage ΔV was measured across the two inner probe pins. Current was provided by incrementally increasing the current to the sample while the multimeter recorded the voltage in the LabVIEW program. For each set, ten points were collected: five points for positive voltage, and five points for negative voltage. For the reduced samples, the current range was from -60 mA to 60 mA; the current increment was 10 mA, and the settling time was 20 s. For the samples before reduction the range for the current was from -0.2 mA to 0.2 mA; and the current increment was 0.02 mA. By using Ohm's law, the resistance (*R*) of the sample was calculated according to Equation 2.1:

$$
R = \frac{\Delta V}{I}
$$
 2.1

The four-point probe is a suitable instrument for the measurement of resistivity of conductors and semiconductors but depending on the shape, size and the thickness of the sample, corrections are needed [16]. Equation 2.2 was used for calculating the conductivity of the pellets [17].

$$
\sigma = \frac{1}{\rho} = 1 / \left[\frac{\Delta V}{I} w C \left(\frac{d}{s} \right) F \left(\frac{w}{s} \right) \right]
$$
 2.2

Here σ represents the conductivity, ρ is the resistivity, *I* is the current, ΔV is the potential difference measured by the inner pins, w is the thickness, d is the sample diameter, s is the probe tip spacing (0.102 mm), and C and F are the correction factors for finite sample diameter and thickness [[18], [19], [20], [21]], given by Equations 2.3 and 2.4.

$$
C = \frac{\pi}{\left[\ln 2 + \ln\left\{\left[\left(\frac{d}{s}\right)^2 + 3\right] / \left[\left(\frac{d}{s}\right)^2 - 3\right]\right\}\right]}
$$
 2.3

$$
F = 1 + 4 \frac{s}{w} \left[\sum_{n=1}^{\infty} (-1)^n \left(\frac{1}{\sqrt{(\frac{s}{w})^2 + (2n)^2}} - \frac{1}{\sqrt{(2\frac{s}{w})^2 + (2n)^2}} \right) \right]
$$
 2.4

2.5 Thermopower

Thermopower was measured to study the electron concentration of the samples and to determine the type of majority carriers [3]. The thermopower Q is related to m^* and N_e as shown in Equation 2.5

$$
Q \propto \frac{1}{E_F} \propto \frac{m^*}{N_e^{2/3}}
$$

The effective mass of the donors (m_d^*) depends on the energy and the density of states in the conducting band. The N_e dependence of m_d^* is given by

$$
m_d^* \propto N_e^{1/3} \tag{2.6}
$$

Therefore

$$
Q \propto N_e^{-1/3} \tag{2.7}
$$

To measure thermopower, the sample was placed between two pieces of gold foil, which were attached to *S*-type thermocouples. A soldering iron was placed on the top sheet while the bottom sheet was in contact with a metal block resting on a refractory brick at room temperature. The soldering iron was used to heat the top of the sample to create a 200°C temperature differential. The sample was then allowed to cool to room temperature and follow a decayed thermal gradient. Data corresponding to a temperature gradient range

around thermal equilibrium (Δ*T* ≤ 20) were used for calculating the thermopower, *Q*. The data were analyzed using Equation 2.8 below with a method of least squares.

$$
Q = -\lim_{\Delta T \to 0} (\Delta V / \Delta T) \tag{2.8}
$$

A correction was applied to *Q* to remove the contribution of the platinum wires from the thermocouples. The negative sign of *Q* indicates that the samples are n-type semiconductors [3].

2.6 X-ray fluorescence (XRF)

The presence of impurities and secondary phases affect the electrical properties of materials. Impurities and secondary phases can change dramatically during thermal and gas treatments, therefore it is important to monitor these changes. X-ray fluorescence is a non-destructive technique used for determining and quantifying the types of impurities both on the surface and in the bulk of the sample. Every element has a characteristic electron configuration. When atoms are bombarded by x-rays, electrons get ejected from inner *K* and *L* shells leaving holes that will be filled back by higher shell electrons. During this transition the atom radiates x-ray photons with a characteristic energy related to the difference between the two shells. This radiation is referred to as x-ray fluorescence (XRF) [22].

The impurities of the untreated and treated samples were measured at DePaul University's Physics Department by using a handheld XRF Bruker, Tracer III-SD instrument (Kennewick, WA). XRF data were collected on treated and untreated powders. The untreated powder was placed between two Prolene films during XRF measurements. These films are mostly transparent to x-rays but contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti, Al. Therefore a background spectrum was collected with a Prolene film having no powder to establish the baseline of the radiations from Rh and Pt of the x-ray tube and Si from the detector. The treated powders were measured in pellet form.

The XRF instrument can be used with four filters. Each filter is optimized for the measurement of a certain region of electromagnetic spectrum. A yellow filter with composition of 0.001" Ti and 0.012 Al was used for measuring the metal elements Ti to Ag (K lines) and the W to Bi lines. A red filter with composition 0.001" Cu, 0.001" Ti, .012 Al was used for measuring higher Z elements (Hg, Pb, Br, and As). For Mg, Al, Si and P to Cu and any *L* and *M* lines for the elements that fall between 1.2 and 8 keV a vacuum pump (and no filter) was used [23]. The spectrum of each filter was obtained without any sample for the baseline. The sample spectrum was superimposed on its corresponding filter spectrum, in order to identify unique peak(s) of various elements. Finally with the help of the Artax software, which is an x-ray analysis program provided by Bruker[22], each spectrum was analyzed to identify the impurities.

2.7 Scanning electron microscopy (SEM)

A scanning electron microscope is an instrument capable of reproducing the topography of the surface of samples through the use of electron beams. When electrons interact with the atoms of the material, information about the grain size, the shape, and the texture of the specimen is obtained. Samples for SEM need to be electrically conductive to obtain sharp images. Insulating specimens would result in blurry micrographs and may require a layer of conductive material.

SEM experiments were conducted at the Electron Probe Instrumentation Center (EPIC) of Northwestern University using the Surface Scanning Electron Microscopy with LEO Gemini 1525 high-resolution instrument. Micrographs with different magnifications (100 KX, 200 KX, and 300 KX, where KX stands for a 1,000 magnification) were recorded to investigate the homogeneity of the samples and the morphology of the nanoparticles. A small amount of powder was placed on conductive carbon tape and then introduced inside the vacuum chamber of the SEM instrument. No additional coating was deposited. Therefore the sharpness of the images was closely related to the conductivity of the samples.

2.8 X-ray diffraction (XRD)

In a diffraction experiment, x-rays interact with the electron cloud of atomic planes producing regions of constructive and destructive interference. X-ray diffraction (XRD) is a technique that gives information about phase purity, lattice parameters, structural arrangement of the atoms, and the grain sizes of the samples.

After grinding treated samples, XRD data were measured at Northwestern University at the Jerome B. Cohen XRD facility (Evanston, IL) and at the Advanced Photon Source (APS) at Argonne National Laboratory (Chicago, IL). XRD data were analyzed to check the phase purity of the samples using the x-ray machine Scintag XDS2000 at Northwestern. In order to get high-resolution and high-statistics data the samples were also measured at the APS. The high-resolution APS data were used to obtain the average grain size and anisotropy for each sample.

2.8.1. Ex-situ experiments at 11-BM

To obtain phase purity and grain size information from the x-ray diffraction pattern, the powder samples were measured at the 11-BM beamline at the APS of Argonne National Laboratory. This beamline takes advantage of the APS bending magnet source and offers high resolution of $\frac{dQ}{Q} \approx 2 \times 10^{-4}$ (*min. 20 step size* = 0.0001°) with a range of energies between 12 and 35 keV ($\lambda \approx 1.0 - 0.34$ Å). The flux was $\sim 5 \times 10^{11} \frac{p_{10}^{1000} m_{s}^{1000}}{sec}$ at 30 keV. The wavelength used was 0.4 Å, and the scan time was 50 minutes. For measurements at 11- BM, the samples were loaded into Kapton capillary tubes with inner diameter of 0.80 mm. Kapton is transparent to x-rays so the background signal due to the sample holder is negligible. The experiments at beamline11-BM were collected at two different temperatures: 298 K and 100 K. At low temperatures, the thermal vibrations of the atoms

are reduced; therefore for some experiments this setup is preferred. For the present study both sets of data gave identical grain size results.

2.8.2. In-situ experiments at 1-BM:

The 1-BM beamline at the APS allows the collection of x-ray diffraction data at elevated temperatures under various annealing conditions. The source of the 1-BM beamline is a bending magnet, providing a ($\Delta E/E$) resolution of 1.5×10^{-4} and a flux of 9× 10¹¹ photons/ The energy range of the beamline is from 8 to 22 keV. *In-situ* x-ray diffraction data were collected at 0.60685 Å on N5 and N6 samples. For the first 10 minutes, one image was collected every minute, and for the rest of the experiment (up to 18 hours) one image was collected every two minutes. Untreated N5 and N6 powders were heated inside a hightemperature cell that allowed the flow of gases. The measurements were done at 500°C under various gas conditions (He/H₂ and O₂ for N6; and HeH₂, O₂, and H₂N₂ for N5). The capillary used for the samples was glass since Kapton is not stable at this temperature. The x-ray diffraction spectra were analyzed using the Matlab program [24] in order to remove the background spectrum due to the glass capillary and to integrate the images. Grain size and the phase-purity of the samples were investigated with these data.

2.8.3 Matlab analysis

Figure 2.1 shows a typical 2D x-ray diffraction image. The black line is the shadow of sample mount.

Figure 2.1 X-ray diffraction pattern, N5 in nitrogen (1BM)

About 900 files were analyzed with Matlab macros. Each 2-D image was radially integrated to obtain a 1-D data set of intensity vs. diffraction angle. The spectrum of the empty capillary was subtracted from each XRD 2-D image. This output became the input for the FullProf software [25]. Figure 2.2 shows the integrated x-ray pattern of N5 in nitrogen for 1 BM.

Figure 2.2 X-ray diffraction pattern, N5 in nitrogen (1BM)

2.8.4 FullProf

FullProf is an x-ray diffraction analysis program that implements the Rietveld method [26]. The program models the peak shapes and intensities of the diffraction pattern to provide accurate simulations of the structural arrangement of atoms and the microstructure of the sample. This is specifically helpful when the diffraction data are influenced by structural defects such as anti-phase domains and poor crystallization.

The instrumental broadening of the x-ray diffractometer was obtained by measuring the diffraction pattern of the NIST LaB6 standard SRM 660a. Grain size information, including anisotropy, was then extracted from the refinement of the width and shape of the diffraction peaks. FullProf allows the simulation of sphere, needle, cubic, and other irregular shapes using spherical harmonic functions [27]. For this study, anisotropic broadening was refined using the Scherrer formula that considers a linear combination of spherical harmonics. The size broadening is given by:

$$
\beta_h = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} y_{lmp(\Theta_h, \Phi_h)} \tag{2.9}
$$

where β _h is the size contribution to the integral breadth of reflection **h**, y_{lmp} (Θ_{h} , Φ_{h}) are the real spherical harmonics with normalization, a_{imp} are the refined coefficients, and the arguments are the polar angles of the vector **h** with respect to the Cartesian crystallographic frame. If an instrumental broadening input is given, the program calculates the apparent size along each reciprocal lattice vector (h k l), and a microstructural file (*.mic) is created, which contains grain size and strain information due to the sample only.

This is an example of a mic file for sample N5_1 treated for 1 hour:

MICRO-STRUCTURAL ANALYSIS FROM FULLPROF (still under development!) A summary of Micro-structural model is given at the end of the file.
FWHM (HG, HL, ...) are given in the same unit as that of the scattering variable
Integral breadths (Beta) are given in reciprocal lattice units (1/angst An apparent size equal to 99999 means no size broadening
The following items are output:
 $s=1/d$: reciprocal distance, $\begin{array}{cc} H G_0, H G_1 : 0.05 \text{ per} \text{ word} \text{ and} \end{array}$ e rollowing items are output:
s=1/d : reciprocal distance, HGo, HGi: observed and instrumental Gaussian FWHM
HLo, HLi: observed and instrumental Lorentzian FWHM
betaG, betaL, beta: Gaussian, Lorentzian and total Sample I

"beta" is calculated using the De Keijser formula (J.Appl.Cryst. 1982, 15, 308-31)
For internal calculations we use beta_TCH (see below)

betaVo, HpVo, eta: Integral Breadth, FWHM and eta values of the total observed pseudo-Voigt profile

The apparent sizes/strains are calculated for each reflection using the formula:

App-size (Angstroms) = 1/(Beta-size)
Max-strain (%%) = 1/2 (Beta-strain) * d(hkl) = 1/4 eta(app-strain Stokes-Wilson)

(Beta-size) is obtained from the size parameters contributing to the FWHM:
FWHMA2 (G-size) = HgzA2 = IG/cosA2(theta)
FWHM (L-size) = H1z = (Y + F(Sz))/cos(theta)
(Beta-strain) is obtained from the strain parameters contri

In both cases (H,eta) are calculated from TCH formula and then Beta-pV is calculated beta-pV= $0.5*H/$ (eta/p i+ $(1.0-eta)/sqrt(pr/Ln2)$)

The standard deviations appearing in the global average apparent size and strain is
calculated using the different reciprocal lattice directions.
It is a measure of the degree of anisotropy, not of the estimated error!

……..

Grain size (Å) Anisotropy (Å)

Figure 2.3 Mic (Microstructural) file for sample N5_1 treated for 1 hour

All the average grain sizes and anisotropy values were extracted from the mic files with the help of a "c sharp" program. The code is provided in Appendix Ι. Anisotropy is the deviation from the average distribution of grain size along different axes. A large value for anisotropy corresponds to non-spherical grains and/or to a wide distribution of crystallite sizes in the sample volume that is measured.

As Figure 2.3 shows the mic file provides microstructural information for each individual diffraction direction. For example, for this specific sample, the biggest apparent size of 252 nm was in the (4 0 1) direction, while the smallest size was 111 nm along the (3 1 7) direction. The average grain size was 163 nm and due to the wide range of sizes the anisotropy was 39 nm, which in this case corresponds to 24 % of the average size.

3. Results and discussions

3.1 X-ray fluorescence (XRF) results and discussion

Figure 3.1 shows the x-ray fluorescence data for the N5 and N6 samples, which were annealed in air at 900°C for one minute and then reduced at 500°C for 10 hours. The spectra were collected using the red filter, which is optimized for the detection of heavy elements. A spectrum with no sample is shown in blue in Figure 3.1. The Rh and Pt lines, which are not labeled in the figure, come from the x-ray tube while the Si lines are due to the detector.

Figure 3.1 Spectra for N5 (1 min, red spectrum), N6 (1 min, green), and background (blue) using the red filter

The spectrum for N6 did not contain any detectable impurities, while the spectrum for N5 showed the presence of Zr in the sample. Similar results were obtained for the untreated batches indicating that this heat treatment at 900°C and the reductions at 500°C did not alter the elemental composition of the pellets. Furthermore, superposition of the spectra for the N5 samples fired at 900°C for one minute and for 48 hours followed by reduction (Figure 3.2), shows that the elemental composition did not change. Zr impurities are observed in both spectra and their concentrations remained the same.

Figure 3.2 Spectra for N5 (1 min, green and 48 hrs, red)

XRF data in vacuum were also collected for these samples. The vacuum system allowed the detection of lighter elements. The XRF spectra of N6 samples fired at 900°C for 1 minute and 68 hours and then reduced were very similar (Figure 3.3). The fluorescence lines for the two spectra seemed identical showing that the overall elemental composition in the N6 samples did not change even after a 68-hour anneal at 900°C.

Figure 3.3 Superimposed XRF spectra of N6 samples prepared with various firing times at 900°C (1 min, green and 68 hrs, magenta) and a background spectrum (red)

Therefore, the results from XRF show that N5 had Zr impurity atoms. Since zirconium has two more valence electrons than zinc, this impurity could potentially act as an n-type dopant, increasing the conductivity of the samples compared to undoped ZnO.

3.2 Scanning electron microscopy (SEM) results and discussion

Figures 3.4 and 3.5 show the SEM images of the N5 and N6 powders before any treatments. Based on XRD information the initial grain size of untreated N5 was 24 nm \pm 1 nm with an anisotropy of 3 nm. The initial grain size of the untreated N6 powder was 75 nm \pm 1 with an anisotropy of 15 nm.

Figure 3.4 SEM image for sample N5 before any treatment: Magnification=100 KX

Figure 3.5 SEM image for sample N6 before any treatment: magnification=100 KX

Figures 3.6 and 3.7 show the SEM micrographs of N5 and N6 samples fired at 900°C for 1 minute followed by the reduction treatment. Comparison of the SEM images for both N5 and N6 samples prior to and post treatment shows that grain growth occurred during heating from room temperature up to 900 °C.

Figure 3.6 SEM for N5 fired at 900°C for 1 minute in air and reduced at 500°C for 10 hours:

magnification=100.53 KX

Figure 3.7 SEM for N6 fired at 900°C for 1 minute in air and reduced at 500°C for 10 hours:

magnification =150 KX

Figures 3.8 and 3.9 correspond to images of N5 and N6, respectively, heated at 500°C for 10 hours and then reduced for an additional 10 hours at this same temperature.

Figure 3.8 SEM for N5 fired for 10 hours at 500 °C in air and then reduced: magnification

=100.05 KX

Figure 3.9 SEM for N6 fired for 10 hours at 500 °C in air and then reduced: magnification

=100.18 KX
Figure 3.10 is a micrograph of N5 after 48 hours at 500°C in air followed by a reduction anneal for 10 hours at the same temperature.

Figure 3.10 SEM for N5 after a 48-hour anneal in air at 500 °C and a reduction at 500°C for 10 hours: magnification =100.18 KX

Figures 3.8, 3.9 and 3.10 show that the grains of N5 and N6 did not grow substantially at 500°C compared to those heated at 900°C first and then at 500°C under the reduction gas. Even in Figure 3.10 where N5 was heated for 48 hours at 500°C and then reduced, the grains exhibited only modest growth. Therefore, as expected, the first step of heating at 900°C had the most dramatic effect on grain growth due to the higher temperature.

Figure 3.11 and Figure 3.12 show the SEM images for N5 and N6 that were fired at 900°C for 55 hrs in air and reduced at 500°C for 10 hours.

Figure 3.11 SEM for N5 fired at 900°C for 55 hrs in air and reduced at 500°C for 10 hours:

magnification =150.00 KX

Figure 3.12 SEM for N6 fired at 900°C for 55 hrs in air and reduced at 500°C for 10 hours:

magnification= 150.00 KX

A comparison of these SEM images reveals that the N5 powder exhibited a more pronounced grain growth compared to N6. Different grain growth kinetics can be a result of several parameters such as the initial grain size and shape, impurities, and the synthesis method by which the nanoparticles were prepared. Since these nanopowders were purchased, this study had no control over these parameters.

3.2.1 Histograms

3.2.1.1 Histogram of N5 at 48 hours

Figure 3.13 and Figure 3.14 show two SEM images for the same N5 sample annealed for 48 hours at 900 °C and then reduced. Histograms of the grain size distribution obtained from SEM were prepared to compare with the XRD results. The volume of grains that x-rays diffract from was bigger compared to the SEM volume. Therefore, in order to have a better representation of the distribution of grain sizes, two SEM images of N5 with the same magnification were chosen.

Figure 3.13 SEM for N5 fired at 900°C for 48 hrs in air and reduced at 500°C for 10 hours:

magnification= 200.37 KX

Figure 3.14 SEM for N5 fired at 900°C for 48 hrs in air and reduced at 500°C for 10 hours:

magnification= 200.37 KX

Figure 3.15 shows the histogram of N5 annealed for 48 hours. For the histogram, the shapes of the grains were assumed to be spherical. The adjustment for magnification of the image was taken into account when calculating the radius of the spherical grain. The average of the grain circumference from the histogram was 550 nm, with a standard deviation of 38 nm. The grain size obtained from the XRD data was 312 nm and the anisotropy was 67 nm.

Figure 3.15 Histogram of the grain circumference of N5 after 48 hours at 900 °C

3.2.1.2 Histogram of N5 for 24 hours

Figure 3.16 shows an SEM picture for N5 annealed for 24 hours at 900 °C.

Figure 3.16 SEM for N5 fired at 900°C for 24 hrs in air and reduced at 500°C for 10 hours:

magnification= 201.49 KX

Figure 3.17 is the corresponding histogram for Figure 3.16.

500°C for 10 hours

From the histogram, the average grain size for N5 after 24 hours at 900 °C was 430 nm with a standard deviation of 44 nm. The grain size of N5 for 24 hours from the XRD data was 225 nm and the anisotropy was 45 nm. Discrepancies in the XRD and SEM values could be due to the inhomogeneity of the samples. As the SEM images show the shape of the grains was not spherical, and there was a wide distribution of sizes. Furthermore, the SEM images sampled only a very small fraction of the grains, while the XRD data was obtained from a larger sample volume [28].

A complete set of SEM images for various treatment times of samples is provided in Appendix ΙΙ.

3.3 The electrical conductivity results and discussion

3.3.1 Conductivity before forming gas reduction

The conductivity of each side of the four pellets was measured after being annealed in the high-temperature box furnace. As mentioned earlier, each set of the four pellets was annealed for different lengths of time to study the kinetics of grain growth. Electrical experiments were performed on quenched samples. This procedure was performed on the two batches of nanopowders (N5 and N6) which have different impurities and different initial grain sizes.

Tables 3.1 and 3.2 summarize the relationship between the durations of time and the conductivity for N5 and N6 before reduction. The conductivity of one side of a pellet differed from the other side by 10 % to 100 % for both batches. For the samples with BN (below noise) the conductivity was too low, and due to the sensitivity of the equipment, the measured values were below the threshold of the instrument $(5.7 \times 10^{-4} \text{ S/cm})$. As the results show, the conductivity values were very small and close to the noise level.

Table 3. 1 Relationship between the durations of time and conductivity for N5 pellets before reduction treatment

N ₅ Time durations	Average of conductivity before reduction gas (S/cm)
1 min	$(1.8\pm0.9)\times10^{-6}$
30 mins	$(8.4\pm4.3)\times10^{-5}$
1 hr	$(1.2\pm0.8)\times10^{-5}$
3 hrs	$(3.2 \pm 1.3) \times 10^{-5}$
8 hrs	ΒN
18 hrs	$(3.1\pm0.6)\times10^{-5}$
24 hrs	$(5.6 \pm 1.1) \times 10^{-5}$
48 hrs	$(9.2 \pm 3.1) \times 10^{-5}$
55 hrs	ВN

Table 3. 2 Relationship between the durations of time and conductivity for N6 pellets before reduction treatment

For both N5 and N6, after annealing in forming gas, the conductivity improved by 4 to 5 orders of magnitude. Figure 3.18 shows the conductivity as a function of annealing time for N5.

forming gas reduction

As shown in the above figure from 1 minute to 3 hours the conductivity increased gradually and then reached a plateau. The error bars on the conductivity graphs represent the standard deviation of the measurements for both sides of the two pellets that underwent the same treatment. The large error bars for some samples can be attributed to discrepancies in the conductivity due to the roughness of the pellets' surfaces.

Figure 3.19 shows that the conductivity for N6 increased gradually from 1 minute to 3 hours, and at 3 hours there was a more pronounced increase followed by a plateau.

Figure 3.19 Relationship between the durations of time at 900 °C and conductivity for N6 pellets after forming gas reduction

The conductivity as a function of time for both samples exhibited similar shapes. In the long term, the conductivity values for N5 and N6 were the same within the uncertainties. However their behavior at small grain sizes was different. For example, the conductivity of N5 at 1 minute was 3.5 S/cm while the conductivity of N6 at 1 minute was only 0.2 S/cm. N5 started to grow faster at 1 minute in comparison to the grains of N6 at 1 minute and yet untreated N5 had a smaller initial grain size. As a result the conductivity of N5 improved more than N6 once the sample reached 900 °C.

It should be pointed out that the conductivity values for these samples are comparable to those of undoped indium oxide powders. Furthermore, the values reported in this study have not been corrected for porosity. The N5 pellets were 55 % dense, while the N6 samples were 66 % dense. If the conductivity is corrected for porosity, the values would be larger.

3.3.2 Thermopower results and discussions

3.3.2.1 Thermopower before reduction treatment

As seen in Equation 1.1, both the electron concentration and the mobility of the carriers contribute to the electrical conductivity. To determine the majority carrier type and its concentration, the thermopower of each pellet was measured for N5 and N6. Tables 3.3 and 3.4 below summarize the effect of firing for different time intervals on the thermopower prior to reduction.

The negative sign of the thermopower measurements indicated that the samples were ntype. The magnitude of the thermopower is inversely related to the electron carrier concentration, therefore the results show that the number of carriers increased with grain size.

Table 3. 3 Relationship between annealing time and thermopower for N5 prior to reduction

N ₅ Time durations	Thermopower before treatment $(\mu V/K)$
1 min	-795
30 mins	-548
1 hr	-633
3 hrs	-668
8 hrs	-652
18 hrs	-533
24 hrs	-340
48 hrs	-330

Table 3. 4 Relationship between annealing time and thermopower for N6 prior to reduction

N ₆ Time durations	Thermopower before treatment $(\mu V/K)$
1 min	-697
30 mins	ΒN
1 hr	ΒN
3 hrs	ΒN
8 hrs	-517
18 hrs	-553
24 hrs	-548
48 hrs	-655
86 hrs	-529

Typical uncertainties due to the instrumental setup are on the order of 10 % for thermopower. The data showed that before reduction carrier concentration was very low for both N5 and N6. For N5 the number of carriers consistently increased with annealing time since the magnitude of *Q* decreased.

3.3.2.2 Thermopower results and discussion after reduction gas treatment

Figure 3.20 shows the effect on the thermopower of N5 and N6 after firing at 500 °C for 10 hours under reduction gas. As seen in this graph the concentration of carriers increased after exposure to reduction gas for both samples. However, the carrier concentration in N6 was higher than in N5 (the thermopower difference was on the order of 50μ V/K).

Figure 3.20 Thermopower for reduced N5 and N6 vs. annealing time at 900 °C

Figure 3.21 shows both the conductivity and thermopower of N5 as a function of grain size.

Figure 3.21 N5 conductivity and thermopower vs. grain size

Figure 3.22 shows the conductivity, grain size, and thermopower of N6.

Figure 3.22 N6 conductivity and thermopower vs. grain size

The above figures show that N6 and N5 had a similar mechanism for the enhancement of conductivity and carrier concentration as a function of grain size.

3.4 X-ray diffraction results and discussion

3.4.1 Ex-situ diffraction results and discussion of 11-BM data

The untreated N5 batch was not phase pure. The amount of hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ secondary phase was small compared to the primary ZnO, as shown in Figures 3.23 and 3.24. The secondary phase transformed to ZnO during heating prior to reaching 500°C as seen in Figures 3.25 and 3.26.

Figure 3.23 Rietveld refinement for untreated N5

In these Rietveld figures, the vertical lines of the first row mark the positions of the Bragg peaks for ZnO, while the second row corresponds to the secondary phase. The blue line shows the difference between the observed and calculated intensities.

Figure 3.24 focuses on the region where the strongest reflections from the secondary phase were found.

Figure 3.25 shows the full pattern of x-ray diffraction for the N5 sample that was annealed at 900°C for 1 minute and then reduced for 10 hours at 500°C.

Figure 3.25 Rietveld refinement for N5 after 1 min at 900 ^o C

Figure 3.26 presents the XRD pattern for N5 after 1 minute at 900 °C in the low-angle region where the secondary phase was detected prior to heating. The reflection peaks below 7.5° disappeared and only the ZnO wurtzite peaks were present. This confirms that the secondary phase transformed to ZnO prior to reaching 900 °C.

Phase purity for every sample was studied using Rietveld analysis with the FullProf program. The complete Rietveld fit for the N6 sample annealed for 1 hour at 900 $^{\circ}$ C and then reduced for 10 hours at 500 $^{\circ}$ C is found in Figure 3.27.

Figure 3.26 Low-angle region of the XRD pattern for N5 after 1 min at 900 ^o C

Figure 3.27 Rietveld refinement for N6 after 1 hour anneal at 900 ^oC followed by reduction

Tables 3.5 and 3.6 list the refined grain size and anisotropy results for the N5 and N6 samples, respectively. Both sets of data show that the grains grew as the firing time increased. The Rietveld refinement uncertainties reported on the second column are due to fits of the peak widths and shapes based on the experimental data collection parameters. The uncertainties given by the Rietveld refinement were very small (most were less than 1 %) due to both the high statistics of the data and the instrumental resolution. The error bars shown in the figures represent the grain anisotropy, which depended on the deviations from spherical shapes.

Table 3.5 Rietveld results for grain size and anisotropy of N5 samples fired in air at 900°C

followed by reduction

Table 3. 6 Rietveld results for grain size and anisotropy of N6 samples fired in air at 900°C

followed by reduction

Figures 3.28 and 3.29 summarize the grain size as a function of annealing time for N5 and N6.

Figure 3.28 Average grain size of N5 powder vs. annealing time in air at 900°C

Figure 3.29 Average grain size of N6 powder vs. annealing time in air at 900 °C

Figure 3.30 compares the grain size between N5 and N6. The crystallites of N5 grew faster and larger than N6 even though the initial size of N5 was smaller than N6, as confirmed by the SEM pictures. Also the anisotropy in the sample increased when the grains grew at this temperature.

Figure 3.30 Average grain sizes of N5 and N6 powders vs. annealing time

The kinetics of grain growth were analyzed using Equation 3.1.

$$
r_t^n - r_0^n = k_0 \text{texp}(-\text{Q/RT}) \tag{3.1}
$$

where r_0 the initial grain size at the annealing temperature is, r_t is the average grain size at time *t*, *n* is the grain growth kinetic exponent, k_0 is a constant, *Q* is the activation energy for the process of grain growth, *T* is the temperature, and *R* is the gas constant [$[29]$, $[9]$, $[10]$, [11]]. The values of *n* for N5 and N6 were obtained from the slope of ln-ln plots as shown in Figures 3.31 and 3.32.

Figure 3.31 Grain growth kinetics model (Equation 3.1) for N5 at 900 ^o C

The grain growth kinetic exponents are typically used to determine the dominant type of mechanism for grain growth and coarsening in ceramics and metals. For example, for ideal grain growth *n* =2, while for a diffusion-controlled mechanism *n* = 3. Literature reports in similar temperature ranges but with initial grains in the $0.1 \mu m$ to $0.25 \mu m$ range have obtained *n* =3 and attributed the grain growth mechanism to the lattice diffusion of zinc

atoms [9]. However, Qin *et al.* [11] obtained $n = 4$ to 6 for growth at 700 °C to 900 °C and attributed the large grain growth kinetic exponents to a more complex mechanism for the sintering of ZnO nano-materials.

Figure 3.32 Grain growth kinetics model (Equation 3.1) for N6 at 900 ^o C

From the linear fits of the data, the grain growth kinetic exponents were *n* = 6.7±1.3 for N5 and *n* = 4.5±0.6 for N6 suggesting that complex mechanisms governed the grain growth of the ZnO nanopowders at this temperature. Mayo [34] found that the presence of porosity in oxide samples resulted in exponents higher than *n* = 4. Pores limited the grain growth, and for some samples values of *n* up to 16 were obtained. As mentioned earlier, the density of the N5 pellets was 55 % while the density of the N6 pellets was approximately 66 %. Porosity was therefore 45 % and 34 %, respectively. The larger *n* value for N5 is consistent with a higher degree of porosity. Furthermore, the increased anisotropy in the N5 powder could have also contributed to the slow growth kinetics. Values for the activation energy for grain growth were not calculated in the present study since only one temperature was studied in air leaving both *Q* and *k⁰* convoluted in the *y*-intercept.

3.4.2 In-situ diffraction results and discussions of 1-BM data

High-resolution XRD data were collected *in-situ* from room temperature up to 500^oC using a 2-D MAR detector. The annealing treatment was performed under $O₂$, forming gas, and He/H₂ gases. The purpose of these experiments was to study *in-situ*, isothermally at 500 °C, the kinetics of grain growth under different gases: $He/H₂$, and $O₂$ for N6; and He/H₂, $O₂$ $He/H₂$, and $H₂/N₂$ for N5.

As seen in Figure 3.33 the annealing environments affected the rate of grain growth. In oxygen, the grains grew slower than in reducing atmospheres. Helium/hydrogen had the largest growth-enhancing effect. These results agree with the theoretical work of Erhart and Albe [30] who calculated that the most mobile defects in ZnO were zinc interstitials followed by oxygen interstitials, zinc vacancies, and oxygen vacancies. In a reducing environment the amount of zinc interstitials must be enhanced while the oxygen species are suppressed, and since zinc are the most mobile species, the grains grew faster.

Figure 3.33 *In-situ* **grain growth of N5 under different annealing gases at 500 ^o C**

The kinetics of grain growth were also analyzed using Equation 3.1. After plotting the data, it became apparent that there were two distinct regions with different slopes: one for the initial region where the grains grew faster, and a second region for later times when the grains grew at a slower rate. Figures 3.34 and 3.35 show the results for N5 in HeH² gas. The initial region covered up to $t = 63872$ seconds. The second region included from $t =$ 63872 seconds up to *t* = 143077 seconds.

Figure 3.34 Grain growth kinetics model fitted for N5 under H2He in the initial region

Figure 3.35 Grain growth kinetics model fitted for N5 under H2He in the later region

As for the *ex-situ* experiments the uncertainties given by the Rietveld refinement were very small (most were less than 1 %) because of the high statistics and instrumental resolution. The large error bars shown in the figures are due to grain anisotropy, which depended on the intrinsic shapes of the crystallites and their deviations from spherical grains as well as the wide range of size distributions. At this temperature and under the hydrogen/helium atmosphere, the anisotropy of the N5 sample increased with annealing time from 20 % up to 60 %. This enhancement of anisotropy was less dramatic for the sample annealed in forming gas and became even smaller for the oxidized sample.

Under hydrogen/helium, initially *n*=4.55±0.02 and then decreased to *n*=3.1±0.1. As mentioned before *n* =3 means that the grain growth was limited by diffusion [31] [32]. The higher exponent for the early stages of growth is consistent with other literature reports where more complex mechanisms dominate at smaller particle sizes [11] but diffusion overtakes for coarse grains. For the oxidized sample the exponent was *n* = 14.3±0.8 for the first region and *n*=11.1±0.2 for the second region.

The *n* values at 500°C were bigger compared those at 900°C. These results can also be attributed to the role of pores in grain growth. The *in-situ* samples were not pressed pellets. The powders were loaded into the glass capillaries and packed manually before inserting them in the high-temperature cell. It is expected that their density was much lower compared to the pressed pellets resulting in more sluggish kinetics due to a higher degree of porosity.

As mentioned before, the initial grain size for N6 at 500 °C was 74 nm and the anisotropy was 15 nm. Figure 3.36 shows that the N6 grains did not exhibit significant growth at this

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temperature. A similar behavior was observed for both oxygen and hydrogen/helium environments. Probably, this temperature did not provide enough kinetic energy for the growth of these nano-grains. *In-situ* experiments at higher temperature would be helpful in providing more insight on the effect of gases and temperature on grain growth for bigger particles also [33].

Figure 3.36 *In-situ* **grain growth of N6 under different annealing gases at 500 ^o C**

4. Conclusions and future experiments

The purpose of this study was to investigate the effect of grain growth and impurities on the electrical properties of ZnO semiconductors. Two batches of ZnO nanoparticles were chosen based on their structural, microstructural, and electrical characteristics. X-ray diffraction, x-ray florescence, scanning electron microscopy, four-point DC probe, and thermopower measurements were performed on these two nanopowders in order to study the kinetics of grain growth and their effect on conductivity.

N5 and N6 nanopowder batches were annealed for different durations of time at two temperatures: 900°C and 500°C. It was observed that the higher temperature promoted grain growth for both batches, whereas the lower temperature did not provide enough energy for significant grain growth of N6 (initial size was 74 nm). The study of reduction treatments on the samples indicated that the electrical conductivity of materials improved significantly after annealing them in forming gas. The mechanism responsible for this enhancement of reducing gases is a matter of debate among several theoretical models, but experimental studies are currently undergoing to provide experimental validation to the theoretical predictions [3].

The electrical conductivity increased as the grains grew. This can be attributed to both the decrease in scattering from grain boundaries, and the increase in electron concentration. The decrease in grain boundary scattering for larger grains results in a higher mobility. For both batches, the magnitude of the thermopower, which is an indication of the carrier concentration, decreased suggesting that the number of carriers increased. The conductivity for large grains was similar for both N5 and N6 (around 4 S/cm). A smaller

magnitude of the thermopower for N6 corresponds to a slightly higher carrier concentration.

X-ray fluorescence and x-ray diffraction results showed that the N6 nanopowder had no impurity elements and was phase pure. However N5 nanopowders had a small amount of Zr impurity atoms and also the untreated powder had a small amount of hydrozyncite secondary phase. It should be noted that the amount of Zr was very small and could not be detected as a secondary phase in the XRD patterns neither untreated nor after treatment. Furthermore, the hydrozyncite phase transformed into ZnO during heating and was absent at both 500 oC and 900 oC.

For the *in-situ* study, grains of N5 (untreated powder 27 nm) exhibited grain growth at 500 ^oC. The gas environment affected the growth rate. In oxygen the grains grew slower than in reducing atmospheres. Helium-hydrogen had the largest growth-enhancing effect. These results agree with the theoretical calculations of Erhart and Albe, who predicted that the most mobile defects in ZnO are zinc interstitials followed by oxygen interstitials, zinc vacancies, and oxygen vacancies. In a reducing environment the amount of zinc interstitials must be enhanced while the oxygen species are suppressed, and since zinc are the most mobile species, the grains should grow faster, as was experimentally confirmed by the present study.

The grain growth kinetics for N5 at 500 °C can be well described by the Arrhenius-type model. The grain growth exponents for N5 were large for $O₂$ conditions where smaller grains were present. The exponents decreased with reducing conditions and the presence of bigger grains. The larger *n* values have been attributed in the literature to porosity and to complex mechanisms that are currently not well understood. The present study found

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that in more porous samples higher exponents were indeed obtained. For He/H₂, $n = 3$ suggest that the growth in later stages was limited by diffusion in agreement with literature reports.

Grains of N6 (untreated powder 78 nm) did not exhibit growth at 500° C under oxygen or helium-hydrogen gas. This temperature did not seem to provide enough energy for the growth of these bigger grains. The shape of the grains might have also had an effect. Similar data were also collected for N3 under the same gas exposures as N5. Untreated N3 and N5 have comparable initial grain sizes. The data need to be analyzed, but the results can provide more insight on the grain growth kinetics under different gases.

In the future, it would be interesting to study *in-situ* the conductivity in the same temperature range and conditions to correlate the electrical and microstructural results. Another study could focus on the effect on grain growth and gas anneals on the optical properties and transparency of ZnO. Also more investigations on the effect of impurities and dopants (such as Al) on grain growth could be useful.

The highest value of the conductivity in ZnO obtained in this study is comparable to that of undoped indium oxide. A few parameters, such as the annealing time and temperature and the type of reducing gas still need to be optimized to maximize the conductivity of undoped ZnO. These results would be valuable to understand the mechanisms responsible for the improvement of the electrical behavior of ZnO and other TCOs.

5. Appendixes

5.1 Appendix I Data parsing code

```
Program that parses data from APS files. 
using System;
using System.Collections.Generic;
using System.ComponentModel;
using System.Data;
using System.Drawing;
using System.Linq;
using System.Text;
using System.Windows.Forms;
```

```
// user-added namespace(s)
using System.IO;
using System.Reflection;
using System.Text.RegularExpressions;
```

```
namespace ReadData
```
{

```
 public partial class frmReadData : Form
 {
   public frmReadData()
   {
     InitializeComponent();
  }
```

```
 private void btnInputDirectory_Click(object sender, EventArgs e)
 {
   // launch window for navigating to directory with data
   FolderBrowserDialog dlgInputDirectory = new FolderBrowserDialog();
   if (dlgInputDirectory.ShowDialog() == DialogResult.OK)
  {
     txtInputDirectory.Text = dlgInputDirectory.SelectedPath;
  }
 }
 private void btnOutputDirectory_Click(object sender, EventArgs e)
 {
   // launch window for navigating to directory for storing results
   FolderBrowserDialog dlgOutputDirectory = new FolderBrowserDialog();
   if (dlgOutputDirectory.ShowDialog() == DialogResult.OK)
  {
     txtOutputDirectory.Text = dlgOutputDirectory.SelectedPath;
  }
 }
 private void btnReadData_Click(object sender, EventArgs e)
 {
   btnReadData.Enabled = false;
  string[] listOfFiles = FullPathsOfAllFiles(txtInputDirectory.Text);
  string listOfFileNames = txtOutputDirectory.Text + "\\" + "listOfFileNames.txt"; //diagnostics
```

```
 System.IO.File.WriteAllLines(listOfFileNames, listOfFiles);
```

```
int colonIndex = 0; int braIndex = 0; string str1, str2, str3, str4;
 string fileNameNoExtension = "";
List<string> lstStrings = new List<string>();
```

```
 // read each file
 int fileIndex = 0;
List<string[] > summary = new List<string[] > ();
```
foreach (string s in listOfFiles)

```
 {
```

```
 lstStrings = FileToListOfStrings(listOfFiles[fileIndex]);
 fileIndex++;
```
fileNameNoExtension = Path.GetFileNameWithoutExtension(s);

```
 // extract values from line 62
```

```
 colonIndex = lstStrings[62].LastIndexOf(':');
 string line62 = RemoveWhitespace(lstStrings[62].Substring(colonIndex + 1));
 line62 = line62.TrimEnd(')'); // remove closing paranthesis
 braIndex = line62.LastIndexOf('(');
 str1 = line62.Substring(0, braIndex); // get first number
 str2 = line62.Substring(braIndex + 1); // get second number
```
// extract values from line 63

colonIndex = lstStrings[63].LastIndexOf(':');

string line63 = RemoveWhitespace(lstStrings[63].Substring(colonIndex + 1));

line63 = line63.TrimEnd(')'); // remove closing paranthesis
```
 braIndex = line63.LastIndexOf('(');
```

```
 str3 = line63.Substring(0, braIndex); // get first number
 str4 = line63.Substring(braIndex + 1); // get second number
```

```
string[] fileSummaryArray = \{s, str1, str2, str3, str4\};
 summary.Add(fileSummaryArray);
```

```
 }
```

```
 DataTable dtSummary = new DataTable();
 dtSummary = WholeListToDataTable(summary);
 dtSummary.Columns[0].ColumnName = "File Name";
 dtSummary.Columns[1].ColumnName = "Grain Size";
 dtSummary.Columns[2].ColumnName = "Grain Anisotropy";
 dtSummary.Columns[3].ColumnName = "Maximum Strain";
 dtSummary.Columns[4].ColumnName = "Strain Anisotropy";
```
string sepChar = ","; // for convenience, use .csv extension

```
 string pathToFile = listOfFiles[0];
```
string folderName = new FileInfo(pathToFile).Directory.Name;

```
 string fileName = String.Format("DataSummary_" + folderName + 
"_{0:yyyyMMdd_HHmmss}.csv", DateTime.Now);
```
string summaryFileFullPath = txtOutputDirectory.Text + " Υ " + fileName;

```
 DataTableToTextFile(dtSummary, summaryFileFullPath, sepChar);
 MessageBox.Show("Data summary successfully created");
 btnReadData.Enabled = true;
```

```
 }
```
 // method FullPathsOfAllFiles that generates list of all event data results private string[] FullPathsOfAllFiles(string inputDirectory)

{

```
 string[] filePaths = Directory.GetFiles(inputDirectory, "*_1.mic");
 filePaths = SortUsingMyAlgorithm(filePaths);
 return filePaths;
```

```
 } // end method FullPathsOfAllFiles
```

```
 private string[] SortUsingMyAlgorithm(string[] a)
```
{

```
 string[] n = new string[a.Length];
```

```
Dictionary<int, string> dctFiles = new Dictionary<int, string>();
```

```
 string filename, partOfFilename, strFilenameIndex;
```

```
int i = 0; int j = 0; int filenameIndex = 0;
```

```
while (i != a.Length)
```

```
 {
```
}

```
 filename = Path.GetFileNameWithoutExtension(a[i]);
 partOfFilename = filename.Substring(0, filename.LastIndexOf('_'));
 j = partOfFilename.LastIndexOf('_');
strFilenameIndex = partOfFilename.Substring(j + 1);
 filenameIndex = Int32.Parse(strFilenameIndex);
 dctFiles.Add(filenameIndex, a[i]);
 i++;
```

```
 var list = dctFiles.Keys.ToList();
 list.Sort();
```

```
Dictionary<int, string> dctSortedFiles = new Dictionary<int, string>();
  int k = 0;
   foreach (var key in list)
   {
    dctSortedFiles.Add(key, dctFiles[key]);
     n[k] = dctSortedFiles[key];
    k++; }
   return n;
 }
 // alternative method for sorting string array
 private string[] SortUsingLinq(string[] a)
 {
   var res = from item in a
        orderby item ascending
        select item;
   return res.ToArray();
 }
 private List<string> FileToListOfStrings(string fullPathOfInputFile)
 {
  List<string> fileContentsAsAList = new List<string>();
   StreamReader aReader = new StreamReader(fullPathOfInputFile);
   string aLine = "";
```

```
65
```

```
 while ((aLine = aReader.ReadLine()) != null)
   {
     fileContentsAsAList.Add(aLine);
   }
   aReader.Close();
   return fileContentsAsAList;
 }
```
private DataTable WholeListToDataTable(List<string[]> stringList)

```
 {
   // initialize table
   DataTable dt = new DataTable();
```
 // find largest array int rowSize = 0; // size of largest array foreach (string[] strArray in stringList) if (rowSize < strArray.Length) rowSize = strArray.Length; // final value is length of longest string array

 // add as many columns as the length of longest string array for (int columnIndex = 0; columnIndex < rowSize; columnIndex++) dt.Columns.Add();

 // load string arrays to DataTable one row at a time int rowIndex = 0; // row counter foreach (string[] strArray in stringList) {

int columnIndex = 0; // column counter

```
 dt.Rows.Add();
   foreach (string strValue in strArray)
   {
     dt.Rows[rowIndex][columnIndex] = strValue;
     columnIndex++;
   }
   rowIndex++;
 }
```
return dt;

} // end method WholeListToDataTable

```
 // method DataTableToTextFile
```
private void DataTableToTextFile(DataTable table, string filename, string seperateChar)

```
 {
  StreamWriter sr = null;
  try
   {
     sr = new StreamWriter(filename);
     string seperator = "";
     StringBuilder builder = new StringBuilder();
     foreach (DataColumn col in table.Columns)
     {
       builder.Append(seperator).Append(col.ColumnName);
       seperator = seperateChar;
     }
     sr.WriteLine(builder.ToString());
```

```
 foreach (DataRow row in table.Rows)
     {
       seperator = "";
       builder = new StringBuilder();
       foreach (DataColumn col in table.Columns)
       {
         builder.Append(seperator).Append(row[col.ColumnName]);
         seperator = seperateChar;
       }
       sr.WriteLine(builder.ToString());
     }
   }
   finally
   {
    if (sr != null) {
       sr.Close();
     }
   }
 } // end method DataTableToTextFile
 private string RemoveWhitespace(string s)
   try
   { return new Regex(@"\s*").Replace(s, string.Empty); }
   catch (Exception)
   { return s; }
```
{

}

```
 private string CreateHtmlFriendlyString(string s)
```

```
 {
     s = RemoveWhitespace(s);
    s = s.TrimEnd(':');
    s = s.TrimStart('-');
     s = s.Replace('(', 'X');
     s = s.Replace(')', 'X');
     return s;
   }
 }
```

```
}
```
using System;

using System.Collections.Generic;

using System.Linq;

using System.Windows.Forms;

namespace ReadData

{

static class Program

{

/// <summary>

```
 /// The main entry point for the application.
```

```
 /// </summary>
```

```
 [STAThread]
```

```
 static void Main()
```
{

```
 Application.EnableVisualStyles();
```
Application.SetCompatibleTextRenderingDefault(false);

```
 Application.Run(new frmReadData());
```

```
 }
 }
```

```
}
```
5.2 Appendix ΙΙ SEM

Before treatment:

N5

N5-1 N5-2 N5-3 N5-4

N6

N6-1 N6-2 N6-3 N6-4

N7

N7-1 N7-2 N7-3 N7-4

N8

N8-1 N8-2 N8-3 N8-4

N9

After treatment in air and in reducing gas:

N5

8 Hours:

N5 R-8HR-1 N5 R-8HR-2 N5 R-8HR-3

55 Hours:

-
-
- N5 R-55HR-1 N5 R-55HR-2 N5 R-55HR-3 N5 R-55HR-4

N6

1 Minuet:

N6 R-1min- N6 R-1min-2 N6 R-1min-3 N6 R-1min-4

30 Minuets:

N6 R-30min-1 N6 R-30min-2 N6 R-30min-3 N6 R-30min-4

1 Hour:

N6 R-1HR-1 N6 R-1HR-2 N6 R-1HR-3

2 Hours:

3 Hours:

8 Hours:

N6 R-8HR-1 N6 R-8HR-2 N6 R-8HR-3

18 Hours:

55 Hours:

N6 R-55hrs-1 N6 R-55hrs-2 N6 R-55hrs-3

86 Hours:

N6 R-86hrs-1 N6 R-86hrs-2 N6 R-86hrs-3

N7

8 Hours:

N7 R-8hrs-1 N7 R-8hrs-2 N7 R-8hrs-3

55 Hours:

N8

8 Hours:

N8 R-8hrs-1 N8 R-8hrs-2 N8 R-8hrs-3 N8 R-8hrs-4

55 Hours:

N8 R-55hrs-1 N8 R-55hrs-2 N8 R-55hrs-3 N8 R-55hrs-4

5.3 Appendix III, Electrical and thermal properties for N9, N8, N7, N6, N5

Real conductivity is based on 100% density.

Summary of the conductivity of N9, N8, N7, N6, N5 before and after reduction gas:

Unit of Conductivity: S/cm

5.4 Appendix IV Thermopower of N9, N8, N7, N6, N5 before and after reduction gas

5.5 Appendix V pcr file sample

```
Pcr-file for N5, 1 hour, after treatment, using spherical harmonic option, Hexagonal<br>
COMM Zno N5 8396 from August 2010 (N5-1 1 hr)<br>
! Current global Chi2 (Bragg contrib.) = 1.614<br>
l Files => DAT-file: 11bmb_8396.4<br>
150 N
     Resolution file for Pattern#
                                                   \overline{1}LaB6.irf
 Labo.iri<br>!IDP PD I DOC Mat PCP LS1 LS2 LS3 NLI Prf Ins Rpa Sym Hk1 Fou Sho Ana<br>_0 0 1 0 1 0 4 0 0 -3 10 0 1 1 0 0 1
 Bkpos Wdt Cthm muR AsyLim<br>20.000 90.0000 0.9827 0.0000 11.00
                                                                                                              Rpolarz 2nd-muR -> Patt# 1<br>0.1000 0.0000
 :<br>INCY Eps R_at R_an R_pr<br>100 0.01 1.00 1.00 1.00
                                                           Thmin<br>0.5000Thmax<br>45.9950
                                                                                                           PSD<br>90.000
                                                                                                                       Sent0<br>0.000R_g1<br>1.00
                                                                          Step<br>0.001000
 \begin{array}{lll} \text{i} & \text{Excluded regions (LowT HighT) for Pattern\#} & 1 \\ & 0.00 & 5.60 & 45.95 & 180.00 & \end{array}!Number of refined parameters
          24Zero Code SyCos Code SySin Code Lambda Code MORE ->Patt# 1<br>-0.0041 81.0 0.00000 0.0 0.000000 0.000000 0.0000<br>Background coefficients/codes for Pattern# 1 (Polynomial of 6th degree)<br>93.371 44.179 -86.139 -30.148 139.492 -71
 J.
           )3.371<br>21.00
                                                                   51.00101.0031.0041.00
                                                                                     11.00Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1:
                                                                                                               0.00ZnO
 Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth<br>2 0 0 1.0 1.0 1.0 0 0 0 0 0 0
                                                                             ATZ Nvk Npr More<br>23437.266 0 7 0
 \GammaP 63 m c
                                                <--Space group symbol
                TypIn Fin N_t Spc /Codes<br>0 0 0 0 # color green conn 0 0 0.0 3.2
 ! Atom
                                   \mathbf{x}Ÿ
                                                                     \overline{z}Biso<br>0.46119
                                                                                                     0cc
              ZN+20.333330.66666 0.000002.00000
 \mathsf{Zn}0.000.000.00131.00
                                                                                                         0.00\overline{0}0 - 20.33333
                                              0.66666
                                                               0.38072
                                                                                0.42381
                                                                                                   2.00000
                                                                                                                      \mathbf{0}\mathbf{0}\bf{0}0 # color blue
 0.00 0.00 111.00 121<br>!-------> Profile Parameters for Pattern # 1
                                                                 111.00
                                                                                  121.00
                                                                                                         0.00\begin{array}{c}\n 6.66611 \\
 5.00000 \\
 6.00000\n \end{array}Ŧ.
      Scale
                               Shape1
                                                      Bov
                                                                                          Str2
                                                                                                             Str3
                                                                                                                         Strain-Model
   0.15871E-040.000000.000000.000000.00000
                                                                                                                                   \bf{0}91.00000
                                 \frac{0.000}{V}0.0000.0000.0000.000\begin{array}{c}\n\text{Lorsiz } \text{Size-Model} \\
0.000000 \quad 19\n\end{array}GauSiz
                                                                                                   Ÿ
 1
                \mathbf{U}W
                                                                              \mathbf x0.0059730.000000
                                                0.0000000.0953560.033133
                                                                                                               0.000000241.000
                                 0.0000.000
                                                                       171.000
                                                                                           141.000
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                                                                   alpha<br>90.000000<br>0.00000
                                                                                                                                   #Cell Info
       \frac{a}{3.250605}\mathbf{h}rac{c}{5.204281}1
                            \frac{1}{2}, 250605<br>71.00000
                    0.00000<br>
0.00001<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
0.00000<br>
                                                                                                                                   #multiple box -1 1 -1 1 0 1
       71.00000
                                                                                           0.00000
                                                                                                               71.00000
      Pref<sub>1</sub>
                                                                                               Asy4
                                                                                                                  S_L0.000000.00000\frac{0.00}{Y00}0.000.000.00Y66+Y<sub>66</sub>
 ı
     -1.5402750.241330 -0.256149 -1.2017190.010092
                                                                                                               0.038682
                               191.00<br>2Th2/TOF2<br>45.950
          181.00
                                                    201.00
                                                                         211.00
                                                                                             221.00
                                                                                                                  231.00
                                                   \begin{array}{c} 201.00 \\ \text{Pattern} \# 1 \\ 1 \end{array}2Th1/TOF1<br>30.000
 <sup>1</sup>
```
The size-model 19 was chosen

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