Dependence of Annealing Temperature on the Conductivity Changes of ZnO and MgZnO Nanoparticle Thin Films from Annealing in a Hydrogen Atmosphere at Mild Temperatures

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ABSTRACT

We report apparent robust doping of ZnO and Mg$_{x}$Zn$_{1-x}$O (x $\sim$20%) nanoparticle films by annealing in hydrogen gas. The annealing was done at sequentially higher temperatures from about 20 °C to 140 °C. The effect of the annealing was determined by comparing current-voltage measurements of the samples at room-temperature and in vacuum after each annealing cycle. The nanoparticles were grown using an aqueous solution and heating process that created thin-films of ZnO or MgZnO nanoparticles with diameters of about 30 nm. When exposed to hydrogen gas at room-temperature or after annealing at temperatures up to about 100 °C, no measureable changes to the room-temperature vacuum conductivity of the films was observed. However, when the samples were annealed at temperatures above 100 °C, an appreciable robust increase in the room-temperature conductance in vacuum occurred. Annealing at the maximum temperature (~135-140 °C) resulted in about a factor of about twenty increase in the conductivity. Furthermore, the ratio of the conductance of the ZnO and MgZnO nanoparticle films while being annealed to their conductance at room-temperature were found to increase and then decrease for increasing annealing temperatures. Maximum changes of about five-fold and seven-fold for the MgZnO and ZnO samples, respectively, were found to occur at temperatures just below the annealing temperature threshold for the onset of the robust hydrogen gas doping. Comparisons of these results to other work on bulk ZnO and MgZnO films and reasons for this behavior will be discussed.

INTRODUCTION

ZnO and MgZnO having a large band gap of 3.23 eV and 3.6 eV, have a wide range of potential applications such as in solar cells, gas sensors, chemical sensors, electrical devices, and luminescent devices. They have also been used for low voltage and short-wavelength electro-optical device applications due to their large exciton binding energies of ~60 meV.[1] ZnO and MgZnO nanoparticles have also recently been of great interest for the detection of pollutants and toxic gases.[2]

The motivation for this work was to understand how the electrical properties of ZnO and MgZnO semiconducting nanoparticles can be modified through doping by exposure to hydrogen gas. To accomplish this, changes in the electrical properties of films of ZnO and MgZnO nanoparticles were studied as a function of annealing temperature in a hydrogen ambient. Similar work was done by this research team on ZnO nanowires, where a significant response to the presence of H$_2$ gas at elevated temperatures was found.[3]
EXPERIMENTAL DETAILS

The ZnO and MgZnO nanoparticles were synthesized by mixing magnesium acetate and zinc acetate in an aqueous solution followed by heating and annealing in a tube furnace. The resultant average crystalline size was ~30 nm. Evidence of achieving an alloy with a Mg composition of ~20% was observed as a band-shift of about 200 meV in the photoluminescence of the nanoparticle films.[4,5]

To contact the nanoparticle film, a simple non–lithographic technique was used.[6] The substrate on which the nanoparticles were grown was placed on a piece of glass (2.5 cm x 2.5 cm) and the sample was secured with silver paint. Two gold wires 25 µm diameter were placed in parallel with a separation of about 5 mm across the surface of the nanoparticle film. To maintain good electrical contact, the nanoparticles and the gold wires were compressed together with a light spring between the first and a second piece of glass.

The current-voltage (I-V) measurements were taken using a Keithley 236 Source Measure Unit ($Z_{input} \sim 10^{14} \Omega$) using voltage sweeps of 0 to ±5 V and step interval of 0.05 V with a ten-second dwell time per data point. These parameters were found to be slow enough so that the system was in electrical equilibrium and the voltage step was close enough to resolve any important features in the I-V characteristics.

The experiments were performed in an environmental chamber (volume ~ 2 ℓ) equipped with gas supply and a vacuum pump. The chamber could be pressurized to 5 psi above atmosphere and evacuated to ~5 mTorr.[7] The temperature of the sample chuck could be increased from room temperature (RT) to 160 ºC by using heating tape wrapped around a copper extension of the thermal finger that passed through the bottom of the environmental chamber. Temperature stability to within ±2 ºC over several hours was achieved.

![Figure 1. Summary of annealing history and gas exposure. At each step in the annealing cycle the system was allowed to come to thermal and electrical equilibrium before proceeding.](image-url)

A cyclic annealing process was used where the sample was heated and cooled to RT in an H$_2$ atmosphere (~3 psig) at sequentially higher annealing temperatures ($T_{anneal}$) followed by evacuation. The relative temperatures and atmospheres at each step is shown in figure 1. An initial annealing in vacuum up to a temperature of 160 ºC (Stage 1) was performed to drive off any surface adsorbates. Between each annealing step in H$_2$, and after the temperature was returned to RT, the chamber was evacuated (Stage 2). At each stage and before the next annealing step was performed, the I-V characteristics were recorded to verify if the system had...
reached equilibrium by noting no detectable change in consecutive I-V characteristics. The effectiveness of annealing to dope the nanoparticles was determined by recording how the RT current at a bias of 5 V had changed since the initial annealing in vacuum.

**DISCUSSION**

**Experimental results**

In the first stage of the annealing process, while in vacuum and at the maximum temperature of 160 ºC, the current passing through the ZnO and MgZnO nanoparticles increased by about a factor of 15 and 20, respectively, relative to when at room temperature as would be expected for semiconducting materials. After cooling back to RT and the system reached equilibrium, the I-V plots were found to be almost identical to the plots from before the initial heating. This demonstrated that under vacuum, the system was completely reversible and refreshable and that any absorbates present from before the initial heating had no effect on the electrical properties of the nanoparticles. All I-V characteristics were found to be piece-wise ohmic and had the same proportional changes in conductivity about a bias of 0 V.

In the second stage, the nanoparticle films were exposed to H2 gas at successively higher annealing temperatures. At the beginning of each annealing step when the nanoparticle films were exposed to H2 at RT, no detectable change in the conductivity was measured. After annealing in H2 at temperatures up to about 100 ºC, the RT, vacuum conductivity of the films was found to be unchanged. However, after annealing at higher temperatures in H2 the RT conductivity in vacuum increased dramatically. Figure 2 shows the overlaid plots of the currents at 5 V under vacuum at RT after each annealing step for both the ZnO and MgZnO showing that the threshold annealing temperature and the degree of increase were similar for both samples.

![Figure 2](image-url)

**Figure 2.** Currents in films of ZnO (●) and MgZnO (♦) nanoparticles at + 5 V showing significant rise in currents at the same threshold temperature of about 120 ºC.

The ratio of the conductivity of the films while at the annealing temperature to the conductivity of the films after being returned to RT was also found to depend on the annealing temperature, as shown in figure 3. The ratio of the current while at T\text{anneal} to the current at RT after annealing steadily increased and then decreased; the peak being at about 10 to 20 K below the onset of the robust conductivity increase illustrated in figure 2. There is a small variation in the ratios of the RT conductivity with and without H2 present. The maximum variation of the ratios of the conductivity at RT shows no systematic dependence on the annealing temperature. For the ZnO sample, this variation was no more than about 35% and for the MgZnO sample, this
variation was no more than about 17%. These variations are quite small compared to the relative increase in the currents while at the annealing temperature of 710% for the ZnO sample and 450% for the MgZnO sample. The differences in the values of the conductance ratios at T\text{anneal} during the annealing is an artifact of the variation in the ratio of the RT conductance with H\textsubscript{2} and in vacuum. All three ratios were included for completeness.

![Graph 1](image1.png)

**Figure 3.** The ratio of currents as a function of annealing temperature and H\textsubscript{2} exposure for ZnO (left) and MgZnO (right) nanoparticle films.

**Discussion of experimental results**

While at RT, the conductivity of both the nanoparticle films was found to not change while exposed to hydrogen gas. However, after annealing at sufficiently high temperatures, a robust (~days) increase in the RT, vacuum conductivity was observed for both samples (figure 2). These results are qualitatively consistent with previous work on the interaction of ZnO with hydrogen gas where hydrogen has been identified as being able to act as a donor.[3,8–11] The effect of the annealing process was similar for both samples. For each, the threshold temperature was about 120 \degree C and the relative increase in conductivity was by about a factor of twenty. The resemblance of the responses of each sample suggests that the mechanism responsible would be similar for both with the most likely mechanisms for the doping effect falling into two categories: adsorption or inclusion of the H atoms as interstitial or substitutional donors.

Gas molecules adsorbed onto a metal-oxide surface can have a strong chemical bond that will either withdraw or donate electrons to the metal-oxide.[12] This mechanism is normally reversible when the gas is removed making ZnO a candidate for use for gas sensing.[3,13–15] In the case of ZnO and MgZnO nanoparticles, it has been well established that the behavior of negatively charged chemisorbed oxygen on the grain boundaries of metal oxides determines the sensitivity to H\textsubscript{2} gas at higher temperatures.[16] Although, ZnO and MgZnO do interact with gasses through adsorption, this is a reversible process and therefore another mechanism is needed that can provide for a stable (or at least a metastable) state in which the conductivity of the ZnO and MgZnO nanoparticles can be increased.

In general, hydrogen is known as a ubiquitous and amphoteric impurity in common semiconductors. However, in ZnO hydrogen has been found to act as a shallow donor.[4] Theoretical predictions suggest that hydrogen can become an interstitial impurity in ZnO with a hydrogen atom donating its electron to the crystal where the most stable site for the H\textsuperscript{+} was found to be between Zn and O atoms. In addition to single H\textsuperscript{+} ions being incorporated into the lattice, a second mechanism by which a hydrogen atom combines with an oxygen vacancy has also been suggested as a way hydrogen can behave as a shallow donor.[11]
Experimental support for a stable or meta-stable doping effect by hydrogen introduced during crystal growth was first reported in the 1950's.[9] Later, post-growth doping of ZnO has been reported by several groups for both ZnO and MgZnO.[6,10,17] In these studies, the effect of doping was found to necessitate annealing the samples at temperatures of at least 300 °C or up to 700-800 °C.

In contrast to these four studies which were carried out on bulk ZnO samples, the results reported here were carried out on thin films of nanoparticles of ZnO and MgZnO. Additionally, the threshold temperature for doping with hydrogen on the ZnO and MgZnO nanoparticles was found to be little above 100 °C. Since the materials under study are nominally similar to those where the threshold temperature for doping was higher, the difference in the morphology of the samples suggests it as an explanation for the difference in the threshold temperature for doping.

An expected consequence of the much larger surface to volume ratio of the nanoparticle films compared to the bulk samples would be to affect the speed or thoroughness of the absorption of the hydrogen. Although the energies of donor states would not be expected to change as a function of crystal size, the relatively low temperatures for the threshold of robust doping suggests otherwise. It has been reported that for films less than 200 nm thick, compressive strain in the lattice can exist.[18] Having been synthesized using a wet-chemical process, the nanoparticle crystal structure would therefore not be affected by strain with their growth substrate. The differences in the amount of strain could be a possible explanation for the different energy thresholds for the hydrogen incorporation.

The correlation as a function of temperature between the increase in total conductivity (figure 2) and the relative conductivity while at the annealing temperatures (figure 3) provides possible clues as to the doping mechanism. The increase in the RT, vacuum conductivity after successive annealing steps would be consistent with a greater number of H-donor atoms being incorporated into the crystal to act as donors. It would be expected that the number of occupied donor states would eventually saturate as the doping process continued. The observed increase in the ratios could be a reflection of the increasing ease that H can be incorporated as a donor as the annealing temperatures were increased. That there was a maximum to this behavior could be evidence that, although the conditions for incorporation of the H atoms was favorable (i.e. high temperatures), the number of available unoccupied sites could be decreasing. This would indicate a saturation of the doping sites was occurring.

Unfortunately, the work reported here was not able to include structural studies of the undoped and doped nanoparticles nor to investigate the importance of particle size to the doping process. Pursuing such investigations, including extending the experiments to higher temperatures, could shed light on the doping mechanisms and the importance of the morphology and size of the nanoparticles to the threshold temperatures for hydrogen doping in both ZnO and MgZnO nanoparticles.

CONCLUSION

The ability to dope films of nanoparticles of ZnO and MgZnO synthesized from a wet-chemical technique by exposure to hydrogen was explored. Initial exposure to hydrogen gas at room temperature found the nanoparticle films insensitive to its presence. By annealing at successively higher temperatures, a threshold temperature for a dramatic increase in RT conductivity was found. This behavior was found to happen at about the same temperature of about 390 K for both the ZnO and MgZnO nanoparticles films. The conductivity increase was
found to be robust, lasting for several days while stored in the dark at room temperature and under vacuum. The similarity in the behavior of the two samples suggests that the doping mechanism for both materials is the same. That the threshold temperature for these films is lower than that reported by previous studies on bulk ZnO suggests the morphology and/or the method of synthesis of the nanoparticles plays an important role in the doping mechanisms. The increase and then decrease of the ratio of the conductivity of the films while in an H2 atmosphere at the annealing temperature to afterwards at RT could be evidence that the number of available donor sites for irreversible or metastable incorporation of hydrogen donor atoms could be close to saturation. This robust effect could lead to a simple way to modify the conductivity of ZnO and MgZnO nanomaterials, increasing their utility for very many electrical applications.

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REFERENCES