

Hydrogen complexes in ZnO grown by chemical vapor transport

S.J. Jokela, M.D. McCluskey*

Department of Physics and Astronomy, Washington State University, Pullman, WA 99164-2814, USA

Abstract

The renewed interest in zinc oxide (ZnO) has provided a great number of details that could lead to a commercially viable alternative to gallium nitride (GaN) for use in high-efficiency, wide band-gap devices. The difficulty in obtaining such devices is that as-grown, large single crystals of ZnO are n type. Past research has shown that hydrogen plays an important role in the n-type conductivity of ZnO. However, other impurities cannot be eliminated as possible donors in as-grown ZnO. In an attempt to study the controlled doping of ZnO, we grew polycrystalline samples via the chemical vapor transport (CVT) method, using graphite as the transport agent. After diffusing hydrogen into these crystals, some clearly showed both the OH-related infrared (IR) absorption peak at 3327 cm^{-1} , as reported in our earlier publications, and the 3611 cm^{-1} absorption peak reported by Lavrov [Physica B 340–342 (2003) 195]. Additionally, a third hydrogen-related absorption peak appears at 3150 cm^{-1} . Suspecting a contaminant in our original source of graphite, we changed to a high-purity source of graphite. The resulting growth yielded no hydrogen-related absorption peaks after hydrogen diffusion into the sample. However, growing samples in ammonia recreated the 3150 cm^{-1} IR absorption peak.

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1. Introduction

Zinc oxide (ZnO) has a band-gap of 3.3 eV, giving it the potential to efficiently supplement gallium nitride (GaN) [1] for use in high-efficiency, wide band-gap devices [2–5]. The difficulty in obtaining such devices is that as-grown, large single crystals of ZnO are n type. Prior research indicates that hydrogen plays an important role in the n-type conductivity of ZnO [6–10]. However, other impurities cannot be eliminated as possible donors in as-grown ZnO.

Using chemical vapor transport (CVT) we grew our own polycrystals doped with nitrogen and hydrogen. Graphite was used as the transport agent. Ammonia was used as an ambient atmosphere during growth, providing both nitrogen and hydrogen dopants. Nitrogen behaves as an acceptor when located at an oxygen site. By using ammonia, we also incorporate hydrogen into our crystal. Hydrogen passivates the nitrogen acceptors, but gives us a

way to easily detect them through the infrared (IR) absorption of the N–H bond.

2. Experiment

CVT uses a combination of source materials and transport agents to grow high-quality crystals. Single crystals are typically deposited on a substrate or seed. The source materials contain the elements that compose the final crystals and dopants of interest. The transport agents react with the source materials until a temperature-dependent equilibrium is reached. As the products move into a cooler region, the reverse reaction can occur, depositing material onto a substrate. CVT is particularly useful for materials with low vapor pressures, in which case extremely high temperatures may be required to grow crystals without an intermediate reaction.

When growing ZnO crystals, it was found that graphite performs as an excellent transport agent [11]. Graphite, used in conjunction with high purity ZnO microparticles, resulted in high quality and high purity polycrystalline growth. The reactions that assist the growth process are

*Corresponding author. Tel.: +1 509 335 5356; fax: +1 509 335 7816.

E-mail address: mattmcc@wsu.edu (M.D. McCluskey).

suspected to be [12]



and



where the superscripts s and g refer to solid and gas phases, respectively.

In the present work, ZnO microparticles obtained from Sigma-Aldrich were mixed with graphite powder and placed in a fused silica ampoule. The ambient air was evacuated and backfilled with 0.5 atm. of Ar, N₂, or NH₃ gas. The ampoule was then sealed and closed using a hydrogen–oxygen torch. The use of NH₃ as an ambient was an attempt to introduce nitrogen impurities into the crystal growth. The ampoule was placed in a horizontal tube furnace. The source material was heated to temperatures between 850 and 990 °C. The natural temperature gradient in the furnace left the deposition end of the ampoule at a temperature approximately 50 °C lower than the end with the source materials. As CO₂ and Zn vapor travel towards the cooler end of the ampoule, the reverse reaction occurs, depositing ZnO polycrystals. At first, the deposition occurs on the fused-silica ampoule wall, not an ideal substrate for the deposition of ZnO. However, once a thin layer of ZnO is deposited, the energetically favorable structure of ZnO becomes apparent in the shape of hexagonally-faceted growth.

An attempt at seeded growth was made by placing a piece of ZnO from Cermet Inc. at the cooler end of the ampoule. However, this approach was met with little success, as ZnO preferred to grow on the ampoule wall instead. It is possible that the curvature of the ampoule prevented the seed crystal from achieving good thermal contact with the ampoule wall. The seed crystal would then be several degrees warmer than the ampoule wall, possibly accounting for the lack of growth on the seed. Since crystalline growth could be achieved on the ampoule wall, it was decided to proceed without the use of a seed crystal.

A variety of crystal sizes were achieved depending on the growth temperature, impurities, and the amount of graphite and ZnO. ZnO was first mixed with water. Then the water was boiled away, leaving behind aggregates of ZnO. These aggregates led to slower crystal growth, and higher crystal quality, than ZnO powder. We achieved excellent crystal growth using 2.0 g graphite and 1.5 g ZnO.

It should be noted that during the growth process there is an increase in gas pressure inside the ampoule. The ampoule was able to handle the increased pressures during the growth process. However, while the ampoule is being cooled, the ZnO crystal growth contracts with a different thermal-expansion coefficient than that of the ampoule wall. In the process of pulling away from the substrate, ZnO can crack the ampoule wall, causing the wall to succumb to the internal pressure. For this reason we designed a shield that would contain the debris from the explosion.

3. Results

Initially, graphite from an electric motor brush was used. This ‘dirty graphite’ contained impurities, determined from neutron activation analysis (NAA), shown in Table 1. The dirty graphite produced satisfactory results at growth temperatures between 820 and 950 °C. At temperatures above 900 °C, the samples took on a red color, common to that reported for ZnO annealed in Zn vapor [13]. Metallic droplets, identified by energy-dispersive X-ray analysis (EDX) to be Zn, were observed on the surface.

The ampoules had a tendency to explode during the cool down phase of the growth process, but only when the growth took place at temperatures above 900 °C. We attribute this to an increase in pressure most likely due to CO and CO₂ in the ampoule, which becomes weakened when the ZnO crystal growth contracts during cool down. There is generally no explosion when a source of high-purity graphite is used.

In an attempt to dope ZnO crystals with nitrogen, we used NH₃ as an ambient for growth. Growth at temperatures below 900 °C resulted in colorless samples with no new IR absorption peaks. When growing at temperatures above 900 °C, the samples became red in color with the appearance of Zn metal on the surface of the sample. Additionally, IR spectroscopy revealed an absorption peak at 3147.7 cm⁻¹ at room temperature and 3150.7 cm⁻¹ at liquid-helium temperatures (Fig. 1). We have attributed this to an N–H bond in ZnO. Subsequent growth using only dirty graphite, ZnO powder, or aggregate, and Ar or N₂ produced this absorption peak when grown at temperatures above 900 °C. These samples produced varying intensities of the 3147.7 cm⁻¹ absorption peak. Results from growth using high-purity graphite lead us to the conclusion that nitrogen is also present in the dirty graphite source.

In a few of the samples grown in dirty graphite and ammonia then annealed in hydrogen and deuterium, we also observed both O–H (O–D) vibrational modes at 3326.2 (2470.2) and 3611.3 cm⁻¹ (2668.0 cm⁻¹) as reported by McCluskey et al. [14] and Lavrov [15], respectively (Fig. 2). Additionally, the N–D absorption peak was observed at 2339.7 cm⁻¹, at liquid-helium temperatures (Fig. 1).

Table 1
NAA results for isotopes in ‘dirty graphite’

Element	Concentration (ppm by weight)
Sc	0.122 ± 0.012
Cr	0.475 ± 0.167
Co	0.0945 ± 0.0182
Zn	6.55 ± 0.55
Ce	69.2 ± 4.1
Nd	2.12 ± 0.55
Eu	0.0118 ± 0.0042
Ta	0.00537 ± 0.00029

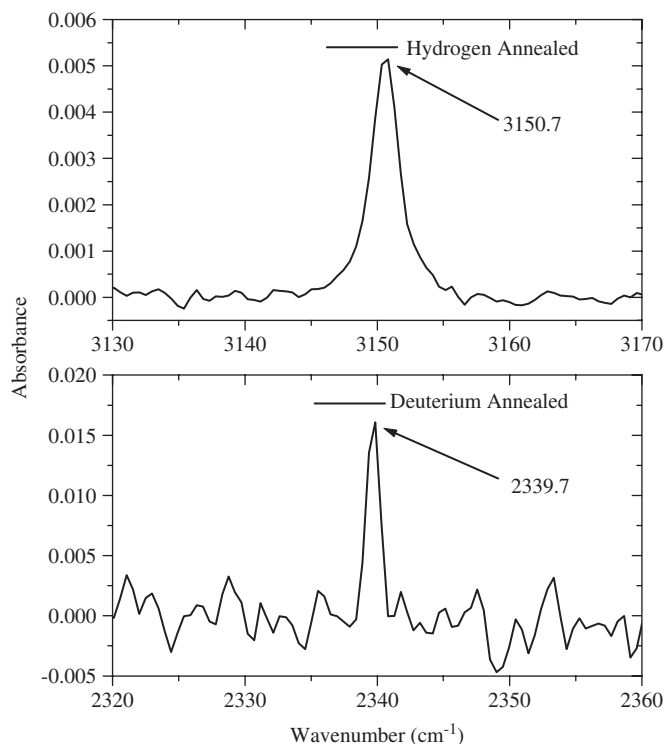


Fig. 1. IR absorption spectra of CVT-grown ZnO using dirty graphite and an ammonia ambient. Pieces of this sample were then annealed in hydrogen (top) and deuterium (bottom). The absorption peaks are attributed to an N–H or N–D bond.

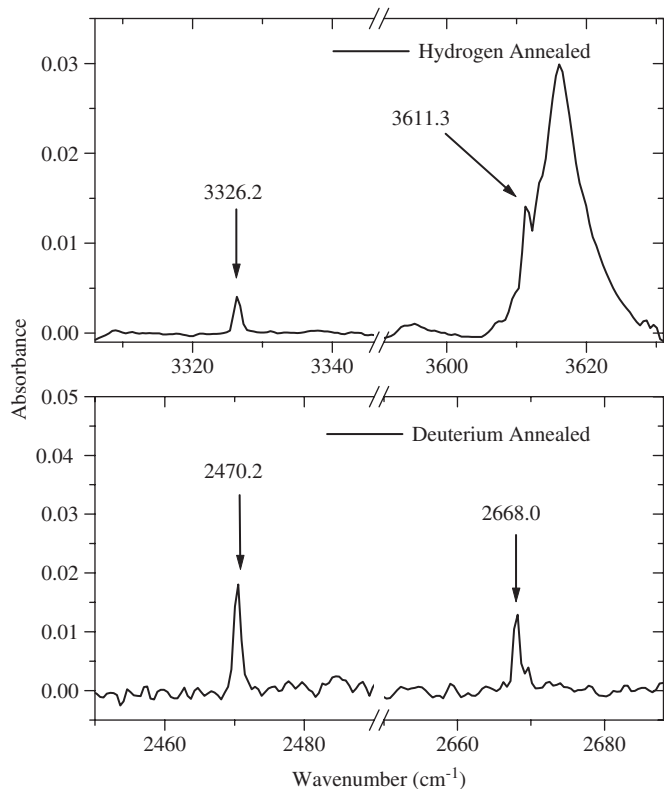


Fig. 2. IR absorption peaks in CVT-grown ZnO annealed in hydrogen (top) or deuterium (bottom). The sample is the same as that shown in Fig. 1.

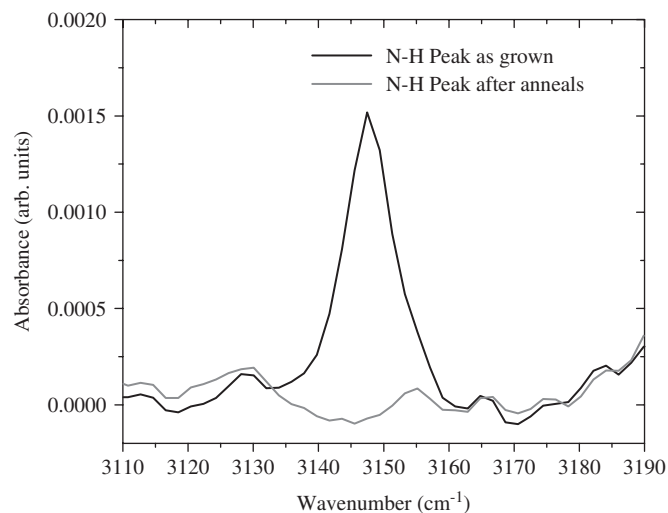


Fig. 3. IR absorption spectra of a CVT-grown ZnO sample using high-purity graphite and an ammonia atmosphere. The as-grown absorption spectrum is shown in black. The sample was annealed in open air for 1 h at 100 °C increments between 200 and 800 °C. The absorption spectrum present after all the anneals at 800 °C is shown in gray.

To confirm that certain anomalies were due to impurities in the dirty graphite, we used high-purity graphite of better than 99.99% purity from Sigma-Aldrich. When using the high-purity graphite, very little growth would occur at temperatures below 900 °C. We attribute this to the boiling temperature of Zn metal at 907 °C. It is unknown what impurity in the dirty graphite was responsible for the growth at temperatures below 900 °C in prior experiments. It is possible that Zn in the dirty graphite assisted the growth by increasing the Zn vapor pressure in the ampoule.

Samples grown in Ar or N₂ ambient between 900 and 950 °C were usually colorless. Adding 0.01 g of Zn metal to the source materials yielded growth that was red in color. This corroborates with our earlier postulation that a Zn-rich atmosphere exists in the ampoule and is responsible for the red color. IR spectroscopy revealed no hydrogen-related absorption peaks, even after diffusing hydrogen into the crystal.

Samples grown in anhydrous NH₃ using high-purity graphite and ZnO aggregate resulted in samples that were slightly red. IR spectroscopy of these samples revealed the presence of the 3147.7 cm⁻¹ absorption peak when analyzed at room temperature. A series of isochronal anneals showed that the peak disappears after annealing at 800 °C for 1 h in open air (Fig. 3).

4. Conclusions

We have successfully introduced N–H complexes into ZnO during growth, a potentially important step toward p-type conductivity. To achieve p-type ZnO, annealing steps could include (1) annealing in an oxygen ambient to remove oxygen vacancies and (2) annealing at higher temperature to dissociate the N–H complexes. When pure

graphite is used, the N-H mode is observed only when NH₃ is used as an ambient but not Ar or N₂. When dirty graphite is used, the N-H mode appears regardless of ambient, suggesting that the dirty graphite contains nitrogen impurities.

We also observed the O–H (O–D) absorption peaks at 3326.2 (2470.2) and 3611.3 cm⁻¹ (2668.0 cm⁻¹) as reported by McCluskey et al. [14] and Lavrov [15], respectively. That both of these hydrogen-related absorption peaks exist in the same sample indicates that either one or both are formed with the assistance of another defect in the ZnO crystal. Ce or Zn impurities in the dirty graphite may play a role.

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