

Infrared Spectroscopy of Impurities in ZnO Nanoparticles

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ABSTRACT

Semiconductor nanoparticles have a range of potential applications in electronic, optoelectronic and spintronic devices. Zinc oxide (ZnO), a wide-bandgap semiconductor, has emerged as an important material for such applications. In this work, impurities in ZnO nanoparticles were investigated with infrared (IR) spectroscopy, and the results show the presence of CO₂ impurities in ZnO nanoparticles. Isotopic substitution was used to verify the frequency assignment and the results demonstrate conclusively that the impurities originate from the precursors. Isochronal annealing experiments were performed to study the formation and stability of the CO₂ molecules. In addition to unintentional CO₂ impurities, we intentionally introduced hydrogen into ZnO nanoparticles. Our results show that post-growth annealing in hydrogen dramatically changes IR transmission, reflection and electrical properties of the nanoparticles.

INTRODUCTION

Zinc oxide (ZnO) has received considerable attention because of its potential applications such as varistors, piezoelectric transducers, and transparent conducting thin films [1-2]. A variety of wet-chemical methods, using zinc salts such as zinc acetate or zinc nitrate as precursor materials, have been used to synthesize the ZnO nanoparticles. Although many approaches have been used to prepare ZnO nanoparticles, the presence of impurities remaining from the precursor materials and reaction products is still a challenging problem. In this paper, we report IR spectroscopy of unintentional CO₂ impurities and intentionally introduced hydrogen in ZnO nanoparticles.

SYNTHESIS OF ZnO NANOPARTICLES

ZnO nanoparticles were synthesized by reaction of zinc acetate dehydrate, Zn(CH₃COO)₂·2H₂O, and sodium hydrogen carbonate, NaHCO₃ [3]. To prevent contamination from ambient the mixture was sealed in an Ar gas filled quartz ampoule. The reaction was performed at 200 °C for 2 hours. After the reaction, the by-product sodium acetate was washed away with distilled water several times. The powder was dried overnight at room temperature and then annealed at 350 °C for 2 hours to remove the remaining water. The TEM image and X-ray diffraction pattern of the nanoparticles are shown in figure 1. The sizes of the particles are about ~15 nm and XRD pattern confirms the wurtzite structure. The powder was pressed into thin pellets (~0.25 mm) to perform the IR spectroscopy.

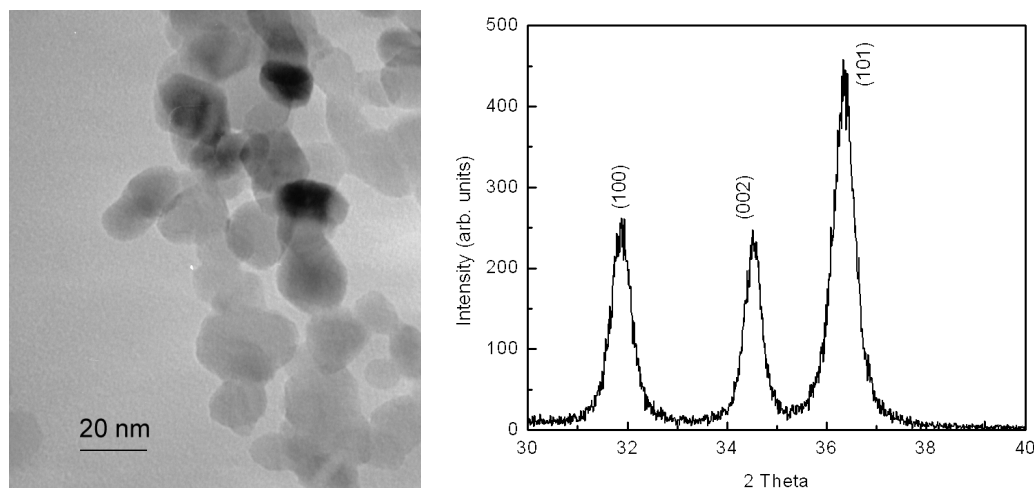


Figure 1. TEM image and X-ray diffraction pattern of ZnO nanoparticles.

INFRARED SPECTRA OF ZnO NANOPARTICLES

Infrared absorbance spectra of the ZnO nanoparticles were taken with a vacuum Bomem DA8 FTIR spectrometer. A strong absorption peak was observed at a frequency of 2342 cm^{-1} (figure 2). In addition a weak absorption was observed at 2277 cm^{-1} . These peaks are assigned to be asymmetrical stretch frequencies (ν_3) of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$, respectively.

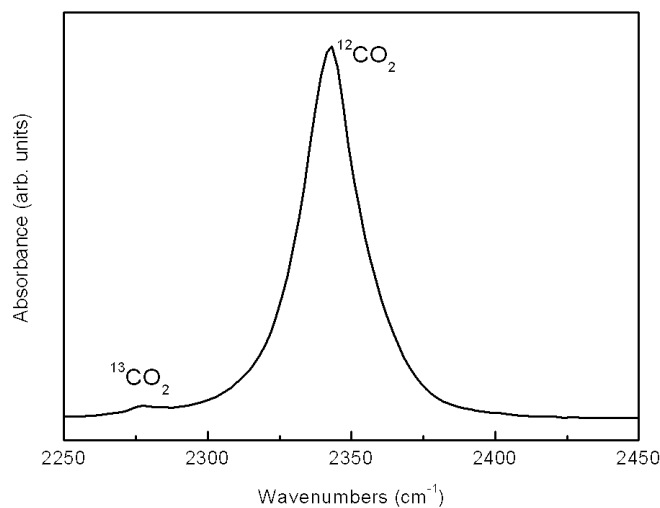


Figure 2. CO_2 absorption peaks in ZnO nanoparticles.

For a linear free CO_2 molecule, the (ν_3) vibrational frequency is estimated by

$$\nu = \sqrt{k \left(\frac{2}{M_C} + \frac{1}{M_O} \right)} \quad (1)$$

where M_C and M_O are masses of carbon and oxygen atoms respectively, and κ is an effective spring constant. The calculated frequency ratio is $\nu(^{12}\text{CO}_2)/\nu(^{13}\text{CO}_2)$ is 1.029, in good agreement with the observed ratio of 1.028.

Isotopic shifts of $^{13}\text{CO}_2$ molecules

Isotopic substitution was used to verify the frequency assignment of CO_2 molecules. IR spectra of ZnO nanoparticles prepared from different precursors containing different ^{13}C compositions are shown in figure 3.

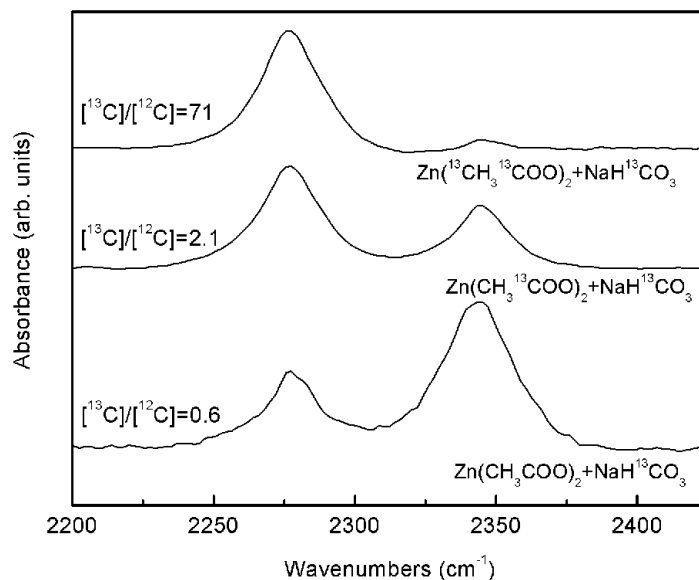


Figure 3. CO_2 absorption peaks in ZnO nanoparticles with different ^{13}C compositions.

It can be seen that peak intensities at 2277 cm^{-1} increase as ^{13}C compositions increase in the precursors. Therefore, we conclude that the CO_2 molecules originate from the precursor materials, not from the ambient.

Formation and stability of CO_2 molecules

To study the formation and stability of CO_2 molecules, isochronal annealing experiments were performed in an open air furnace. A time period of 1 hour for each temperature step was performed over a temperature range $200\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ at $100\text{ }^\circ\text{C}$ intervals. IR spectra were taken after each annealing step (figure 4). The broad band absorption peaks in the region of $1200\text{--}1700\text{ cm}^{-1}$ are due to the vibration of carbonate impurities remaining in the sample.

As shown in figure 4, the peak intensities of the CO_2 peak increase with increasing annealing temperature, and the carbonate peaks decrease upon annealing. This reveals that unreacted carbonate impurities decompose into CO_2 and ZnO, and the CO_2 molecules remain in the samples.

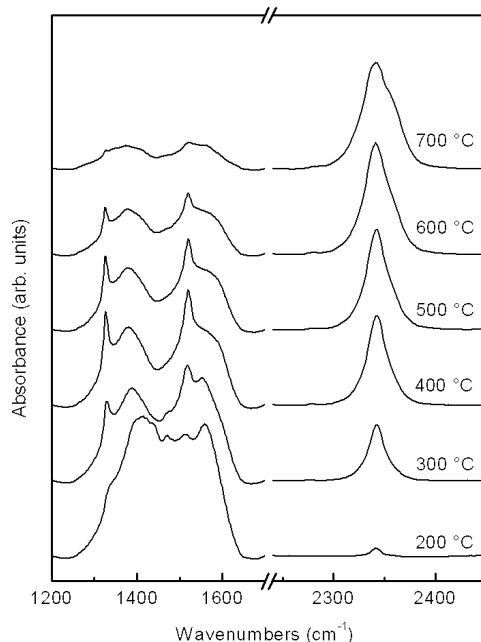


Figure 4. CO₂ and carbonate peaks in ZnO nanoparticles after isochronal annealing.

From the isochronal annealing results, now we can explain the formation of CO₂ molecules with a two-step reaction. First zinc acetate reacts with sodium hydrogen carbonate, forming zinc carbonate ZnCO₃ and sodium acetate. Then zinc carbonate decomposes into ZnO and CO₂ by thermal decomposition. Since zinc carbonate is insoluble in water, one cannot simply remove it by washing with water. The stability of CO₂ molecules are different from that of CO₂ adsorbed on bulk ZnO surfaces [4], where the molecules are unstable at room temperature. However, our results are similar to studies of permanent trapped CO₂ molecules in carbon nanotube bundles [5].

HYDROGEN IN ZnO NANOPARTICLES

Hydrogen is a very common impurity in most semiconductors, introduced easily in host materials either intentionally or unintentionally. Hydrogen can dramatically change the electrical and optical properties of a semiconductor. Both theoretical [6] and experimental [7] works showed that hydrogen can act as shallow donor in ZnO.

Thin pellets of ZnO nanoparticles were annealed at 350 °C for 1 hour under hydrogen ambient. Infrared spectra were taken before and after hydrogen annealing. Differential transmittance was determined as $[(T_0 - T)/T_0]$, where T_0 and T are infrared spectra of the sample before and after hydrogen annealing respectively. As shown in figure 5, it is clear that the hydrogen annealed sample is opaque to infrared radiation due to free carrier absorption.

Infrared reflectance spectra of the samples were also taken with a near-normal incidence configuration. A gold mirror was used as reference. The reflectance spectrum of an as-prepared ZnO sample shows a sharp decrease in reflectance ($R_{\min} \approx 0$) around the longitudinal optical phonon frequency ω_{LO} of ZnO (figure 6). This is the typical reststrahlen band reflection of ZnO

[8], and an indication that the sample is semi-insulating. For the hydrogen annealed sample, the change in reststrahlen band shape and disappearance of R_{\min} around ω_{LO} were observed. These effects are due to an increase in free carrier concentration.

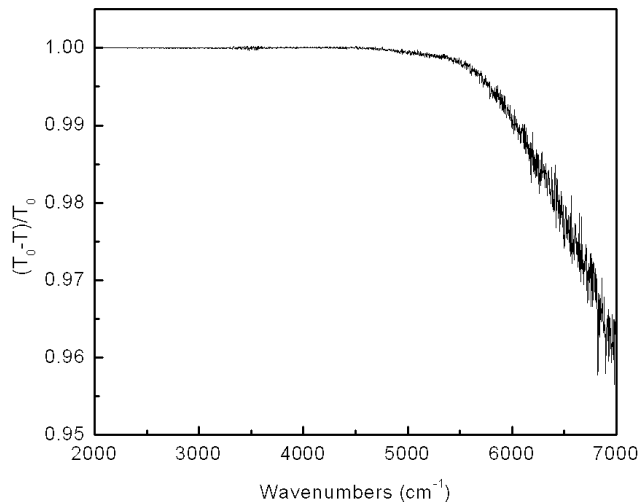


Figure 5. Differential transmittance spectrum of hydrogen annealed sample.

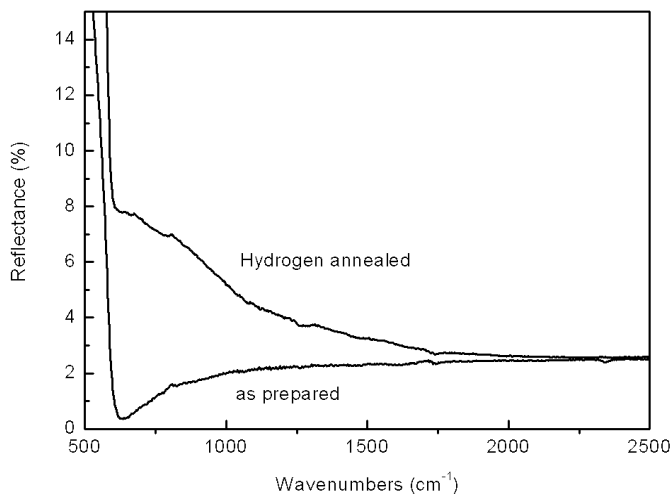


Figure 6. Infrared reflectance spectra of as prepared and hydrogen annealed samples.

In order to determine the electrical conductivity of the nanoparticles, 4-probe measurements, in the van der Pauw geometry, were performed. Electrical contacts were made by conductive silver paint. Figure 7 shows the temperature dependence of electrical conductivity of ZnO nanoparticle samples. The dramatic increase in electrical conductivity after hydrogen annealing is another supporting result for an increase in free carrier concentration.

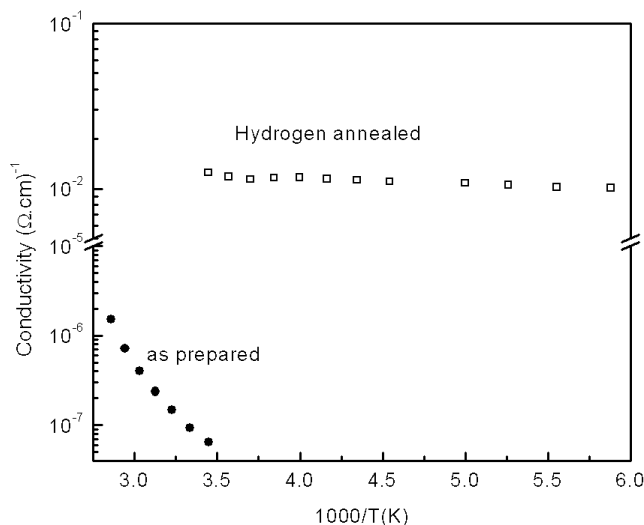


Figure 7. Electrical conductivity results of as prepared and hydrogen annealed samples.

CONCLUSIONS

We observed the presence of CO₂ molecules in ZnO nanoparticles. Isotopic substitution was used to verify the frequency assignments. Results from the isochronal annealing show that CO₂ molecules are formed by thermal decomposition of reaction products, and are believed to be trapped within the particles. Hydrogen also plays an important role in ZnO nanoparticles. Both optical and electrical measurements reveal evidence of an increase in free carrier concentration after hydrogen annealing.

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