Co-Precipitation Synthesis and Characterization of Nanocrystalline Zinc Oxide Particles Doped with Cu$^{2+}$ Ions

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ABSTRACT

Nanocrystalline Cu-doped ZnO particles were synthesized by the co-precipitation method. The composition, structural, optical and magnetic characterizations were performed by energy dispersive X-Ray spectroscopy, X-Ray diffraction, UV-Visible spectrometer, and vibrating sample magnetometer. The results confirmed that nanocrystalline Cu-doped ZnO particles have a hexagonal wurtzite structure with a high degree of crystallization and a crystallite size of 10 - 16 nm. For Cu above 11 at%, the X-Ray diffraction pattern possessed CuO secondary phase which shows the solubility limit of Cu in the ZnO lattice. Up to 11% at Cu, the presence of Cu in the ZnO lattice as Zn substitution indicated by an increase in lattice parameter values. Nanoparticles showed weak ferromagnetic characteristics at room temperature. The absence of secondary phase related to magnetic precipitate shown intrinsic ferromagnetic behaviour.

Keywords: Cu-Doped ZnO; Structural Properties; Room Temperature Ferromagnetism

1. Introduction

Wide band-gap oxide semiconductors, when doped with transition metal ions (Mn, Fe, Co and Ni) have attracted much attention for their promising versatile applications. ZnO based ferromagnetic semiconductor are paid much attention since the theoretical prediction of room temperature ferromagnetism by Dietl et al. in 2000 [1]. They used mean field theory to estimate Currie temperature (T$_C$) of ferromagnetic semiconductor and they predicted that room temperature ferromagnetism can be created by substituting Mn ion in wide band gap semiconductor such as ZnO or GaN. Due to its wide band gap and exciton binding energy of 60 meV, transition metal doped ZnO is attractive for many UV photonic and transparent electronic applications [2]. Numerous experimental studies have proved the existence of room temperature ferromagnetism in Mn-, Fe-, Co- and Ni-doped ZnO [3-6]. Room temperature ferromagnetism has indeed been reported in many of transition metal-doped ZnO. However, the origin of ferromagnetism in transition metal-doped oxide semiconductors remain controversial, some report claims that the room temperature ferromagnetism in TM-doped oxides might come from precipitation of magnetic cluster or secondary magnetic phases [7,8], while others claims that ferromagnetic ordering is intrinsic [9]. Motivated by these contradictory results, experimental studies have addressed the magnetic properties of Cu-doped, since it is known that the metallic Cu as well as all possible Cu-based oxide such as Cu$_2$O or CuO is nonmagnetic [10]. Therefore, several scientists suggested that if any ferromagnetism is observed in Cu-based system, then it will undoubtedly be the intrinsic property of the material [11]. However, the experimental results still remain controversial; Buchholz et al. [12] nonferromagnetism in n-type Cu-doped ZnO sample. On the contrary, other report claimed that, n-type Cu-doped ZnO has ferromagnetic behavior [13]. The same results were also found in theoretical studies. Early theoretical investigation showed that ferromagnetic ordering cannot develop in ZnO doped with 25 at% [14]. Later subsequent studies suggested that ZnO doped with low level of Cu concentration should be more succesful in producing ferromagnetism [15-17]. Furthermore, it is shown that the magnetism is very sensitive to the preparation methods and hence preparation conditions, even magnetic properties of Cu-doped ZnO prepared by the same method for the same doping concentration show the lack of reproducibility.

In this paper, we present our investigation to understand the structural and magnetic properties of Cu doped
nanocrystalline ZnO particles prepared through a coprecipitation method. The structural and magnetic properties were correlated to understand the origin of room temperature ferromagnetism in our samples.

2. Experimental

Nanocrystalline Cu-doped ZnO particles in this work were synthesized by co-precipitation process. This method provides advantages, such as low synthesis temperature, small particle and simplicity of processing. The starting materials used in this experiment were copper sulfate monohydrate (CuSO_4·5H_2O), Zinc sulfate heptahydrate (ZnSO_4·7H_2O), 25% aqueous Sodium hydroxide (NaOH) which are all procured from Aldrich and Merck. All of the chemicals used are GR grade without further purification. To synthesize nanocrystalline Cu-doped ZnO particles, two solutions, one containing the requisite amounts of ZnSO_4·7H_2O and CuSO_4·5H_2O in distilled water, and the other containing 44 mmol NaOH was prepared in 440 ml of de-ionized water. The solution containing ZnSO_4·7H_2O and CuSO_4·5H_2O was then put into an ordinary ultrasonic cleaner using a 57 kHz operating frequency for 2 h at 50°C. Then, this solution was subsequently stirred with a magnetic stirrer at 80°C. The NaOH solution was added until the final pH of the mixed solution reached to 12. The mixed solution was further stirred for 0.5 h with constant stirring. So obtained solution was aged at room temperature for 18 h. This solution was centrifuged and the precipitate that formed was separated from the solution, and washed several times with ethanol and distilled water in order to remove residual and unwanted impurities. The obtained product was dried in a vacuum oven at 200°C for 1 h yielding brown Cu-doped ZnO powder.

The composition of the samples was determined by energy dispersive X-Ray spectroscopy (EDX) using scanning microscope. The crystal structure and phase impurity were analysed using X-Ray diffraction (XRD) measurements at room temperature with a standard X-Ray diffractometer Philips PW 1710 and monochromatic Cu-Kα (λ = 1.54060 Å) radiation operated at 40 kV and 20 mA in the range from 10° to 80°. The calibration of the diffractometer was done using Si powder. Structural properties were further studied using Fourier transform infrared (FTIR) measurements. FTIR spectra of the powder samples were recorded using Shimadzu Fourier transform spectrometer. All spectra recorded on pressed pellet of the prepared samples in potassium bromide (KBr) in the range of 400 - 4000 cm⁻¹ with resolution of 4 cm⁻¹.

In order to study the electronic interaction near the optical band gap due to addition of dopant atoms UV-Vis diffuse reflectance measurements were deployed. In the present work, measurements have been performed using a Shimadzu UV-Vis spectrophotometer with an integrating sphere attachment and spectralon reflectance standard in the wavelength range of 250 - 800 nm. The diffuse reflectance, \( R \), of the sample is related to the Kubelka-Munk function \( F(R) \) by the relation:

\[
F(R) = \frac{(1 - R)^2}{2R}
\]

The band gap energy of the samples were calculated from the diffuse reflectance spectra by plotting the \( F(R)^2 \) vs. energy and extrapolated it to \( F(R)^2 = 0 \).

Magnetic properties were experimentally studied by measuring magnetization as a function of external magnetic field at room temperature using Oxford Type 1.2 T vibrating sample magnetometer (VSM). These measurements were taken from 0 to ±1 Tesla field.

3. Results and Discussion

Figure 1 shows a typical energy dispersive X-Ray (EDX) spectrum of Cu-doped ZnO nanoparticles. In addition to an oxygen peak at 0.53 keV and a Zn signal at 1.01, 8.69 and 9.53 keV, a Cu peak at 8.69 keV was observed. Quantitative results of the Cu/Zn ratio are calculated from the area of the corresponding spectra K lines. The amount of Cu in the nanoparticles has been found to vary between 6 and 23 at%. The inset of Figure 1 illustrates the Cu incorporation in nanoparticles as a function of the initial cations ratio in the starting solution.

Figure 2 shows the results of XRD patterns of nanocrystalline Cu-doped ZnO, undoped ZnO and CuO particle samples.

The diffraction peak for sample doped with 6 and 11 at% of Cu can be indexed to the hexagonal wurtzite
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Figure 2. XRD patterns of undoped, CuO and Cu-doped nanocrystalline ZnO particles synthesized with different concentrations of Cu.

Figure 2. XRD patterns of undoped, CuO and Cu-doped nanocrystalline ZnO particles synthesized with different concentrations of Cu.

structure of ZnO with nine prominent peaks, clearly suggested that the samples are in single phase within detection limit. No detectable diffraction peak for any secondary or impurity phase such as CuO was found in both samples. Moreover, we can see the Bragg peaks of our Cu-doped ZnO slightly move to lower angle side compared to that of the undoped ZnO sample as shown in Figure 3, indicated an important evidence of replacement of Zn$^{2+}$ with Cu$^{2+}$ ions [18].

However, for samples doped with Cu concentration of 18 and 23 at%, reflection (111) of CuO crystalline structure marked by (*) in its corresponding XRD pattern arises. This means a small part of CuO may have been incorporated into the ZnO wurtzite lattice or decompose. This result indicated that the doping limit for our Cu-doped ZnO sample is below 18 at% of Cu. However, there is no noticeable shift in the XRD peak positions towards lower angles for samples doped with 18 and 23 at% compared to samples doped with lower doping concentrations. We have analyzed the effect of doping on the structural changes, such as the lattice parameter, the unit cell volume and average crystallite size. The lattice parameters are estimated from the XRD peaks positions and refined using Rietveld analysis technique. The lattice parameters of undoped ZnO particles were $a = 0.3218$ nm and $c = 0.5155$ nm, which is similar with a standard values [19]. For Cu-doped ZnO samples, the lattice parameters are slightly higher than undoped ZnO.

Lattice parameters ($a$ and $c$), unit cell volume ($V$), and average crystallite size ($<D>$) calculated for different doping concentrations are plotted in Figure 4. The lattice parameters $a$, $c$ and $V$ increased with increasing doping concentrations. The unit cell volume continuously increases, which can be explained by looking at the ionic radii.

The substitution of the smaller Zn$^{2+}$ ion by the Cu$^{2+}$ ion is expected to result in an expansion of the unit cell.
volume. In addition, XRD pattern can be utilized to evaluate lattice strain and stress due to defect or vacancies using Williamson-Hall relation [20]:

\[ \Delta_{hkl}\cos\Theta = \kappa \lambda / <D> + 4 \varepsilon \sin\Theta \]  

(1)

where \( k \) is shape factor (0.89), \( \lambda \) is X-Ray wavelength, \( \Delta_{hkl} \) is line broadening at half-height, \( \Theta \) is Bragg angle of the particles and \( \varepsilon \) is the microstrain.

According to Hooke’s law, the stress is proportional to the strain with the constant of proportionality being the modulus of elasticity or Young modulus denoted by \( \Delta_{hkl} \). Therefore, as a result, the Equation (1) may be modified as:

\[ \Delta_{hkl}\cos\Theta = \kappa \lambda / <D> + 4 \sin\Theta \sigma E_{hkl} \]  

(2)

where \( \sigma \) is the uniform stress. The Equation (2) represents a straight line between \( 4 \sin\Theta \sigma E_{hkl} \) as an x-axis and \( \Delta_{hkl}\cos\Theta \) as an y-axis. The slope of the line gives the uniform stress \( \sigma \) and intercept of this line gives crystallite size \( <D> \). It is observed that the strain in Cu-doped samples varies with doping concentrations. The strain is higher as the dopant is increased. It is seen that more Cu content is introduced into the sample, the stronger tensile is, or more created compression stress is. It is known that the more oxygen vacancies are introduced in the ZnO matrix, the stronger the resulting stress [21]. Accordingly, we believed that our Cu-doped ZnO samples contain oxygen vacancies.

The crystallite size \( <D> \) calculated from Williamson and Hall plot was found to decrease with increasing Cu dopant. The average crystallite size was found to be 18 nm for undoped ZnO and 13.45 for the Cu-doped samples, which indicates that the samples are nanocrystalline.

Optical characterization was carried out by measuring the diffuse reflectance at room temperature. All spectra were taken in the range of 200 - 800 nm. The optical gap was estimated from diffuse reflectance spectra by plotting the square of the Kubelka-Munk function \( F(R)^2 \) given by the relation \( F(R) = (1 - R)^2 / 2R \), where \( R \) is the magnitude of reflectance as a function of energy. Figure 5 shows the \( F(R)^2 \) as a function of energy for all Cu-doped ZnO samples and to obtained the optical gap the linear part of \( F(R)^2 \) curve was extrapolated until it intersects the energy axis at \( F(R)^2 = 0 \). The optical band gap of the various compositions in Cu-doped ZnO samples is shown in Table 1. For undoped ZnO the band gap comes out to be 3.4 eV and is in accordance with the
Table 1. Rietveld refined XRD data and optical gap of Cu-doped nanocrystalline ZnO particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>at%</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>&lt;D&gt; nm</th>
<th>ε (10⁻⁴)</th>
<th>Eg (eV)</th>
</tr>
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<tr>
<td></td>
<td>0</td>
<td>3.2180</td>
<td>5.1550</td>
<td>47.7017</td>
<td>18.0</td>
<td>10.7</td>
<td>3.46</td>
</tr>
<tr>
<td>Cu doped ZnO</td>
<td>6</td>
<td>3.2350</td>
<td>5.1810</td>
<td>46.9570</td>
<td>16.5</td>
<td>11.5</td>
<td>3.32</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>3.2460</td>
<td>5.1990</td>
<td>47.4420</td>
<td>13.1</td>
<td>19.3</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>3.2480</td>
<td>5.2060</td>
<td>47.5590</td>
<td>12.6</td>
<td>26.6</td>
<td>3.23</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>3.2530</td>
<td>5.2070</td>
<td>47.7120</td>
<td>11.6</td>
<td>34.6</td>
<td>3.21</td>
</tr>
</tbody>
</table>

For Cu-doped ZnO the optical gap was obtained as 3.32, 3.30, 3.23 and 3.21 eV, for doping concentration 6, 11, 18 and 23 at%, respectively.

The band gap is found to decrease with increase Cu concentration in ZnO. Similar mitigation of the band gap with increasing Cu concentration has been reported earlier [25,26]. The inherent reason for red shift in band edge in transition metal doped ZnO samples is due to the change of the sp-d exchange interaction between the band electrons and the localized d-electron of the Cu²⁺ ions [27].

Infrared absorbance spectra are employed to study the vibration bands due to Zn-O bond, the changes due to Cu substitution and hydrogen bonding. Typical infrared absorption spectra of samples synthesized at different doping concentrations are displayed in Figure 6. For all Cu-doped samples the strong absorption peaks in the range of 400 - 700 cm⁻¹ could be attributed to ZnO stretching modes [28,29]. These stretching modes are indicative of successful synthesized of nanocrystalline ZnO particles as already confirmed by XRD and EDX studies. At the same time we can also observed an absorption peak around 1646, 1390 and 1121 cm⁻¹ corresponds to OH bending mode, C-OH plane bending and C-OH out-of-plane bending, respectively [30].

A broad band in the region 2900 - 3700 cm⁻¹ can be explained as overlapping of physically absorbed water, O-H stretching modes and C-H stretching modes. C-H local vibrational modes between 2800 and 3100 cm⁻¹ have been observed in a number of semiconductor such as amorphous silicon carbon (a-Si:C:H), GaAs, and GaN [31-33]. In these materials the local vibrational modes are assigned to symmetric and antisymmetric C-H stretching modes. To obtain information more clearly on the local vibrational modes correspond to OH modes we focalized our analysis on the infrared absorption range of interest, namely in a wave number range of 2900 - 3700 cm⁻¹.

All spectra can be deconvoluted into two peaks around 2990 cm⁻¹ attributed to CH stretching mode and 3400 cm⁻¹ associated with physically absorbed water and O-H stretching modes (dashed line in Figure 7). The integrated absorption is evaluated using the sum of the absorption areas from the fits data. As the dopant concentration is increased, the integrated absorption of the OH and CH stretching modes appears to be independent of

Figure 6. The infrared spectra of Cu-doped nanocrystalline ZnO particles synthesized with various doping concentrations.

Figure 7. Representative deconvolution of C-H stretching (dash line) and O-H stretching (dotted line) modes of infrared absorption band in the range of 2400 - 3900 cm⁻¹ for Cu-doped ZnO nanoparticles.
the dopant concentrations in the samples (Figure 8).

The magnetization as a function of magnetic field (M-H loop) measured at room temperature for samples doped with 6, 11, 18 and 23 at% of Cu are studied using VSM in the applied magnetic field range of 0 - 1 T. The maximum value of magnetic moment per Cu atom increased with increasing dopant atoms.

The corresponding curves are shown in Figure 9 reveal the dependence of magnetization on the applied magnetic field for all doped samples. The inset of Figure 9 clearly displays the magnetization data with an open loop for all Cu-doped samples. The variation in saturation magnetization, remnant magnetization and coercivity for different Cu-doped samples is presented in Table 2. However, the magnetization values are much smaller than the 1 μB/Cu expected for Cu²⁺ ions homogenously dispersed in the ZnO bulk.

Since Cu and related oxides are nonmagnetic materials at room temperature, the observed ferromagnetism is thought to be intrinsic properties of the Cu-doped ZnO [34]. A similar result was also found by Sharma et al. [35]. Sudakar et al. [36] reported that Cu-doped ZnO films with concentration lower than 1 at% exhibited ferromagnetic behavior with large saturation magnetization, however, for higher doping concentrations, the saturation magnetization decreased drastically. They proposed that...
According to BMP model, bound electrons in defects like oxygen vacancies, can couple with Cu ions and cause ferromagnetic regions to overlap giving rise to long range ferromagnetic ordering in the samples.

From the energy band point of view, the BMP overlap to produce spin-split impurity band [49], and the electrons are able to transfer from the BMP impurity band to an unoccupied 3 d state of Cu ions at the Fermi level. Therefore, the ferromagnetism of the system will be established.

4. Summary

Cu-doped nanocrystalline ZnO particles have been synthesized using the co-precipitation method and based on the structural, optical and magnetic measurements of our samples the following main point emerge:

1) Structure analysis indicates that Cu ions substitute for Zn ions without changing the wurtzite structure. The determined solubility limit of Cu in nanocrystalline ZnO particles by XRD studies is approximately 11 at%.

2) The optical band gap was found to decrease with increasing doping concentrations, indicating a clear red shift.

3) All samples were found to exhibit ferromagnetic ordering at room temperature. The magnetization results showed that the ferromagnetism behavior is the intrinsic behavior.

4) The infrared absorption measurements showed clear evidence of hydrogen incorporation in our nanocrystalline ZnO particles. It is possible that hydrogen could induce ferromagnetism in our samples. Unfortunately, we do not have experimental evidence of the spin-spin interaction due to the incorporation of hydrogen atoms, and such analysis is beyond the scope of our work.

Table 2. Magnetization value, remanence magnetization, and coercivity of Cu-doped nanocrystalline ZnO particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>at%</th>
<th>(\mu_B/\text{Cu}^{2+})</th>
<th>(H_C) (oe)</th>
<th>(M_R \times 10^{-2}) (emu/gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu doped ZnO</td>
<td>6</td>
<td>0.1008</td>
<td>270</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.1512</td>
<td>329</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0.1862</td>
<td>415</td>
<td>1.14</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>0.2318</td>
<td>235</td>
<td>0.57</td>
</tr>
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REFERENCES


