El Filali, B.; Torchynska, T. V.; Díaz Cano, A.I.; Morales Rodríguez, M.

STRUCTURAL AND RAMAN SCATTERING STUDIES OF ZnO Cu NANOCRYSTALS GROWN BY SPRAY PYROLYSIS


Universidad Autónoma Metropolitana Unidad Iztapalapa
Distrito Federal, México

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1 Introduction

In the last decades, the zinc oxide nanocrystals (NCs) were investigated intensively owing to their important optical and electrical properties, as well as the possibility to be used in a great number of electronic applications, such as photodetectors, acoustic devices, thin film transistors, lasers, white light emitting diodes, mechanical and biomedical sensing nanodevices, sensors and actuators, solar cells,
high-density data storage devices, UV detectors etc (Javed et al., 2014; Kahraman et al., 2013). ZnO NC films are interesting as well for the application in photo catalysis, as transparent conducting and super hydrophobic materials, etc. (Tang et al., 2014; Tarwal et al., 2014; Torchynska et al., 2014; Shinde et al., 2013). The majority of these applications of ZnO NCs are owing to a wide direct band gap of 3.37 eV and a large excitonic binding energy of 60 meV, as well as excellent physical, optical and electrical proprieties (Benharrats et al., 2010; Saidani et al., 2014). The characteristics of ZnO NCs can be modified by the impurity doping, such as aluminum, erbium, silver, gold, copper, etc... The ZnO doping with Cu has attracted an enormous attention recently due to the expected applications in light emitting diodes and magnetic semiconductors (Ghosh et al., 2009; Sahu et al., 2014).

Many techniques have been used to deposit the doped ZnO films, including CVD, sol-gel process and spray pyrolysis. Considering the different techniques, the spray pyrolysis is a simple method and its requirements are inexpensive. By using the spray pyrolysis technique, it is possible to produce the large area films, as well as multilayered or doped thin films. Additionally the Cu doped ZnO NCs are interesting as a white light emission material, because Cu doping at some concentrations stimulates the light emission in the red-green-yellow spectral range, that permits to obtain white light in high quality ZnO NCs with efficient near band edge (blue) emission as well (El Filali et al., 2015). Furthermore, the Cu atoms, as expected, are suitable for obtaining the p-type ZnO material because the Cu atoms can replace of Zn atoms in the ZnO crystal lattice. The Cu atoms in the ZnO crystal lattice are considered as a deep acceptor which affects electrical and optical properties (Bae et al., 2014; Kamalianfar et al., 2014; Kim et al., 2009). A set of recent theoretical and experimental papers report that the Cu atoms substitute preferentially of Zn atoms and provoke a local magnetic moment in the ZnO crystal lattice as well (Xia et al., 2014). Thus the structural and optical studies of ZnO NCs doped by Cu atoms are of great interest owing to a necessity of the development of a simple technological method for their production with controllable optical properties.

2 Experimental details

The ZnO Cu nanocrystals were synthesized from the spraying chemical solution of the 0.1mol of high purity Zinc acetylacetonate hydrate (Zn(C₅H₇O₂)₂) (Aldrich) in chloroform, after keeping this solution for 30 min in the ultrasonic bath for the homogeneous component dissolution. The appropriate volume of copper acetylacetonate (Cu(C₅H₇O₂)₂) (Aldrich) was diluted in chloroform as well and added to a spray solution to obtain the doping Cu concentrations of 5, 10, 15 and 20 wt% in a spray solution. The resulting solution was sprayed with a rate of 7 ml/min, using a pneumatic spray set-up with a compressed air (10 LPM) as a carrier gas (Aklilu et al., 2013). The glass sheets with a size of 25 × 20 × 1 mm previously cleaned in an ultrasonic bath for 10 min were used as a substrate. The deposition temperature was fixed at 400°C for all samples, denoted as S1, S2, S3 and S4 with the Cu concentrations 5, 10, 15 and 20 wt%, respectively. All samples were then thermal annealed at 500°C for 2 hours in ambient atmosphere.

The morphology and a crystal structure of ZnO NCs were characterized by the scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. The scanning electron microscopy JOEL-JSM7800F has been used (Soto et al., 2014). The XRD equipment of a model XPERT MRD with the detector Pixel, three axis goniometry and parallel collimator, with the resolution of 0.0001 degree has been applied. The X-ray beam was from the Cu source, Kα1 line λ=1.5406 A. Raman scattering spectra were measured in Jobin-Yvon Lab-RAM HR800 UV micro-Raman system using an excitation by a solid state light-emitting diode with a light wavelength of 532nm (Luna et al., 2013; Torchynska et al., 2008).

3 Results and discussion

3.1 SEM and XRD studies

SEM images of Cu doped ZnO NC films for different Cu concentrations after thermal annealing are presented in figure 1a-d. The size of ZnO NCs decreases with raising the Cu concentration in the films as it is shown in Table 1. XRD results for the samples with different Cu concentrations are presented in figure 2. The annealing at 500°C for 2 hours in ambient air stimulates the process of ZnO oxidation and crystallization. The comparison of XRD peak positions with the available data base card no. 36-1451 shows that these peaks correspond to the X-ray diffraction from the (100), (002), (101), (102), (110), (103) and (112) crystal planes in the wurtzite ZnO crystal structure.
Table 3. Raman scattering spectrum analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>E² (low) (cm⁻¹)</th>
<th>Raman Active Modes of CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3E²H-E²L (cm⁻¹)</td>
<td>A¹ (TO) (cm⁻¹) E¹ (TO) (cm⁻¹)</td>
</tr>
<tr>
<td>E²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>A¹ (LO) (cm⁻¹) E¹ (LO) (cm⁻¹)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A (cm⁻¹) B (cm⁻¹) B (cm⁻¹)</td>
</tr>
</tbody>
</table>

| Bulk ZnO [31] | 101 | --- | --- | --- | --- | --- |
| Bulk CuO [30] | --- | 296 | 344 | 628 | --- | --- |
| S1             | 100.9 | --- | --- | --- | 333 | --- |
| S2             | 101  | 298.6 | 348.5 | --- | --- | --- |
| S3             | 101  | 298.6 | 348.5 | --- | --- | --- |
| S4             | 100.5 | 293.5 | 343.3 | --- | --- | --- |

Fig. 1. SEM images of the spray deposited Cu doped ZnO thin films at various Cu concentration (a) S1, (b) S2, (c) S3 and (d) S4.

Table 1. The NC size variation versus Cu concentration

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu concentration, %</th>
<th>The average NC size D (estimated in SEM images, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>5%</td>
<td>96.2</td>
</tr>
<tr>
<td>S2</td>
<td>10%</td>
<td>81.4</td>
</tr>
<tr>
<td>S3</td>
<td>15%</td>
<td>54.6</td>
</tr>
<tr>
<td>S4</td>
<td>20%</td>
<td>22.3</td>
</tr>
</tbody>
</table>

When the Cu doping concentration increases, the position of the diffraction peaks shifts monotonically into the higher angle range (Figure 3, Table 2). In the samples S1 and S2 the second phase has not been detected, but in the samples S3 and S4 the second phase of CuO has been revealed as a peak at the angle 38.731° corresponding to the diffraction from the plane (111) in the monoclinic CuO crystal lattice (Fig.2).

The parameters of ZnO crystal lattices were calculated for all studied samples (Table 2) that reveals decreasing monotonically the ZnO crystal lattice parameters with Cu concentration rising in the films. Actually the both “red” and “blue” XRD peak shifts in ZnO Cu crystals in comparison with undoped ZnO were presented in the literature (Chowa et al., 2013; Kulyk et al., 2009; Ligang et al., 2011; Núñez et al., 2011; Yan et al., 2006).
Table 2. XRD peaks and the wurtzite ZnO lattice parameters

<table>
<thead>
<tr>
<th>Crystal planes</th>
<th>Bulk ZnO</th>
<th>S1, 5%Cu,</th>
<th>S2, 10%Cu,</th>
<th>S3, 15%Cu,</th>
<th>S4, 20%Cu,</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ (º)</td>
<td>2θ (º)</td>
<td>2θ (º)</td>
<td>2θ (º)</td>
<td>2θ (º)</td>
<td>2θ (º)</td>
</tr>
<tr>
<td>(100)</td>
<td>31.770</td>
<td>31.897</td>
<td>32.040</td>
<td>32.331</td>
<td>32.439</td>
</tr>
<tr>
<td>(002)</td>
<td>34.440</td>
<td>34.607</td>
<td>34.786</td>
<td>35.077</td>
<td>35.051</td>
</tr>
<tr>
<td>(101)</td>
<td>36.253</td>
<td>36.377</td>
<td>36.628</td>
<td>36.811</td>
<td>36.847</td>
</tr>
<tr>
<td>“a” (Ǻ)</td>
<td>3.2498</td>
<td>3.239</td>
<td>3.217</td>
<td>3.202</td>
<td>3.199</td>
</tr>
<tr>
<td>“c” (Ǻ)</td>
<td>5.2066</td>
<td>5.189</td>
<td>5.154</td>
<td>5.130</td>
<td>5.125</td>
</tr>
</tbody>
</table>

Fig. 2. XRD patterns of ZnO NC films with different Cu concentrations.

Fig. 3. The shift of XRD peaks in ZnO Cu NC films versus Cu concentrations.

Note that the valence of Cu could be +1 or +2 in the ZnO:Cu crystal lattice. The radius of Cu$^{+}$, Cu$^{+2}$ and Zn$^{+2}$ ions are 0.096, 0.072 and 0.074 nm, respectively. Thus the Cu$^{+}$, Cu$^{+2}$ substitution ions and the Cu$^{+2}$ interstitial ions might be the main impurities in ZnO:Cu NCs. The Cu defects would impact on the concentrations of interstitial Zn atoms, of Zn and oxygen vacancies as well (Peng et al, 2008). As Cu$^{+}$ ions substituted Zn$^{+2}$ ions in the crystal lattice, the increase of the lattice constant and inter planar distances will be realized, which would lead as well to decreasing the diffraction angles compared with undoped ZnO NCs. In contrary if Cu$^{+2}$ ions substituted Zn$^{+2}$ ions, the decrease of the lattice parameters and inter planar distances will be detected together with increasing the diffraction angles in XRD in comparison with undoped ZnO. Hence the decreasing monotonically the ZnO lattice parameters in studied samples at rising Cu concentrations in the range of 5-15% testifies that the Cu$^{+2}$ ions substituted Zn$^{+2}$ ions mainly for the studied Cu concentrations. At higher Cu concentration (20%) the variation of ZnO lattice parameters is negligible (Table 2), but the second phase CuO is detected additionally in studied samples at rising Cu concentrations in the XRD in comparison with undoped ZnO. Hence the decreasing monotonically the ZnO lattice parameters in studied samples at rising Cu concentrations in the range of 5-15% testifies that the Cu$^{+2}$ ions substituted Zn$^{+2}$ ions mainly for the studied Cu concentrations. At higher Cu concentration (20%) the variation of ZnO lattice parameters is negligible (Table 2), but the second phase CuO is detected additionally in studied films.
Table 3. Raman scattering spectrum analysis

<table>
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<tr>
<th>Samples</th>
<th>E$_2$ (low) (cm$^{-1}$)</th>
<th>CuO 3E$_2$H-E$_2$L (cm$^{-1}$)</th>
<th>A$_1$(TO) (cm$^{-1}$)</th>
<th>E$_1$(TO) (High) (cm$^{-1}$)</th>
<th>A$_1$(LO) (cm$^{-1}$)</th>
<th>E$_1$(LO) (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk ZnO [31]</td>
<td>101</td>
<td>296 344 628</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S1</td>
<td>100.9</td>
<td>333</td>
<td>---</td>
<td>---</td>
<td>439.6</td>
<td>---</td>
</tr>
<tr>
<td>S2</td>
<td>101</td>
<td>333</td>
<td>---</td>
<td>---</td>
<td>437.8</td>
<td>---</td>
</tr>
<tr>
<td>S3</td>
<td>101 298.6 348.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>440.0</td>
<td>---</td>
</tr>
<tr>
<td>S4</td>
<td>100.5 293.5 343.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>439.5</td>
<td>---</td>
</tr>
</tbody>
</table>

Fig. 4. Raman scattering spectra of ZnO NC films obtained at different Cu concentrations: 5 (a), 10 (b), 15 (c) and 20% (d).

3.2 Raman scattering study

Raman scattering spectra have been measured for the films in order to study how the different Cu atom concentrations change the Raman scattering of ZnO NC films. These ZnO films have a wurtzite structure with $C_{6v}^4$ point group symmetry (Lupan et al., 2011):

$$\Gamma_{opt} = A_1 + 2B_1 + E_1 + 2E_2$$  \hspace{1cm} (1)

The group theory predicts that the ZnO structures present the Raman active optic phonons in Brillouin zone center such as: $A_1$ and $E_1$ symmetry polar...
phonons with different frequencies, transversal optic-(TO) and longitudinal optic-(LO) phonons, and $E_2$ - a symmetry non-polar phonon mode with the frequencies $E_{2L}$ and $E_{2H}$. The B1 modes are infrared and Raman inactive modes. The $E_{2H}$ (high) mode is associated with the oxygen sublattice, also it is characteristic of the wurtzite phase material. The $E_{2L}$ (low) mode is attributed to the Zn sublattice (Ashkenov et al., 2003; Lupan et al., 2011; Torchynska et al., 2014). Raman peak at 100.5-101.0 cm$^{-1}$ detected in studied Cu doped ZnO NCs after thermal annealing (Figure 4) can be attributed to the first order Raman peak in the wurtzite crystal lattice related to $E_{2L}$. The Raman peak at 333 cm$^{-1}$ (Figure 4, Table 3) was attributed to the second order Raman peak arising from the zone boundary phonon $3E_{2H} - E_{2L}$. The Raman peaks 437-440 cm$^{-1}$ and 582-584 cm$^{-1}$ (Figure 4, Table 3) were attributed to the $E_{2H}$ mode and $E_1$ LO phonon mode in ZnO NCs (Torchynska et al., 2014). It is clear in figure 5, that the intensity of $E_{2L}$ and $E_{2H}$ Raman non-polar phonon modes increase with the copper concentration until 10%, and then starts decreasing when the copper concentration increases. This fact indicates that the quality of ZnO NC films can be improved with the copper concentration not more than 10%.

CuO has been characterized by a monoclinic crystal structure and it belongs to space group symmetry of $C_{2h}^5$ (Diaz et al., 2013). There are twelve zone center optical phonon modes defined by 4Au+5Ba+Ag+2Bg; and three of them (Ag+2Bg) are Raman active (Yu et al., 2004). The peaks shown in the figure 4 at 296-305.4cm$^{-1}$ and 343-348cm$^{-1}$, are attributed to the Ag and $B^1_g$ active Raman modes in the CuO monoclinic phase, respectively (Chrzanowski et al., 1989; Diaz et al., 2013; Yu et al., 2004).

Conclusions

Cu doped ZnO nanocrystals have been prepared by the spray pyrolysis method with follows thermal annealing. The X-ray diffraction study shows that the introduction of Cu atoms in the ZnO wurtzite crystal lattice was achieved, which causes decreasing the ZnO lattice parameters. Additionally in the samples S3 and S4 the second monoclinic phase of CuO has been detected in the XRD pattern and Raman scattering spectra. SEM study reveals decreasing the ZnO NC average size from 96.2 nm down to 22.3 nm with rising Cu concentration. It was shown that the quality of ZnO NC films can be improved by copper doping with concentration less than 10%.

Acknowledgement

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