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Effect of Copper Doping on the Growth of c-axis of Zinc Oxide Nanostructure

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Abstract

A simple sol-gel method has been used to synthesize zinc oxide nanoparticles. Using appropriate concentration of copper acetate, different amount of Cu was successfully doped in the synthesized ZnO nanocrystals. X-ray diffraction study revealed the formation of well crystalline and pure ZnO nanoparticles. The growth rate of ZnO nanocrystals along the c-axis i.e., *(0001)* direction was investigated. It was found that on increasing the amount of copper doping, the intensity of *(0002)* plane increases. It indicates that the growth rate gradually decreases on increasing Cu-doping. It is due to the reduction of the growth of ZnO nanocrystals due to the incorporation of less electronegative Cu^{2+} ions.

Keywords: Sol-gel, ZnO, Doping, c-axis, Crystal, Anisotropy

1. INTRODUCTION

Researches on nanostructured materials especially metal-oxide direct band gap semiconductors are in the forefront of research due to their unique optical emission and absorptions properties. These lead their potential applications in optoelectronic devices like light emitting diodes, solar cells, UV-visible optical transducers and optical sensors [1-5]. Besides, optoelectronics, metal oxide nanoparticles are also being investigated as materials in drug delivery, nanomedicine, enhancement of MRI image contrast, therapeutic purposes like destruction of cancer cells, cell repairing, and cell pH balancing [6-9]. Most commonly investigated metal-oxide nanoparticles are zinc oxide (ZnO) and titanium oxide (TiO_2). Amongst these, ZnO is very popular for its unique optical properties. It has a high and direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature. Hence the usual emission from ZnO falls in the UV region. This property can be utilized in designing ZnO based UV lasers and detectors. It is reported that during low temperature growth of ZnO nanostructures, several defect states (Zn_i, ZnO, O_{Zn}, V_{Zn}, V_O, O_+, O^{++}) are generated [10]. These defect states have energy levels between the conduction band and valence band of pure ZnO energy states. These shallow levels defect states lead to longer wavelength visible emission from ZnO nanostructures. Hence analysis of these defect states is very crucial in understanding the luminescence and crystal growth of ZnO. Various type of crystal morphologies of ZnO have been synthesized by the researchers. The most commonly reported structures are ZnO nanorods, nanotubes, nanobelts, nanopencils, nanodiscs and nanoparticles [11-14]. The formation of various morphologies is due different growth rates of various facets of ZnO crystals. By controlling growth along desired direction, the morphology can be modulated. For example, researchers have used non-polar hexamine (HM) during chemical synthesis of ZnO [15]. These non-polar HM molecules are preferentially attached to the non-polar facets of ZnO leading to the preferential growth along the polar (0001) direction. Some researchers have also used polyvinyl alcohol as the capping agent to control the growth of ZnO nanocrystals. However, the effect of doping of foreign elements on the growth rate of various crystal planes of ZnO is not yet investigated.

Here, in this paper, we report a simple chemical method to synthesize undoped and Cu doped ZnO. X-ray diffraction (XRD) analysis was carried out to understand the growth mechanism of ZnO nanocrystals. In this context we have also discussed the effect of Cu^{2+} ion doping on the growth of the *(0001)* plane of ZnO which is not yet reported.

2. EXPERIMENTAL

2.1 Materials Preparation

The precursor materials used in this experiment was as supplied by Merck (99.99% pure) without any further purification. For synthesis of pure ZnO, zinc acetate dihydrate aquatic solution was prepared by dissolving 2.195 g in predetermined amount of deionized water. We dissolved 1.048 g of LiOH in predetermined amount of deionized water to prepare 1 M solution. Under constant magnetic stirring of zinc acetate dihydrate aquatic solution, LiOH solution was added drop-wise and the stirring was continued for further *2* hr. A white precipitate was observed at the bottom of the flask. The precipitate was filtered, and dried in an ordinary furnace at 100 ˚C for further characterization. For doping of Cu in ZnO, we added predetermined amount of $CuCl_2$ during the stirring and then by varying the amount of $CuCl_2$, the doping concentration was varied.

2.2 Materials Characterization

X-ray diffraction (XRD) measurement was carried out in PROTO X-ray diffractometer over the angular range $30° < 2\theta < 60°$. The detector used in the equipment is solid-state detector.

3. RESULTS AND DISCUSSIONS

ZnO usually crystallizes in wurtzite form, although some researchers have reported very rarely observed cubic phase of ZnO [16, 17]. Wurtzite ZnO belongs to space group C6mc with lattice parameters $a = 3.249$ Å and $c = 5.207$Å [16]. The wurtzite of ZnO can be represented by the stacking of tetrahedral coordinated O^{2-} and Zn^{2+} ions along c-axis placed alternatively (see Fig. 1 and 2).

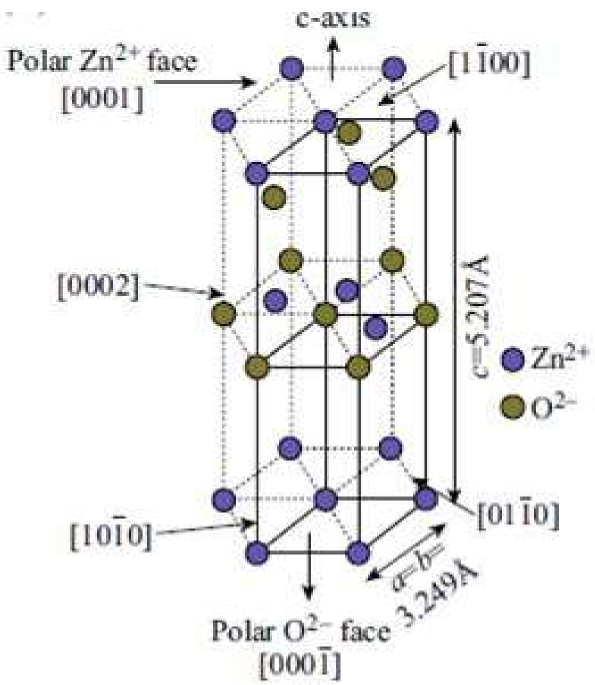

Fig. 1 – Wurtzite ZnO crystal structure [Reproduced from [16] under the terms of the Creative Commons CC BY license]

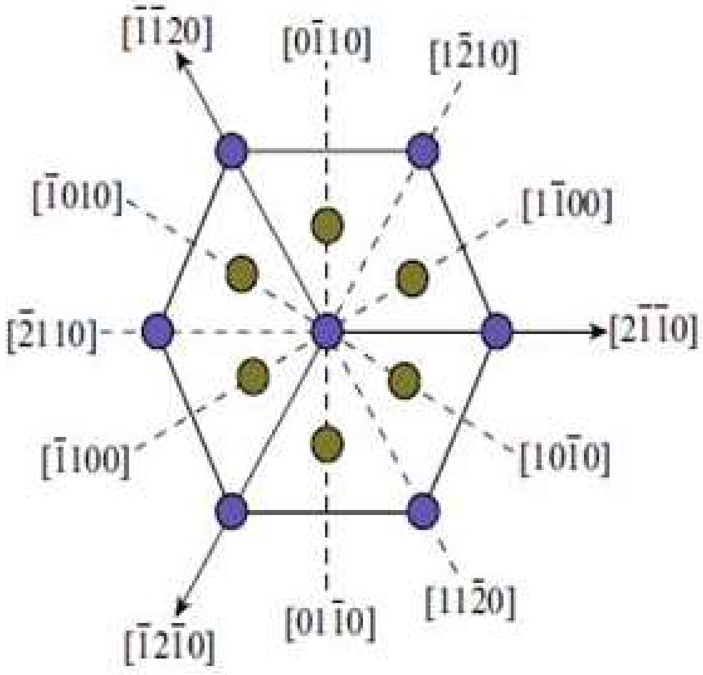

Fig. 2 – Crystal planes of ZnO. [Reproduced from [16] under the terms of the Creative Commons CC BY license]

This leads to the polar nature of wurtzite ZnO. There are various crystal planes in wurtzite structure. The (0001) plane is the basal polar plane. One side of this plane contains Zn^{2+} ions while other face $(000\bar{1})$ is terminated by O^{2-} ions [18]. The rest six facets namely, $[\bar{1}010]$, $[0\bar{1}10]$, $[1\bar{1}00]$, $[10\bar{1}0]$, $[01\bar{1}0]$ and $[\bar{1}100]$ are non-polar and lies parallel to c-axis (see Figure 1). Due to the polar nature, there exists inherent dipole moment along c-axis of the crystal. Reconstruction of the polar surfaces occurs in wurtzite structure for stability [18]. However, the (0001) surface is found to be flat and stable without any surface reconstruction. Hence it is of great importance to the researcher to understand the super stability of this plane.

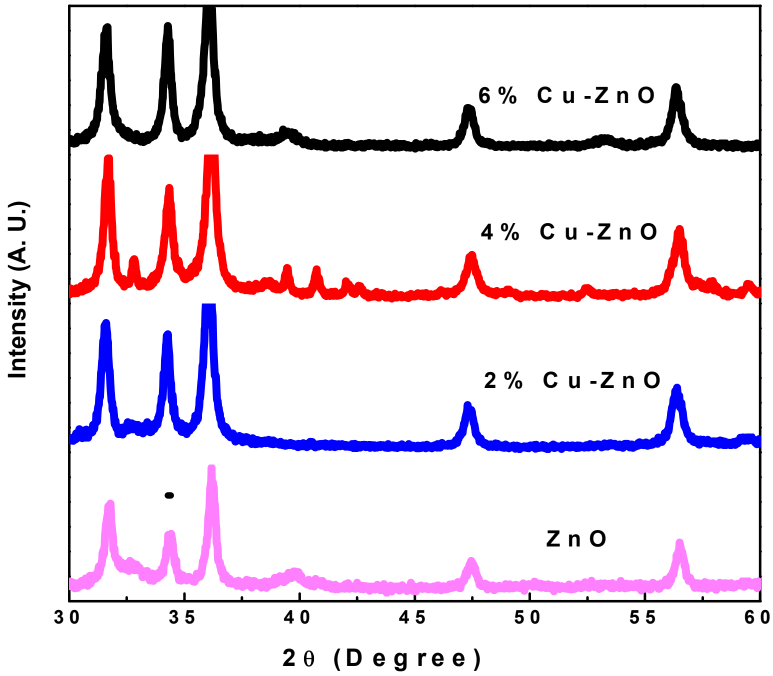

Fig. 3 – XRD pattern of undoped and Cu doped ZnO.

Typical XRD patterns of synthesized undoped and Cu doped ZnO are shown in Figure 3. Sharp peaks appear indicating well crystallinity of the synthesized material. The XRD pattern was indexed with wurtzite (hexagonal) unit cell structure with the presence of the peaks (100), (002), (101), (102) and (110) within the angular range 30° < 2θ < 60°. A small left shift (Δ2θ) of ~ 0.12° of (0002) peak is observed in case of Cu doped ZnO (see Figure 4).

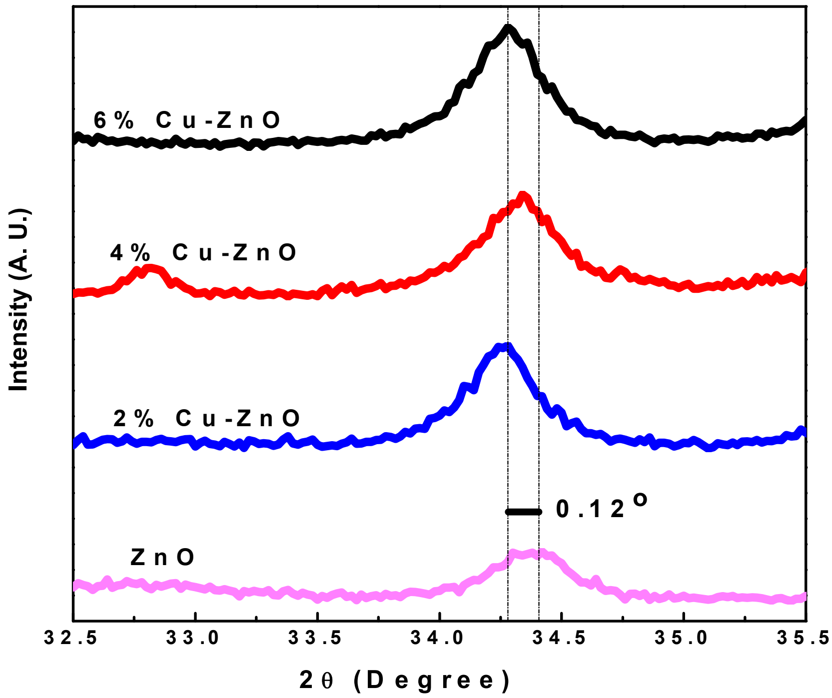

Fig. 4 – Shift of the (0002) peak in the XRD pattern.

It is because of the smaller size of the Cu atom compared to Zn. The intensities of different diffraction peaks are different indicating that the growth of the crystal is anisotropic. This anisotropic growth is characterized by a parameter known as the degree of orientation (χ_{hkl}) as defined below (for (002) plane) [3]

$$\chi_{002} = \frac{I_{002}}{\sum I_{hkl}}$$

The values of χ_{002} for undoped and 2%, 4% and 6% Cu-doped ZnO are 0.50, 0.56, 0.61 and 0.72 respectively. This indicates that for higher doping concentration, the degree of orientation increases. It is due to the lower growth rate of (0002) plane for larger Cu doping concentration. It has been observed that the relative intensity of (0002) plane gradually increases with increasing Cu doping concentration (see Figure 5).

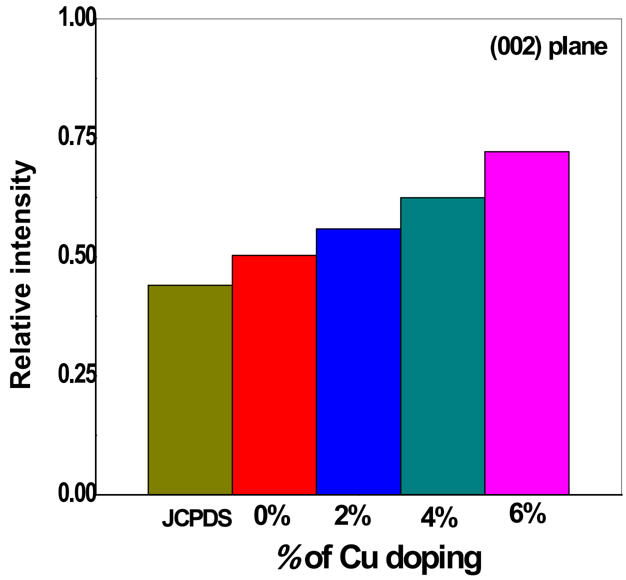

Fig. 5 – Normalized intensity of (0002) peak.

It is very well known that the faster growing layer vanishes out rapidly from the structure [3]. Hence, the doping of Cu in ZnO reduces the growth rate of (0002) plane. This is because; Cu^{2+} is less electronegative than Zn^{2+}. When some of the Zn^{2+} ions of (0002) plane are replaced by Cu^{2+} ions (see Figure 6), the electrostatic force between Cu^{2+} ions with O2- ions reduces. Hence the growth rate decreases.

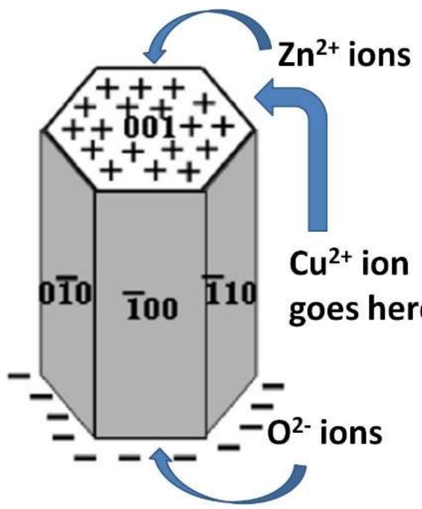

Fig. 6 – Mechanism of Cu doping in ZnO.

4. CONCLUSIONS

In conclusion, we have successfully synthesized undoped and Cu doped ZnO nanostructures using a simple sol-gel method. The crystallinity and purity were very evident from the XRD pattern. The XRD pattern revealed anisotropic growth of the wurtzite ZnO. The growth rate of (0002) plane is modified due to Cu doping. The growth along (0001) decreases on increasing Cu doping concentration due to substitution of Zn ions by less electronegative Cu ions.

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