

Full Length Research Paper

Effect of Co doping on structural, morphological, electrical and optical properties of nanocrystalline zinc oxide films

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We report the effect of cobalt doping on the structural, morphological, electrical and optical properties of nanocrystalline ZnO films fabricated by chemical spray pyrolysis technique (CSPT). The structural studies reveals that films have strongly c-axis oriented wurtzite structure. However with the increase (at 5%) in Co doping percentage, an inclination from (0 0 2) to (1 0 1) orientation has been observed. This may be due to the fact that, in addition to substitutional sites, Co may start to occupy interstitial sites due to the deformation of lattice structure caused by substitution of nearby Zn atoms by other Co atoms. This will also result in an increase of lattice constant. The films appear to be homogeneous and single-phase material, where cobalt enters the ZnO structure as Co²⁺ rather than forming metallic clusters. Self-assembly of particles are clearly displayed in Atomic Force Microscope (AFM) micrograph. The particle size and roughness of the films are found to decrease with the increase in Co doping percentage. Optical transmittance spectra showed red shift at higher doping. A sharp increase in transmittance occurs at 375 nm for all films, which correspond to band edge absorption. In addition to the band edge, absorption bands are also observed for all Co doped samples at 573, 606 and 666 nm, which are attributed to d-d transitions of tetrahedrally coordinate Co²⁺. The absolute strength of these absorption bands increases almost linearly with the increase in Co concentrations. Band gap values are found in the interval between 3.26 to 3.16 eV. Resistance are found to decrease at 15% of Cobalt doping.

Key words: ZnO, Co, Chemical Spray Pyrolysis Technique (CSPT), Atomic Force Microscope (AFM).

INTRODUCTION

Majority of semiconductors can only absorb UV light with the wavelength equal to or less than 385 nm. It is noted that visible light with spectral wavelength between 400 and 700 nm accounts for 45% of the total energy of the solar radiation, while UV light occupies less than 10% (Liao et al., 2006). Therefore, it is necessary to improve the photo catalytic efficiency for practical applications by broadening the absorption spectral range. From the view point of solid state physics, the spectral absorption is

directly determined by the structure and moreover the band gap energies. However, semiconductors like, ZnO and TiO₂, have shown merits of high photosensitivity, non-toxic nature and low cost (Wu and Tseng, 2006; Wang et al., 2007). Many elaboration works have been done to modify the structures of semiconductors with an aim to significantly enhance the optical absorption by doping with various metal or non-metal ions (Asahi et al., 2001; Mozia et al., 2005; Ekambaram et al., 2007; Sayilkan, 2007; Li and Haneda, 2004; Nakano et al., 2005.). Therefore, it would be interesting to investigate the effect of cobalt doping in ZnO films on the structure, electrical and optical properties (Wang et al., 2004;

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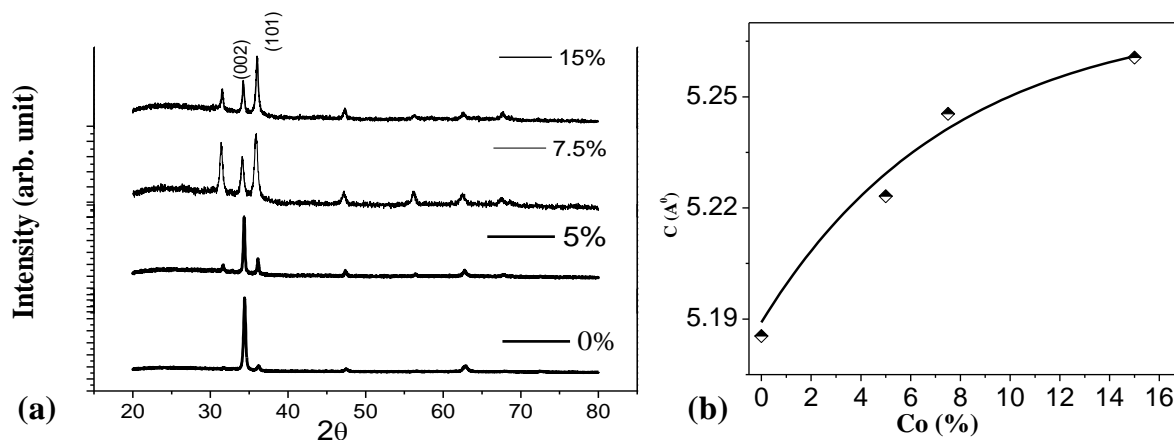


Figure 1. (a) XRD pattern of Co doped ZnO films at different Co doping concentrations, (b) lattice constant “C” at different Co doping concentrations.

Hoffmann et al., 1995). This is particularly important because Co^{2+} doping in ZnO can produce a significant red shift in band gap energy and, most importantly, the additional optical absorption bands could extend to the visible range of solar energy (Kim and Park, 2002; Qiu et al., 2006). In the present work, we report the effect of cobalt doping on the structural, morphological, electrical and optical properties of nanocrystalline ZnO films deposited onto glass substrate at temperature $380 \pm 5^\circ\text{C}$ by using chemical spray pyrolysis technique (CSPT).

EXPERIMENTATION

Undoped ZnO and Co doped ZnO films at various dopant percentages were deposited by chemical spray pyrolysis technique (CSPT). Aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been used for spraying. The doping was achieved by the addition of cobalt chloride to the precursor solution, and the whole mixture was sprayed on to the microscopic glass slides. The structural and morphological characterization of the prepared film was carried out by X-ray diffractometer and Atomic Force Microscope (AFM). The electrical and optical studies have been done by using four-probe set-up and UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Figure 1(a) shows the XRD pattern of Co-doped ZnO films at different Co doping concentrations. XRD is done by using Rigaku Diffractometer with $\text{CuK}\alpha$ ($\lambda=1.5405\text{\AA}$) radiation. From the figure one can observe that the crystal structure remains hexagonal even with maximum doping that is, at 15% Co doped ZnO. However an inclination from (0 0 2) to (1 0 1) orientation has been observed with the increase (at 7.5 and 15%) in Co doping percentage. This may be due to fact that, in addition to substitutional sites, Co may also start to occupy interstitial sites due to the deformation of lattice structure caused by

substitution of nearby Zn atoms by other Co atoms. This will also result in an increase of lattice constant Figure 1(b).

The AFM micrographs [Figure 2 (a-f)] of Co doped ZnO films show uniform polycrystalline nature. The self-assembly of particles (Ring and rod formation) with the increase in Co percentage are clearly shown in AFM micrograph (Figure 3). The values of roughness Figure 4 and grain size Figure 5 (a-f) are found to decrease with the increase in cobalt doping percentage.

A sharp increase in transmittance occurs at 375 nm for all films, which correspond to band edge absorption shown in Figure 6. In addition to the band edge, absorption bands are also observed for all Co doped samples at 573, 606 and 666 nm. The absolute strength of these absorption bands increases almost linearly with the increase in Co concentrations are clearly displayed in figure. This is attributed to d-d transitions of tetrahedrally coordinate Co^{2+} (Maureen et al., 2006). The values of optical band gap (E_g) are found to vary from 3.16 to 3.26 eV as shown in Figure 6(b). As can be seen from the figure as the cobalt doping increases the values of band gap decreases this may be attributed to the sp-d exchange interactions between the band electrons and the localized electrons of the Co^{2+} ions (Diouri et al., 1986). Also, as the cobalt content increases, so does the absorption band intensity. This gives clear evidence that cobalt enters in the tetrahedral sites of the wurtzite structure as Co^{2+} rather than forming metallic clusters which is consistent with the XRD data. The value of resistance are found to decrease with the increase in cobalt doping percentage. This behaviour of resistance could be understood from the fact that with the increase in Co doping, initially the Co atoms occupy interstitial position thus increasing the scattering from the defects. While at higher doping the carrier concentration become much larger and it dominates the contribution from scattering and gives rise to decrease in resistance.

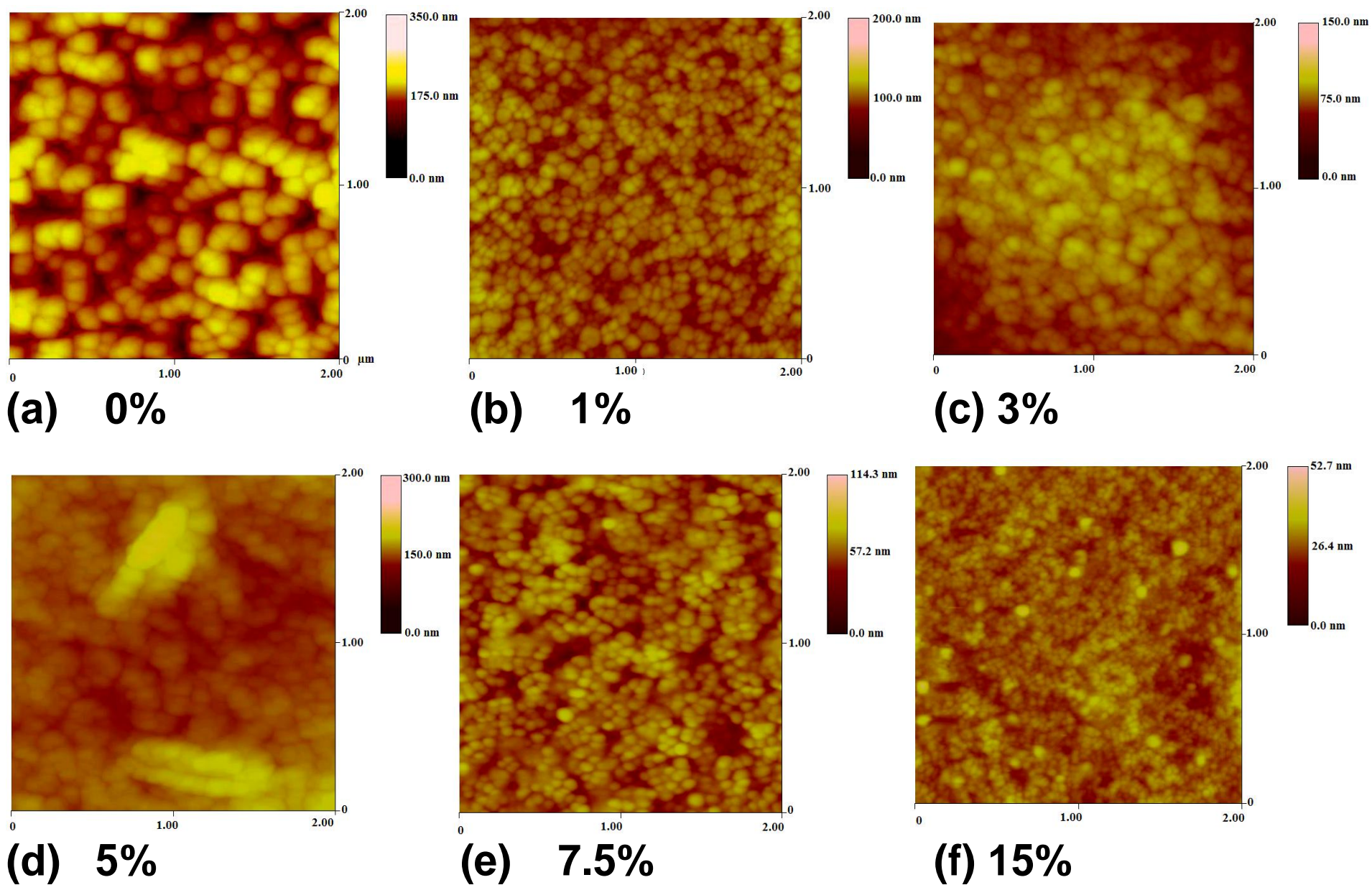


Figure 2. (a-f) AFM micrograph ($2 \times 2 \mu\text{m}^2$) of Co doped ZnO films at different Co doping concentrations.

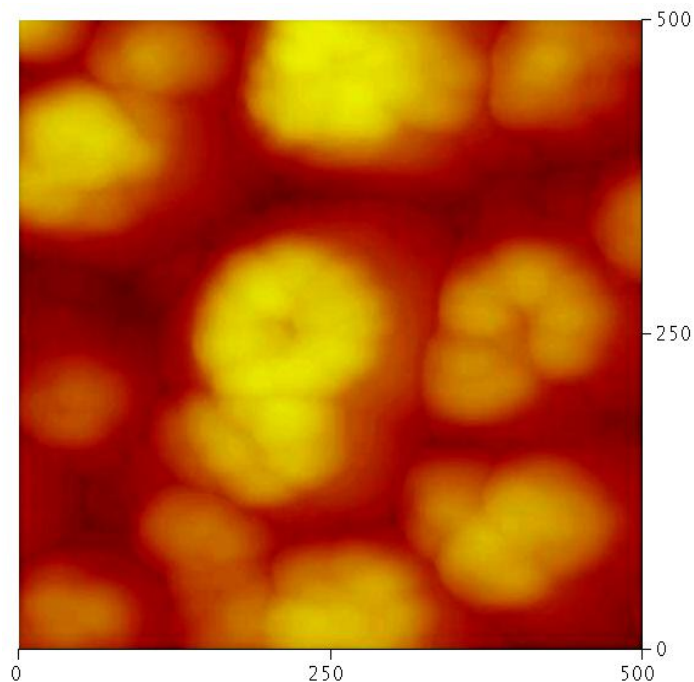


Figure 3. Self assembly of 1% Co doped ZnO nanoparticles (in 500 nm image).

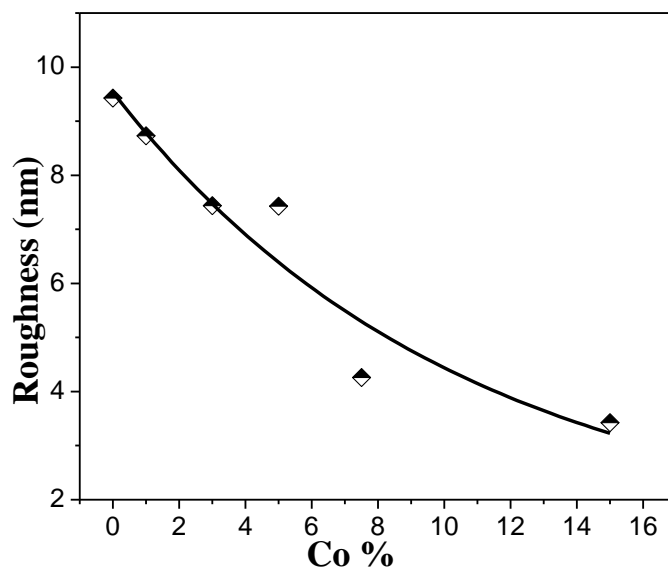


Figure 4. Roughness as a function of Co dopant percentage.

Conclusion

A systematic study has been carried out to investigate structural, morphological, electrical and optical properties of Cobalt doped ZnO films. All films are found to have preferred orientation along (0 0 2) plane. However, an

inclination from (0 0 2) to (1 0 1) orientation has been observed with the increase in Co doping percentage. This is because of the fact that, in addition to substitutional sites, Co may start to occupy interstitial sites due to the deformation of lattice structure caused by substitution of nearby Zn atoms by other Co atoms which also result in

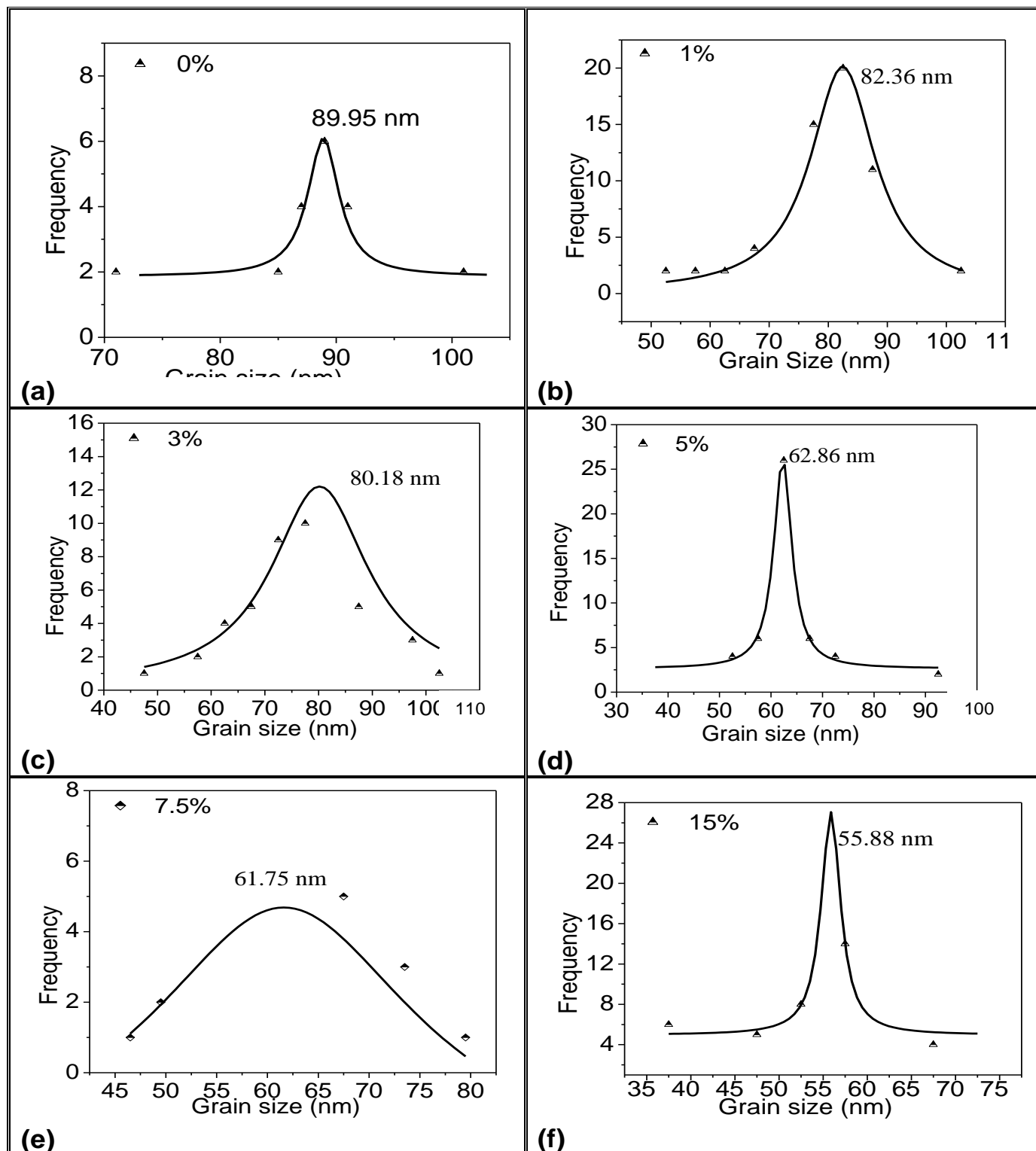


Figure 5. Grain size distributions for Co doped ZnO films for (a) 0 (b) 1 (c) 3 (d) 5 (e) 7.5 (f) 15% Co concentration.

of lattice constant. The films appear to be homogeneous and single-phase material, where cobalt enters the ZnO structure as Co^{2+} rather than forming metallic clusters.

Self-assembly of Co doped ZnO particles are clearly displayed in AFM micrograph. Optical transmittance spectra showed red shift at higher doping. Optical band

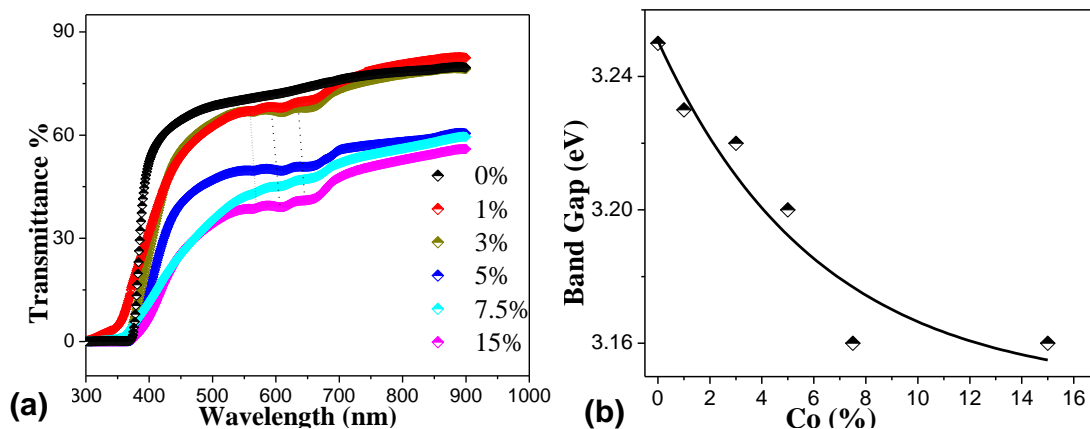


Figure 6. (a) Optical transmittance spectra of Co doped ZnO films (b) Optical band gap Vs Co% curve for Co doped ZnO thin films.

gap values are found in the interval between 3.26 to 3.16 eV. Resistance are found to decrease at 15% of Cobalt doping.

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