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Dedicated to Professor Mircea Diudea on the Occasion of His 65th Anniversary

EFFECTS OF Cu DOPING ON NANO STRUCTURE, MORPHOLOGY AND PHOTOCATALYTIC ACTIVITY OF ZnO THIN FILM SYNTHESIZED BY SOL-GEL METHOD

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ABSTRACT. Zinc oxide has been investigated due to its large band gap and several applications in science and industry. However, doping extrinsic impurities would change the resistivity of ZnO films which enhance their properties. In the present study, nano-structured ZnO and Cu-doped ZnO photocatalysts were successfully prepared on glass substrates by sol-gel dip-coatig method. Various techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and UV-VIS absorption spectroscopy were used to investigate the effect of the Cu-doped on ZnO thin film. The results showed that the doping greatly changed the microstructure, morphology and optical properties of ZnO, which may contribute to the enhancement of photocatalytic activity. The photocatalytic activity of the prepared pure ZnO and Cu-doped ZnO photocatalyst was investigated by the degradation of Methylene Blue solution. The results indicated that Cu-doped ZnO had a higher photocatalytic activity and Cu dopant greatly increased the photocatalytic activity of ZnO. Using C# programming language, we developed a software for more analyzing results.

Keyword: *Cu-doped ZnO, Thin film, Sol-Gel, Photocatalyst.*

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INTRODUCTION

As a very low cost and environmental friendly material, zinc oxide is an n-type semiconductor that has a wide band gap (3.3 eV) and exciton binding energy (60 meV) [1]. It is one of the most important metal oxide semiconductors that found applications in many fields such as transparent conducting oxide (TCO) [2], photocatalyst [3], piezoelectric anogenerators [4], solar cells [5], gas sensors [6], UV detectors [7], optoelectronic devices [8], and so on. Also TiO_2 is a very good photocatalyst but, in some cases, ZnO presents higher advantages [9], because of the mobility and separation of its photo induced electrons and holes and non-expensive, high yield production [10]. Owning to aforementioned applications of ZnO, various methods such as chemical vapor deposition (CVD) [11], sputtering [12], metal organic chemical vapor deposition (MOCVD) [13], pulsed laser deposition [14] and sol-gel have been used to prepare ZnO thin films. Among these methods, sol-gel technique is very popular, since it is non-expensive and reliable technique, that needs simple equipment [15]. In this work we report the influence of Cu doping on the microstructure, morphology, optical properties and photocatalytic activity of ZnO thin films prepared by sol-gel method. Also pristine ZnO thin films were produced and their properties compared with Cu doped samples.

RESULTS AND DISCUSSION

Structural and Morphological Characterization

Figure 1 (a & b) shows the XRD patterns of un-doped and Cu-doped thin films. From this figure, three main diffraction peaks of (111), (002) and (101) planes can be seen, indicating the films have a polycrystalline hexagonal wurtzite structure (JCPDS card no. 36-1451) while the diffraction peaks of copper oxides (CuO or Cu_2O) were not detected. Moreover, Figure 1 indicates that Cu doping shifts the XRD peaks to higher angles. The average crystallite size was estimated by using of Scherrer equation [16]:

$$d = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is a constant (0.9) and d, λ, θ and β are the average crystallite size (nm), wavelength of X ray radiation (0.1546 nm), Bragg's angle of diffraction and full-width at half maximum intensity of the peaks, respectively. According to calculations, Cu doping decreased the average crystallite size from 21.245 nm to 17.514 nm.

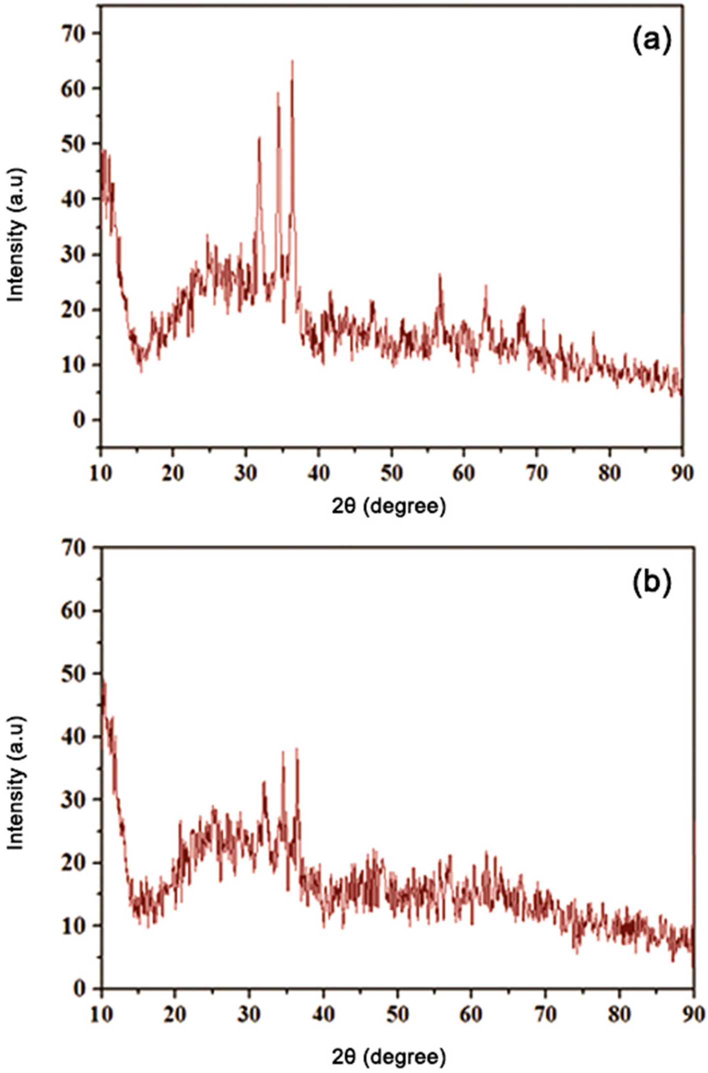

Figure 1. XRD patterns of: (a) ZnO thin film, (b) Cu-doped ZnO thin film.

The surface morphology of pristine ZnO and Cu doped ZnO thin film is shown in Figure 2. The ZnO thin film shows a wrinkle morphology, with an approximate width of 0.5-1 µm, whereas the Cu-doped ZnO film has a spherical morphology, where diameter of the spheres is about 0.5-1 µm.

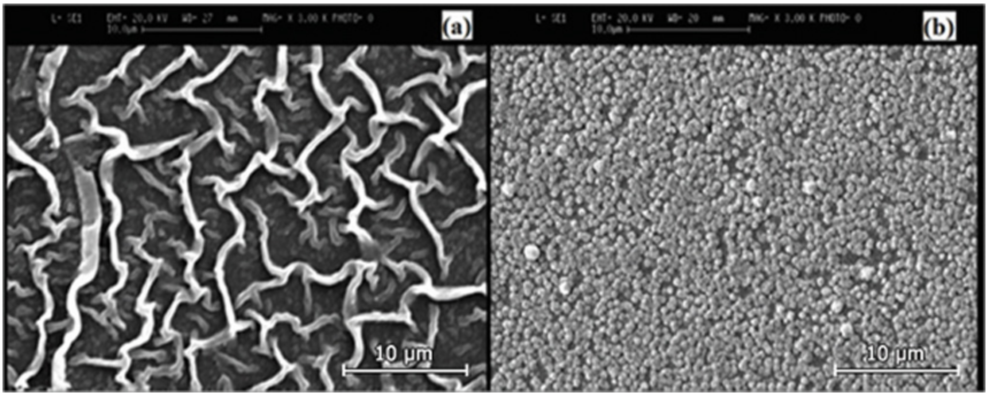

Figure 2. SEM micrographs of (a) pristine ZnO thin film and (b) Cu-doped ZnO thin film.

Cross-section FE-SEM micrographs of pristine and Cu-doped ZnO thin films is shown in Figure 3. It is obvious that thickness of ZnO thin film increased by Cu doping. It is well-known that in dip coating process, thickness of films is controlled by the viscosity of the liquid, the solid content and the withdrawal speed [17]. Since the total dissolved solids in the solution of Cu doped ZnO is larger than in that of pristine ZnO, the thickness of doped ZnO thin film is expected to be higher, while the viscosity of the liquid increased.

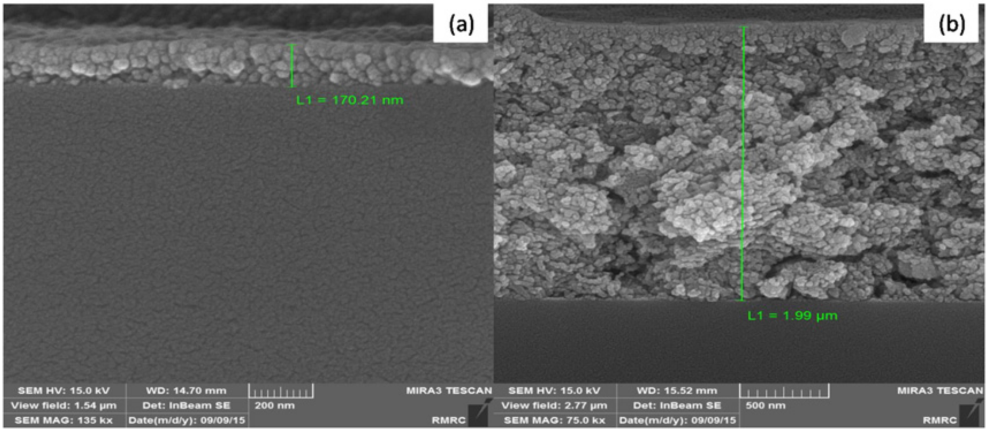

Figure 3. FESEM micrographs of (a) pristine ZnO thin film and (b) Cu-doped ZnO thin film.

Figure 4 shows the optical absorbance spectra of pristine and Cu doped ZnO thin films deposited on glass substrates. It seems that band gap energy of ZnO thin film decreased by Cu doping. According to [18] by increasing in thickness of sample, UV absorbance will increase. Therefore, as shown in Figure 4, the absorption edge of ZnO thin films has moved toward longer wavelength by Cu doping.

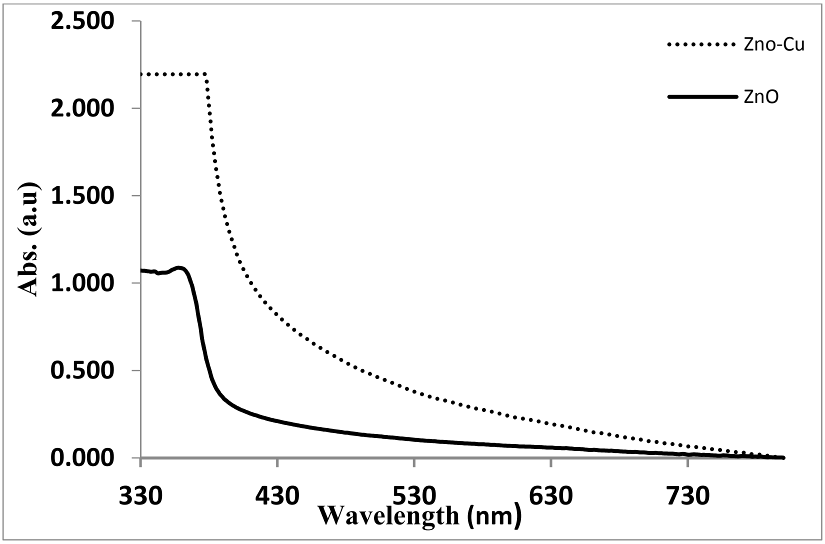

Figure 4. Absorbance spectra of non-doped and Cu-doped ZnO thin films.

Photocatalytic Activity

The photocatalytic activity of pristine and Cu doped ZnO thin films were measured by degradation of methylene blue (MB) in an aqueous solution. Curves of degradation of methylene blue (%) versus time, for pristine and Cu doped ZnO are shown in Figure 5. According to the photocatalytic activity principles, when photons with energy equal or greater than ZnO band gap hit on the surface, the valence band electrons are excited and go to the conduction band therefore a hole is created in the valence band. The mechanism of photocatalytic activity of ZnO thin films is presented as follows [3]:

$$ZnO \rightarrow {e_{cb}}^{-} + h_{vb}^{+} \tag{2}$$

$$e_{ch}^{-} + O_2 \rightarrow {}^{\cdot}O_2^{-} \tag{3}$$

$$h_{vb}^{+} + OH^{-} \rightarrow {}^{\cdot}OH \quad (4)$$

$${}^{\cdot}O_2^{-} + H_2O \rightarrow HO_2^{\cdot} + OH^{-} \quad (5)$$

$$HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + {}^{\cdot}OH \quad (6)$$

$$H_2O_2 \rightarrow 2\,{}^{\cdot}OH \quad (7)$$

$${}^{\cdot}OH + organic\ \ compound \rightarrow CO_2 + H_2O \quad (8)$$

It is seen that the catalytic efficiency of the thin films increases with Cu doping. In the case of Cu-doped ZnO thin film, Cu can improve the photocatalytic activity of ZnO thin film by the following mechanism [19]:

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + OH^{-} + {}^{\cdot}OH \quad (9)$$

$$Cu^{2+} + e^{-} \rightarrow Cu^{-} \quad (10)$$

Also the surface to volume ratio of Cu-doped ZnO thin film is higher in comparison with pristine ZnO thin film. This is an advantage that may improve the photocatalytic activity of Cu-doped ZnO thin films [20].

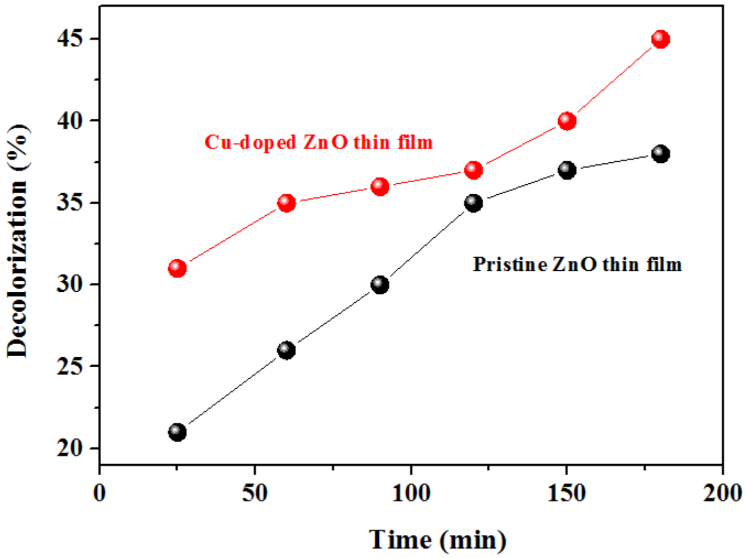

Figure 5. Time dependence of the decolouring efficiency of MB solution by doped and undoped ZnO thin films.

CONCLUSIONS

Pristine ZnO and Cu doped ZnO thin films were prepared by sol-gel followed by dip coating techniques. The thin films (doped and undoped) were characterized by XRD, SEM, FESEM and UV-VIS spectroscopy. The results showed that thin films had ZnO crystallite with a hexagonal wurtzite structure. It was observed that the surface morphology of ZnO thin film transformed from wrinkle morphology to spherical morphology by Cu doping. Furthermore Cu doping increased the thickness of thin film and the absorption edge was shifted to longer wavelengths. The photocatalytic activity of Cu doped ZnO thin film was greater than the activity achieved by pristine ZnO thin films under UV-light illumination.

EXPERIMENTAL SECTION

ZnO and Cu-doped ZnO thin films were synthesized by the sol-gel dip coating on the glass slides. To prepare a solution for coating, 0.3M zinc acetate dehydrate was dissolved in 10 ml iso-propanol containing monoethanolamine (as a stabilizer). The mole ratio of Zn^{2+} to MEA was kept 1:1. The required amounts of copper acetate was dissolved into the above solution to obtain a mole ratio of Cu^{2+} to $Zn^{2+}=0.1$. Then the mixed solution was stirred at 70°C for 1 h to accelerate the hydrolysis reaction. Final solution was clear and homogeneous which after being aged for 24h was used as the coating solution. Thin films were deposited by dip coating method on glass substrates (10mm × 15mm ×1.5mm) at room temperature. After each successive coating, the layers were dried for 10 min in an oven at 80 °C to remove the solvent. The coating and drying process were repeated ten times. Then the gel films were calcined at 400 °C for 60 min and finally the thin films cooled to room temperature to obtain the pristine ZnO and Cu-doped ZnO thin films.

The crystal structure of the un-doped and Cu-doped ZnO thin films was identified by using of an X-ray diffractometer (XRD, D-8 Advanced). Surface morphology of the thin films was determined by scanning electron microscopy (SEM, S-360 Cambridge). UV-VIS spectrophotometer (UV-4802UNCO) was used for the measurement of UV-Vis absorbance spectra of thin films.

The photocatalytic activity of thin films was quantified by means of the degradation of methylene blue (MB) in an aqueous solution. 5 mL of MB solution at an initial concentration of 10 mg/lit (10 ppm) was put in a glass container. Then the thin films were submersed in the glass container and this disposition was exposed to UV radiation. The light source of illumination was two parallel UV lamp in a dark space. After irradiating for 0.5, 1, 1.5, 2, 2.5 and 3 h, the concentration of residual MB was determined in the same UV-VIS spectrophotometer used for measuring the optical transmission spectra of the thin films.

Developing Software

To make better use of this research, a software was developed (in C# language programming) by “Visual Studio 2012”, and the results were categorized by this software, named "ZnO Master". Physical properties, optical properties, etc. of ZnO, and the Method of doping ZnO are categorized in this software (Figure 6).

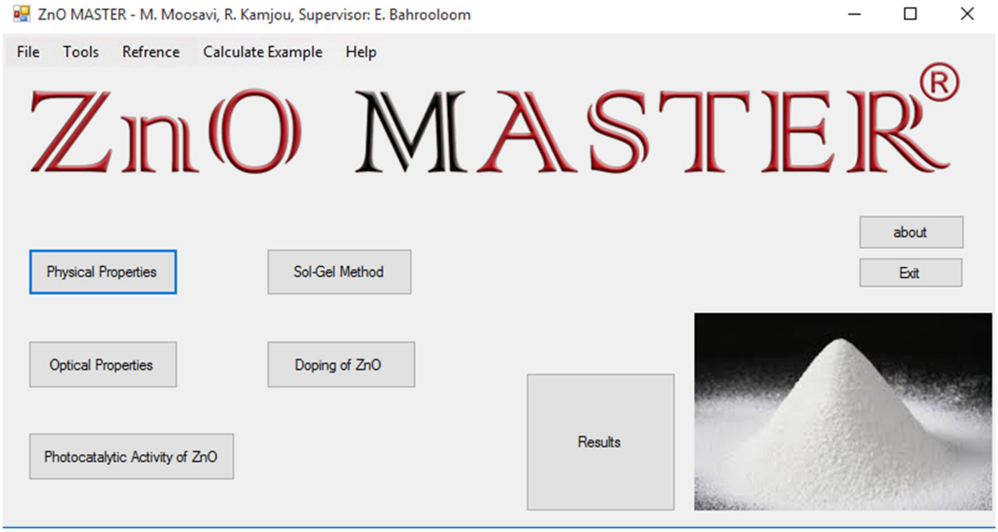

Figure 6. ZnO Master software environment.

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