Fabrication and characterization of sulfur doped zinc oxide thin films

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In this work we present a new chemical bath deposition method to fabricate thin films of ZnO:S type deposited on glass and polymer substrates. The reaction was controlled using a stable metal complex. Additionally, the optical and structural characterization of the obtained materials was performed. The films exhibit an emission peak around 417 nm. The scanning electron microscopy images show a polycrystalline nature of these films.

Keywords: Zinc oxide; Thin films; Semiconductors

1. Introduction

Semiconductor inorganic thin films play a central role in the development of the novel technology that modern society demands, mainly in the field of optic and electronic devices [1-3]. In this field, zinc oxide thin films have been proposed to be used as blue-violet optical emission devices, wide band gap high power devices, surface acoustic wave devices and ferroelectric memories, among other [4]. ZnO thin films have been deposited by a variety of techniques such as sputtering, molecular beam epitaxy, pyrolysis and chemical deposition. Among the thin films deposition methods, chemical bath deposition (CBD) from aqueous solutions is the simplest and most economical one. Another advantage of the CBD method with respect to other methods is that films can be deposited on different kinds, shapes and sizes of substrates.

In this work we present a new chemical bath deposition method to fabricate ZnO:S thin films carrying out a controlled chemical reaction.

2. Experimental

The synthesis of the films was carried out from a controlled chemical reaction using thiourea and a stable zinc complex, $Zn(en)_3SO_4$ (en: ethylenediamine), which slowly releases the zinc ions. Thiourea releases sulfur ions by means of an alkaline hydrolysis process. $Zn(en)_3SO_4$ metal complex was prepared by adding an ethylenediamine aqueous solution to a $ZnSO_4$ aqueous solution in a 3:1 ratio. The synthesized complex was purified by means of a recrystallyzation process. The films were synthesized as follow: 80 ml of a 0.1 M $CS(NH_2)_2$ aqueous solution were added to 250 ml of a 8 mM $Zn(en)_3SO_4$ aqueous solution. Then, 40 ml of a 1 M NaOH aqueous solution were added. The resulting solution was allowed to stand stirred at 60 ^oC for 8 h. Polyethylene (PE), polyethyleneterephthalate (PET) and glass substrates were immersed into the solution. White thin films on the substrates and white powder were obtained from this reaction. The films were removed from the solution and the powder was separated by filtration. The materials were washed with deionized water and vacuum dried. The films were annealed at 125 ^oC for 3 h under N_2 atmosphere. The characterization was performed on the coated glass films because simplicity, although the films were grown on PE, PET and glass substrates.

The optical transmission and fluorescence measurements of the obtained films were performed in a Perkin Elmer Lambda 2 UV-VIS spectrometer and a Perkin Elmer LS50 B luminescence spectrometer, respectively. The X-ray diffraction paterns were collected with a Rigaku Geirgerflex diffractometer by using Cu-Kα radiation (λ = 1.542 Å). Secondary electron images and the composition of the films were obtained using a JEOL JSM-5410LV scanning electron microscope.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of a film deposited on glass from the conditions indicated above. The $Zn(OH)_2$ diffraction pattern (wuelfingite, JCPDS 38-385) is included for comparison. In this figure can be noted that the X-ray diffraction pattern of the film coincides with that of $Zn(OH)_2$. Thus, a $Zn(OH)_2$ thin film was obtained during the reaction. Figure 2 shows the X-ray diffraction pattern of the film after annealing at 125 ^oC for 3 h under N_2 atmosphere, compared with that of ZnO (zincite syn, JCPDS 36-1451). After annealing, the X-ray diffraction pattern of the film coincides exactly with that of ZnO and the peaks attributed to $Zn(OH)_2$ disappear. By annealing, $Zn(OH)_2$ changed to ZnO.

The SEM image illustrated in the figure 3 reveals that the film, such as synthesized, exhibits a polycrystalline nature. On the film surface large crystals with sharp edges are observed. The EDS analyses performed by SEM revealed

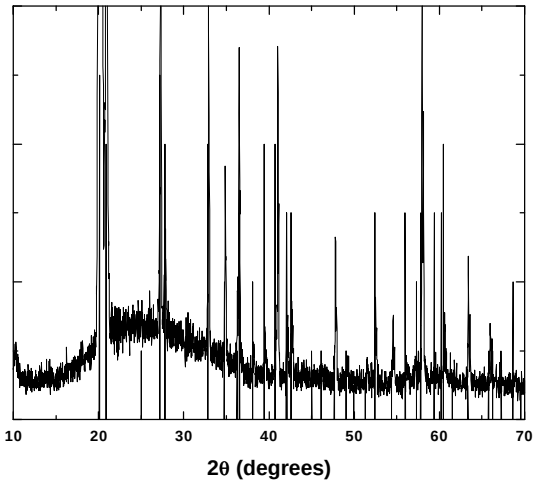

Figure 1. X-ray diffraction pattern of a thin film deposited on glass. The vertical lines show the diffraction pattern of $Zn(OH)_2$ (wuelfingite, JCPDS no. 38-385).

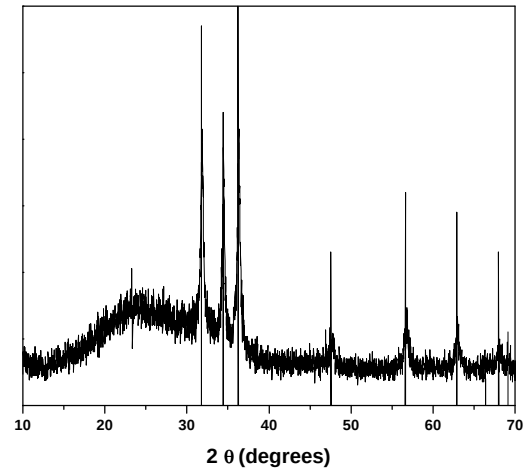

Figure 2. X-ray diffraction pattern of the annealed thin film corresponding to figure 1. The vertical lines show the diffraction pattern of ZnO (zincite syn, JCPDS no. 36-1451).

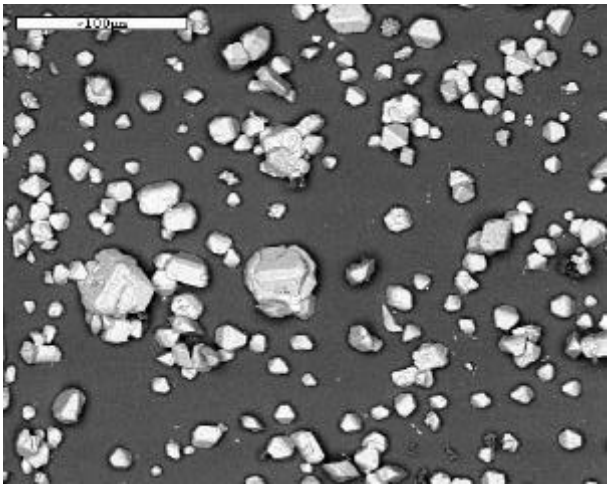

Figure 3. Secondary electron image of a thin film synthesized on glass. The scale bar of the image is *ca.* 100 µm.

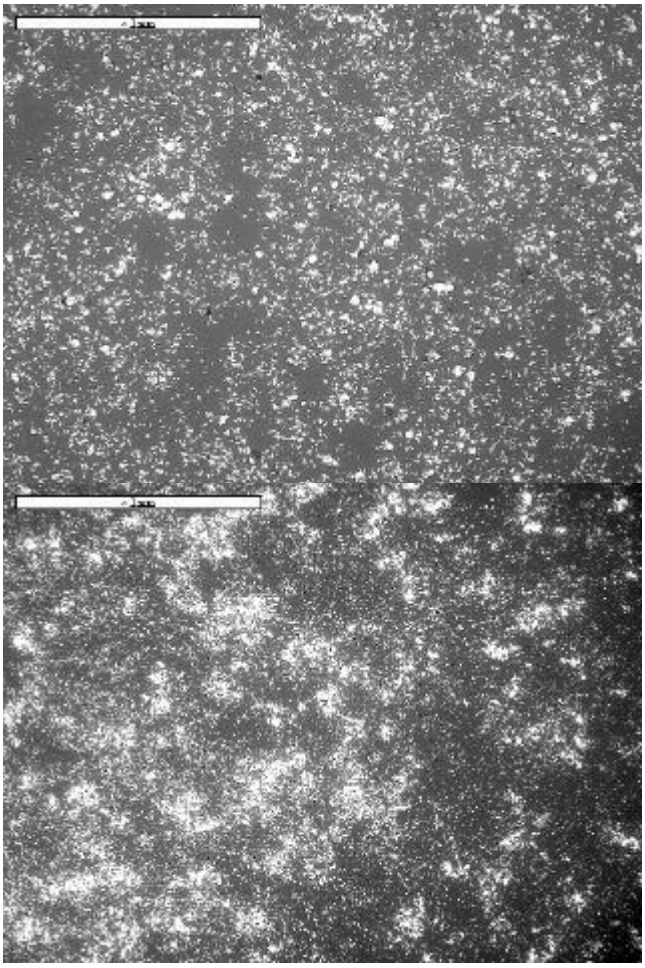

Figure 4. Secondary electron images of films: (a) thin film such as synthesized (b) thin film after annealing. The scale bar of these images is *ca.* 1 mm.

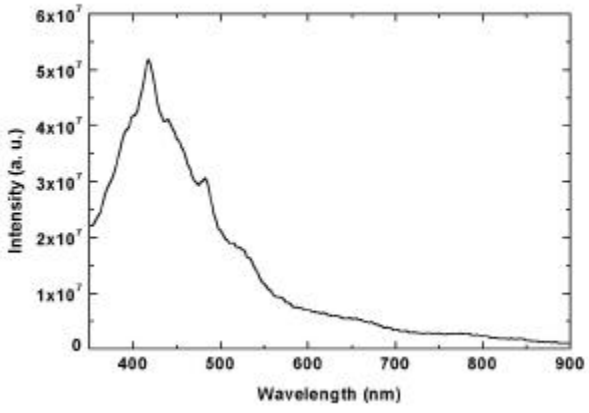

Figure 5. Fluorescence spectrum of an annealed thin film (excitation wavelength = 260 nm).

the presence of Zn and S in the film, with a Zn:S ratio of *ca*. 32:1. Sulfur is included as an impurity in the film.
Figure 4 shows the SEM images of a film before and after annealing. The crystals on the surface of the annealed film are smaller than those of the film before annealing. This change in the morphology of the films agrees well with the results obtained by X-ray diffraction. The EDS analyses of the annealed films did not reveal appreciable change of the Zn:S ratio in relation to the films before annealing. These results suggest that after the annealing, sulfur remains as dopant in the film.

In previous works have been reported that ZnO is capable of producing red and green luminescence. It has been found that doping ZnO with tungsten produced a intense peak at 476 nm. Figure 5 shows the fluorescence spectrum of a film synthesized by the CBD method and then annealed. The film exhibits an emission peak around 417 nm when excited with light of 260 nm. The properties of the films depend strongly on the employed method for the synthesis.

The film synthesized from the reaction conditions stated above exhibited a strong absorption in the ultraviolet region of the spectrum up to 350 nm. It presented a transmittance of *ca*. 85 % over 350 nm. The optical absorption of the thin film remains closely constant in all the visible region of the spectrum.

4. Conclusions

In this work, ZnO:S thin films have been obtained by means of an economical and simple chemical bath deposition method followed by annealing. The ZnO:S polycrystalline films present an emission peak at 417 nm and a constant optical absorption in the visible region of the spectrum. Thin films can be deposited on PE and PET films with different shapes and sizes by the method used in this work. This method could be used to introduce different kinds of impurities in the ZnO thin films by adding a variety of metal complexes in the reaction, which could lead to interesting new properties of the materials.

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