Deposition of Ag doped Zinc Oxide Thin Films for p-type semiconductor

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Abstract – This paper aims to optimize and fabricate high-quality Ag doped zinc oxide (ZnO) thin films using a low-cost sol gel deposition method. The study demonstrates the successful implantation of single crystalline ZnO on a glass substrate as well as Ag doped ZnO at 1at%, to 5 at% using the sol gel method. The XRD spectra show the formation Ag embedded ZnO films on glass. The embedding of Ag in ZnO was confirmed from the SEM image. The UV-Vis transmission spectra show high transparency and uniform deposition of doped ZnO at different doping levels. The energy band gap of the deposited sample is ~3.2eV. The surface morphology of the Ag-doped ZnO is also studied using SEM characterization.

Index Terms – Ag doped ZnO, solgel deposition, XRD spectra, UV-VIS spectra, SEM

I. INTRODUCTION

Ag-ZnO thin film is one of the important semiconductors materials used in optical electronics, sensors, solar cells, and antibacterial coatings[1-5], and has attracted considerable attention for its unique properties. ZnO has been already a widely accepted semiconducting material in the applications of photodetectors, sensors, light emitting devices etc [6]. The epitaxial growth of ZnO has led to the development of quantum wells and other heterostructures for excellent ultraviolet and blue light emitters [7]. The success of zinc oxide based devices would not have been possible without the dopant materials like Cu [8], Al [9] and Sb [10], N [11] for fabrication of n-type and p-type ZnO semiconductor from III and V group atoms. The fabrication of undoped and doped ZnO material has been reported using various chemical assisted deposition and physical vapor deposition techniques previously [12]. Several attempts have been made to fabricate the stable p-type ZnO semiconducting material and doping of silver can also assist in the fabrication of stable p-type ZnO [13-15]. The Ag doping can improve the conductivity, transparency and photocatalytic activity of ZnO thin films by introducing extra electrons and scattering centers in the film.

However, one of the problems that arise in Ag doped ZnO thin films is to control the stable electrical and optical properties by adjusting several parameters. These parameters could be the deposition method, the substrate temperature, the doping concentration, and the post-deposition treatment etc. These parameters affect the structure, morphology and composition of the films, which in turn influence their electrical and optical properties. In this paper, an attempt has been made to optimize and fabricate stable high-quality Ag doped ZnO thin films of desired properties with a very low cost sol gel deposition method. This method is not only simple and cost effective, but also, it also provides various parameters to control the doping concentration and annealing temperatures. Further the deposited samples were characterized for its distinctiveness using XRD, UV-Vis spectrophotometer and SEM.

II. EXPERIMENTAL PROCEDURE

The sol-gel spin coating approach, which was previously utilized to deposit doped and undoped ZnO [16-17], is used in this study to deposit Ag doped ZnO. The solution was made with zinc acetate dihydrate and silver acetate as zinc and Ag sources respectively. 2-Methoxyethanol was employed as a solvent, while ethanolamine was used as a reagent. By dissolving zinc acetate dihydrate and silver acetate in 2-methoxyethanol, a clear solution was formed, and 5 to 7 drops of ethanolamine were added to the solution at the same time, which served to improve the rate of reaction and preserve stability. The solution was then continually stirred on a hot plate at 80°C for an hour, yielding a translucent and clear solution. The obtained solution was cooled at room temperature followed by the deposition of films on microscopic glass and silicon substrate with a homemade spin coating system. Each time after the deposition process, films were preheated in the open air at 300°C for 10 minutes for evaporation of any organic elements present in the films. After cooling the substrate to room temperature, the next layer was deposited. Finally, all the samples were post-annealed at 375°C for an hour in the open air. For the investigation of the optical property, multiple coated films of undoped and doped ZnO were deposited for 1 at% to 5 at% silver doping concentrations.

The deposited Ag doped and undoped films on glass substrate were characterized to study percentage of transparency and energy bandgap using transmittance spectra, recorded by Shimadzu UV spectrophotometry. Structural property of undoped and doped films were investigated by XRD pattern recorded using Bruker AXS-D8 X-ray diffractometer. The X-ray diffractometer was equipped with a Cu-kα x-ray source having wavelength 1.54059 Å. Samples deposited in silicon substrate were used to measure the refractive index on silicon substrate.

III. RESULT AND DISCUSSION

Structural Properties

As recorded XRD spectra of undoped and 4 at% silver doped ZnO thin film on glass substrate using the sol gel method are shown in Figure 1 and Figure 2 respectively. In Figure 1, the peak at 34.8º corresponds to (002) plane orientation of the wurtzite hexagonal structure whereas no other significant peaks were observed [18]. It indicates that a c-axis oriented single crystalline ZnO was successfully deposited on the glass using the sol gel deposition method at optimum conditions.

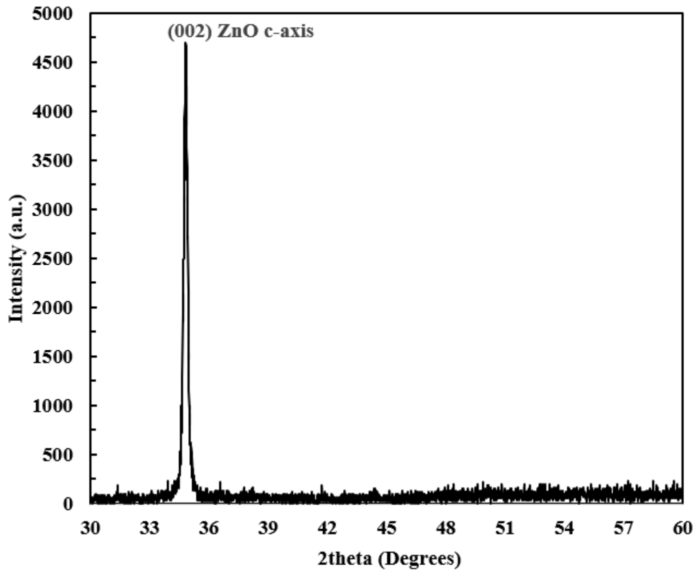


Figure 1 XRD spectra of ZnO film deposited using solgel

The recorded spectra of Ag doped ZnO are shown in Figure 2. The peak at 38.2° and 44.46° are associated with the (111) and (002) plane respectively of silver crystal [19]. The same peaks were reported for the formation of face centered cubic structure silver crystal elsewhere [20-22]. The increased intensity of peaks of silver crystal may be attributed to the 4 at% dopant value of silver acetate in the solution. However, for lower atomic concentrations the negligible height of the peak was reported [23]. It became evident from the XRD results that the Ag was successfully incorporated in ZnO with low cost solgel technique.

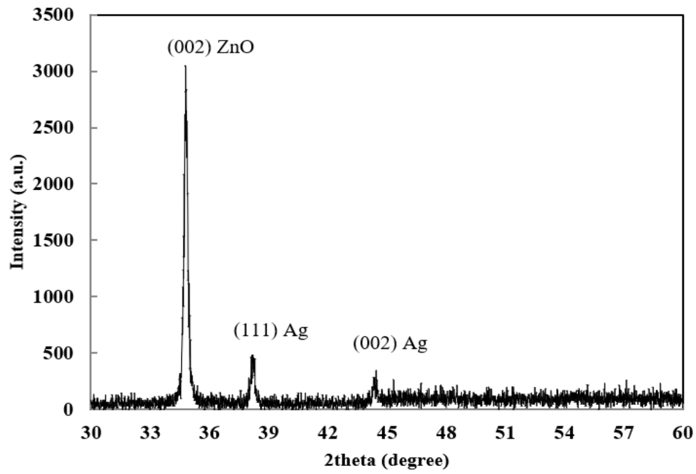


FIGURE 2 XRD spectra of silver doped ZnO film using solgel

Optical properties

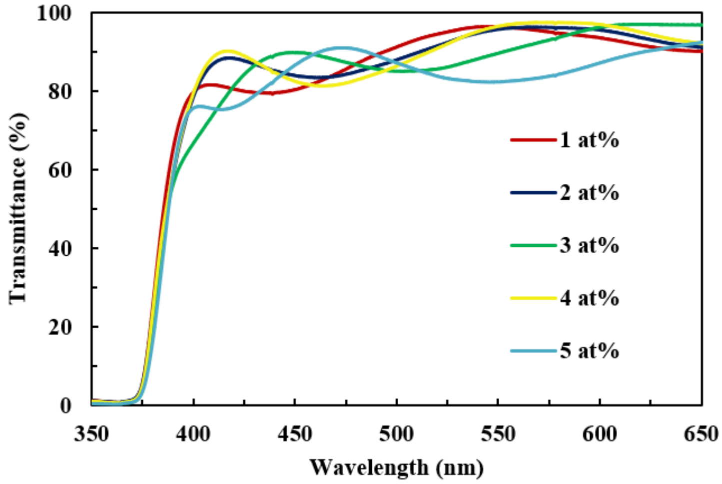


Figure 3. UV-VIS transmittance spectra of silver doped ZnO thin film at various at%

The UV–visible transmission spectra of Ag-doped ZnO films deposited on a microscopic glass substrate are shown in figure 3 as a function of wavelength. The transmission spectra show that deposited films were highly transparent and the oscillating nature of the spectra indicates uniform deposition of doped ZnO at various at% doping of silver. From these transmission spectra, various parameters like thickness and energy band gap were determined as calculated previously [24]. Since an equal number of coatings were applied under optimum deposition parameters on the glass surface, it was expected to get the equal thickness of the sample in this study. The thickness of sample, determined using well known swapnoel method, was calculated to be ~489 nm.

The bandgap energy of the deposited 4at% silver doped ZnO film was determined using a plot of absorption coefficient versus energy bandgap as shown in Figure 4. From the plot, it was observed that Ag doped ZnO showed a direct bandgap nature. With the help of extrapolation taken on the absorption coefficient curve, the energy bandgap was found to be ~3.2eV. The transmittance spectra and absorption coefficient of the deposited film also indicated that the higher transparency could be maintained even after ZnO was doped with silver atoms.

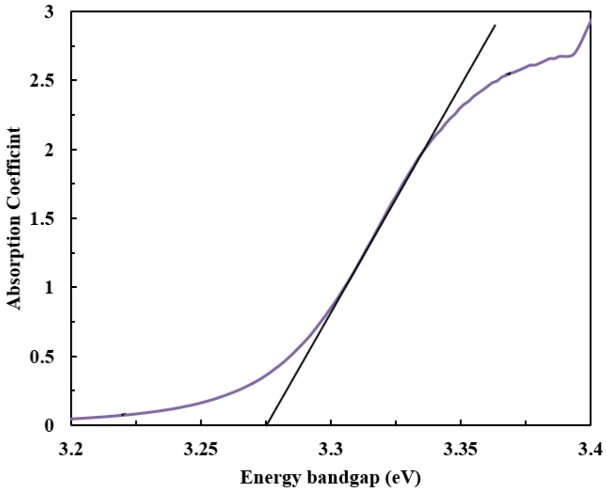
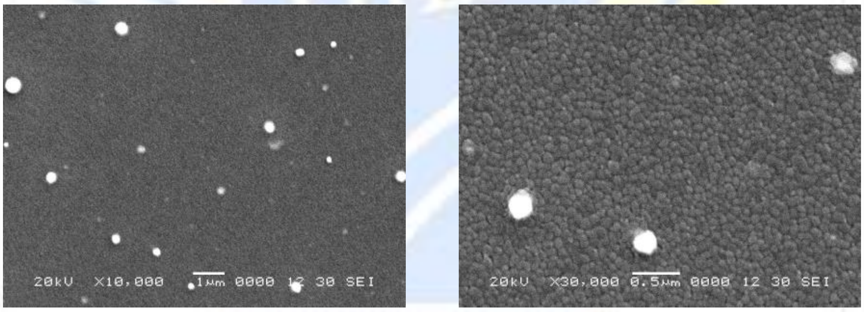


Figure 4. Plot of absorption coefficient versus energy bandgap of 4 at% Ag doped ZnO

Surface Morphology

The surface morphology of the silver doped ZnO was studied using SEM characterization. The white spots appearing in the image are attributed to the formation of silver crystals embedded in ZnO. The appearance of these crystal in Ag doped ZnO in SEM image indicates the formation of metallic silver nanoparticles. The SEM image shows that the silver crystal has a spherical shape and a uniform size distribution, with an average diameter of about 10 to 20 nm. Such type of silver embedded in ZnO may enhance the optical and electrical properties of the material. It is reported that such silver nanocrystals were helping in the increase in the conductivity of the doped ZnO material [25].



(a) (b)

Figure 5 (a) and (b) SEM images of silver doped ZnO thin film at 1µm and 0.5µm respectivaly

IV. Conclusion

Ag doped ZnO thin films of various concentrations were grown on the microscopic glass with the sol gel method. Out of them, the effect of 4at% doped ZnO thin film was investigated for structural and optical properties. The XRD spectra of undoped and 4 at% silver doped ZnO thin films on a glass substrate show the formation of wurtzite hexagonal structure and the formation of face centered cubic structure silver crystal. The large peaks of silver crystal may be due to the 4 at% dopant value of silver acetate in the solution. The UV-visible transmission spectra of Ag-doped ZnO films deposited on a microscopic glass substrate showed uniform deposition of doped ZnO at various at% doping of silver. The thickness of the samples was determined to be 489 nm. SEM characterization of silver doped ZnO revealed the formation of silver crystals embedded in ZnO, with a spherical shape and uniform size distribution. These silver nanocrystals may enhance the optical and electrical properties of the material. Further research work will be carried out to measure the impact of the Ag doping in ZnO on electrical, optical and structural properties for detailed investigation.

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