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Comparative Analysis of Cu and Ag doped ZnO: Influence of Doping Concentration and Annealing Temperature on Optical and Electrical Properties

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Abstract: ***In this work, Cu-doped and Ag-doped zinc oxide films were deposited using the sol-gel method. The impact of annealing temperature and doping concentration on optical and electrical properties were examined. It was noted that the annealing temperature has less effect on both the Cu-doped and Ag-doped zinc oxide films optical band gap energy. The minimum resistivity for Ag doped ZnO was From the study it was understood that Ag doped ZnO has lower resistivity as compared to Cu doped ZnO both at different doping concentrations and annealing temperatures.***

Keywords: Solgel method, Ag doped ZnO, Cu doped ZnO , Annealing temperature, Electrical resistivity

1. Introduction

Zinc oxide, abbreviated ZnO, is an inorganic substance possessing semiconductor properties. As an element of the II-VI semiconductor group, it is composed of the two group VI elements (oxygen) and group II elements (zinc). Given its large band gap of approximately 3.3 eV, ZnO finds use in transparent electronics, optoelectronics, and sensors. ZnO can have its electrical and optical properties changed by simply doping it with various impurities. However, as a result of intrinsic flaws like oxygen vacancies or zinc interstitials, zinc oxide usually has the n-type, indicating that it has more electrons than holes [1].

Therefore, various dopants such as trivalent (Al, Ga, In) [2-4], pentavalent (N, P, As) [5-7], or rare earth (Er, Gd) [8-9] elements have been used to achieve different types of doping in ZnO. Doping can affect the structural, optical, and magnetic properties of ZnO depending on the dopant concentration, ionic radius, electronegativity, and valence state [10].

One of the challenges in ZnO-based devices is to achieve p-type doping, which is essential for creating p-n junctions. N-type ZnO has an excess of electrons, while p-type ZnO has a deficiency of electrons. One of the methods to achieve p-type doping in ZnO is to use copper (Cu) as a dopant [11]. Cu has one less valence electron than Zn, so it can substitute Zn atoms in the ZnO lattice and create acceptor levels. The Cu-doped ZnO can be synthesized by various techniques, such as sol-gel, hydrothermal, spray pyrolysis, and sputtering [10]. The electrical and optical properties of Cu-doped ZnO depend on the Cu concentration, annealing temperature, and ambient atmosphere. Cu-doped ZnO can exhibit enhanced photoluminescence, photocatalytic activity, and gas sensing performance compared to undoped ZnO.

One way to enhance the electrical properties of ZnO is to introduce dopants, such as silver (Ag), that can create free carriers and modify the band structure. Silver (Ag) is an attractive candidate because of its high conductivity, antibacterial activity, and plasmonic properties [12]. Ag doped ZnO (Ag-ZnO) can exhibit enhanced electrical, optical, and catalytic performance compared to pure ZnO.

Therefore, it is important to optimize the synthesis conditions and characterization methods of silver-doped ZnO for achieving high-quality p-type material. In this study, doped ZnO films with different concentrations were annealed at different temperatures to study optical and electrical properties.

2. Experimental Process

The sol-gel spin coating method, which was earlier used to deposit doped and undoped ZnO, is used in this work for the deposition of Cu and Ag doped ZnO [13-14]. Since this study involves study of two different dopants in ZnO, copper acetate and silver acetate were used for synthesis of Cu doped ZnO and Ag doped ZnO respectively. The solution was prepared by dissolving zinc acetate dihydrate in 2-Methoxyethanol used as a solvent, while ethanolamine was used as a reagent with the appropriate amount of copper acetate and indium acetate for depositing Cu doped and In doped ZnO respectively. Then the solution was continuously stirred on the hot plate at 80°C for an hour, and a transparent and clear solution was obtained. The obtained solution was cooled to room temperature, followed by the deposition of films on glass substrate and silicon substrate with a homemade spin coating system for optical and electrical measurements respectively. Each time after the deposition process, films were preheated in the open air at 300°C for 10 minutes for the evaporation of organic elements present in the films. After cooling the substrate to room temperature, the next layer was deposited. Finally, samples were post-annealed at 375°C for an hour in the open air. For the investigation of the optical property, multilayered (10 coatings) films were deposited at various dopant concentrations.

Shimadzu UV spectrophotometry was used to record the transmittance spectra of the sample to study its optical properties. The optical band gap was further determined using a tauc plot. The resistivity of the samples were measured using four probe methods. The surface morphology was investigated using SEM.

3. Result and Discussion

Figure 1 depicts the graph of a square of the absorption coefficient versus photon energy for copper and silver doped ZnO films. The optical band gap energy was estimated using the linear extrapolation method from the absorption coefficient. It was noted that the optical band gaps of copper and silver doped ZnO were found to be lower than those of pure ZnO. A band gap of 3.08 eV was observed for copper-doped ZnO, whereas it was found to be 3.18 eV for silver doped ZnO. Reddy et al. found a similar type of reduction in band gap after copper doping [15].

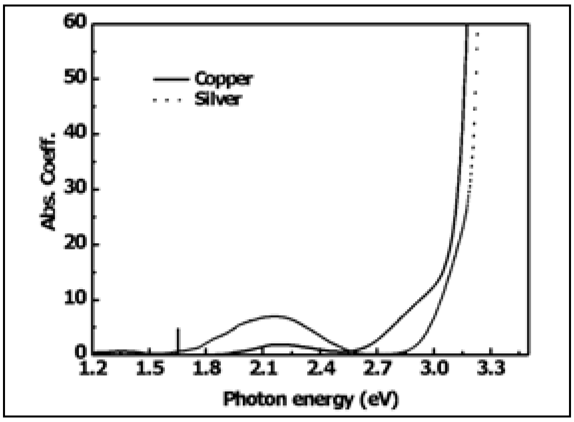

Figure 1: Absorption coefficient versus photon energy for copper and silver doped ZnO films

To study the effect of copper and silver impurities in ZnO, the resistivity of the films was calculated using the following equation:.

$$\rho = Rs \times t \quad (1)$$

Where *Rs* is sheet resistance, ρ is the resistivity, and *t* is the thickness of the film.

Figure 2 depicts the effect of dopant concentration on the resistivity of silver and copper doped ZnO films deposited on a silicon substrate. For both the dopants (silver and copper) at lower doping concentrations, resistivity was noted to be large. As the doping concentrations increased, resistivity gradually decreased and attained a minimum value of 4 at%. The minimum resistivity of ~4.5106 Ω-cm and ~1.7105 Ω-cm are measured for Cu and Ag doped ZnO, respectively, at 4 at%. The measured resistivity values are in good agreement with values reported by Wang et al. [16].

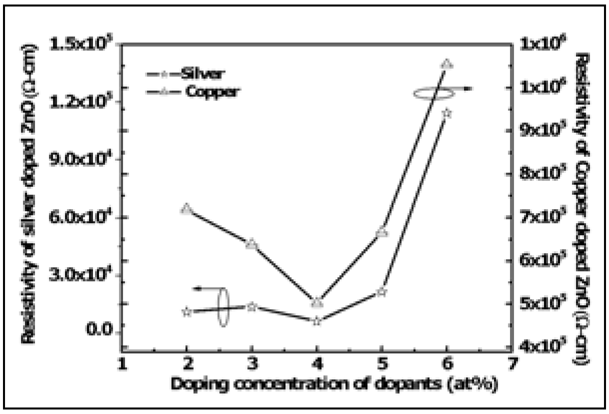

Figure 2: Effect of doping concentration on resistivity of copper and silver doped ZnO films deposited on silicon substrate

Figure 3 illustrates the effect of post annealing temperature on the resistivity of copper and silver doped ZnO films deposited on silicon substrates. Initially, a reduction in resistivity was observed when the temperature was varied from 350°C to 375°C. This may be due to the improvement in crystallinity after annealing at 375°C. Above 375°C, resistivity was found to be increased due to the scattering effect or may be due to the reduction in carrier concentration. From the results of resistivity, it has been concluded that silver doping is a better choice to achieve lower resistivity.

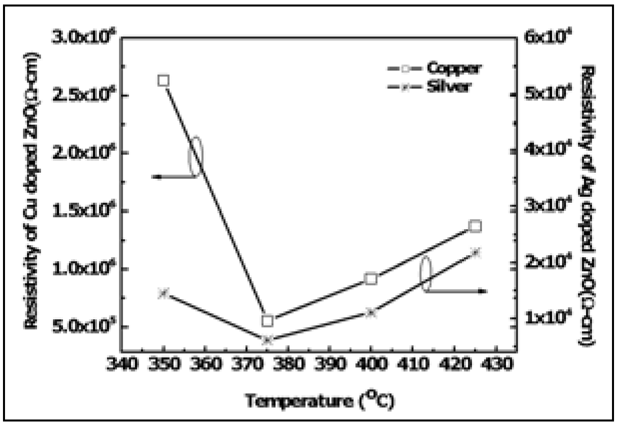

Figure 3: Effect of annealing temperature on resistivity of copper and silver doped films deposited on silicon substrate

4. Conclusion

Cu and Ag doped ZnO films are successfully deposited using a low cost sol gel technique for different molar concentration dopings and annealing temperatures. From the absorption coefficient plot, it is deduced that the optical band gap of ZnO remains approximately the same even after Cu and Ag doping. With the help of a probe method, deposited samples are successfully investigated for electrical properties. For both 4 at% Cu and Ag doped ZnO, the resistivity is found to be minimum, whereas at 375°C annealing temperature, the minimum resistivity is noted due to an improvement in the crystallinity.

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Author Profile

Vrushali Shelke received the B.Sc. in general science and M.Sc. Degree in Electronics from Sant Gadge Baba Amaravati University in 2001 and 2003. She Completed her M.Phil. and Ph.D. from North Maharashtra University, Jalgaon (INDIA). She is currently working as Assistant Professor in the Department of Electronics, Shri. Dnyaneshwar Maskuji Burungle Science and Arts College, Shegaon, Dist: Buldhana (INDIA). Her topics of research interest are optoelectronics devices and photonics devices etc.