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Opto-electrical characterization of transparent conducting sand dune shaped indium doped ZnO nanostructures

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ABSTRACT

Low resistive highly transparent indium doped ZnO films have been deposited by spin coating technique. Effect of doping concentrations and post annealing temperatures were studied by optimizing the films on the silicon and glass substrates. The sand dune shaped nanostructures were observed by atomic force microscopy and other structural properties were examined with scanning electron microscopy and X-ray diffraction. Low resistivity value of 1.27 Ω cm was achieved for film deposited on silicon substrate. Films deposited on the glass substrate showed the high transmittance above 80%. Effect of annealing temperature on band gap, figure of merit and refractive index are highlighted in the study.

1. Introduction

Transparent conducting oxide (TCO) exhibits both the properties of optical transparency in the visible region as well as electrical conductivity. This simultaneous combination is effectively used in the most of optoelectronics applications. Various types of transparent conducting oxides are used in industry. Among all these ZnO is emerging material. Its physical properties like stability, non toxic nature, low cost and availability in abundant makes it suitable and attractive material in the field of TCO. It served as the best alternative to tin doped indium oxide (ITO) [1]. Besides this, its direct band gap of 3.2 eV [2] is promising for short wavelength applications and large exciton binding energy of ~60 meV ensures exciton emission even at room temperature [3].

When ZnO is doped with various elements, it proves its utility in different application areas e.g. Li doped ZnO shows ferroelectric behavior [4] and Cu doping modifies the ferromagnetism [5]. When ZnO is doped with ions such as Al^{3+} or In^{3+}, it becomes a highly transparent and electrically conducting n type semiconductor [6]. Doped ZnO can be deposited with different deposited techniques like Sol–gel process [7], sputtering [8], chemical vapor deposition [9], atomic layer deposition [10], pulsed laser deposition (PLD) [11] etc. Among all these methods sol gel is effective and low cost deposition technique.

Present work describes the role of indium doping concentration and the post annealing temperature variation on the structural, electrical and optical properties of sand dune shaped indium doped ZnO nanostructures. The growth of nanocrystalline, highly transparent and electrically conducting films optimized in open air annealing were discussed in detail.

2. Experimental process

Transparent conducting indium doped zinc oxide films were deposited using spin coating method. Transparent solution was obtained by dissolving zinc acetate dihydrate and indium acetate in 2-methoxyethanol simultaneously few drops of ethanolamine were added in the solution. It helps to increase the rate of reaction and to maintain the stability of the solution. Solution was continuously stirred on the hot plate at 80 °C. After an hour, transparent and clear solution was obtained. Acquired solution was deposited on microscopic glass and silicon substrate with homemade spin coater system. Deposited films were preheated in open air at 300 °C for 10 min. This preheating is necessary for evaporation of organic elements present in the films. To enhance the conductivity, next coat was deposited on the film after cooling the substrate to room temperature. Finally, samples were post annealed in open air. To study the doping concentration effect, the post annealing temperature was kept constant at 375 °C for an hour and indium concentration were varied. To study temperature effect, post annealing temperature was varied from 350 °C to 425 °C while indium concentration of 6 at.% was kept same for all the samples.

The chemical reactions for the formation of ZnO in this process were

$$Zn(Ac)_2 \cdot 2H_2O \rightarrow Zn(Ac)_2 + 2H_2O,$$

$$Zn(Ac)_2 + 2OR\text{-}OH \rightarrow Zn(OR)_2 + 2Ac\text{-}OH,$$

$$Zn(OR)_2 + 2H_2O \rightarrow Zn(OH)_2 + 2R\text{-}OH,$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O.$$

Deposited sample were characterized to study various properties. Transmittance spectra were recorded by Shimadzu UV spectrophotometer. Refractive index was measured by using ellipsometry Philips SD 1000 at 632.8 nm wavelengths

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Sheet resistance was estimated with *I–V* Keithley instrument equipped with Signatone 1160 series probe station. Structural properties were investigated by XRD and spectrum was recorded using Bruker AXS-D8 X-ray diffractometer. Surface morphology was investigated with JEOL scanning electron microscopy. NT-MDT Solver Pro atomic force microscopy system was utilized for the characterization of the sand dune shaped nanostructures.

3. Results and discussion

Resistivity variation of indium doped ZnO films as function of indium doping concentration is elucidated in Fig. 1a. It shows the results of films deposited on silicon and glass substrate. The resistivity of the films was calculated by using the following equation:

$$\rho = R_s \times t, \quad (1)$$

where R_s is sheet resistance, t is the thickness and ρ is the resistivity of the films. Sheet resistance was measured by current–voltage Keithley instrument equipped with Signatone probe station. For both the substrates, the resistivity was observed to be decreased with corresponding increase in indium doping concentration and minimum value of resistivity was achieved for 6 at.%. Initially, with an increase in indium doping concentration, more and more free carriers were available for conduction mechanism. Indium atoms might occupy Zn-sites substitutionally, because of the similarity of the radius of zinc (0.74 Å) and indium (0.81 Å) and this results in an enhanced concentration of free carriers, which results in reduction of resistivity [12]. Minimum resistivity of 1.27 Ω cm was obtained for the film deposited on the silicon substrate while for glass substrate it was deduced to be 13.19 Ω cm. Resistivity was noted to be increased above 6 at.%. This may be due to solubility limits of indium that leads to segregate the dopants and further act as traps for carriers [13].

As discussed above, minimum resistivity for indium doped ZnO film was obtained for 6 at.%. Effect of annealing temperature was studied by annealing the films at different temperature in open air by keeping doping concentration of 6 at.%. Resistivity of films is greatly influenced by thickness of film, deposition techniques, annealing temperature and annealing environment like vacuum annealing, nitrogen, hydrogen, oxygen, air, etc. In the present work, annealing is carried out in open air which leads to adsorptions of oxygen on the surface of film. These adsorbed oxygen act as trap center for the electrons in the grains and thus affects the resistivity [14]. Fig. 1b shows effect of annealing temperature on the films deposited on silicon and glass substrates. It was observed that for both the substrates, with an increase in annealing temperature, resistivity was tending to be reduced and attend minimum resistivity at 375 °C.

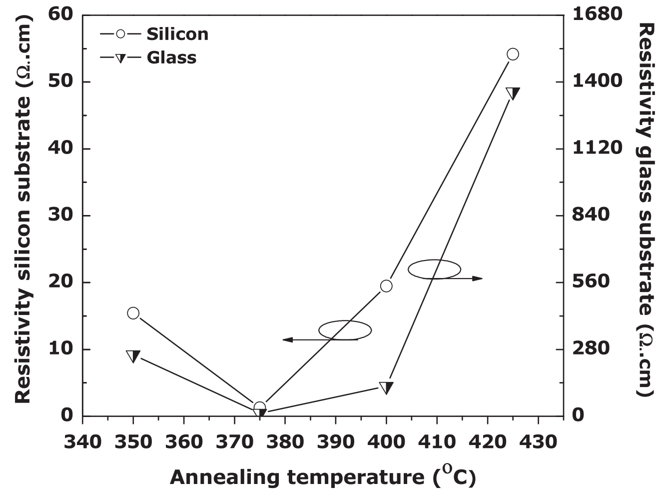

Fig. 1b. Effect of annealing temperature on the resistivity of indium doped ZnO films.

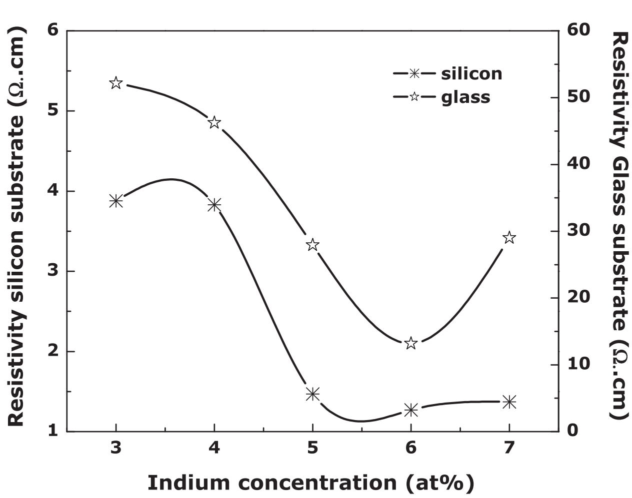

Fig. 1a. Effect of indium doping concentration on the resistivity of indium doped ZnO films annealed at 375 °C.

Atomic force microscopy 3D image of indium doped ZnO nanostructures deposited on silicon substrate and post annealed at 375 °C are depicted in Fig. 2. NT-MDT Solver Pro atomic force microscopy system was utilized for the characterization. Scanning was carried out in semi-contact mode with 1 μm × 1 μm area. The film surface is almost flat and no sharp peaks were observed. 3D image indicates sand dune type nanostructures with almost uniform height.

Fig. 3 illustrates the scanning electron microscopy image of indium doped ZnO film deposited on silicon substrates for 6 at.% and annealed at 375 °C. Image of the film was recorded by keeping scale of 1 μm with a magnification of 10,000×. Homogeneous worm like uniform morphology was observed for the films deposited on silicon substrates.

We performed X-ray diffraction (XRD) measurement. Fig. 4 showed the XRD patterns of indium doped ZnO films deposited on glass substrate and annealed at different temperatures. Blurred diffraction peak was observed for the film annealed at 350 °C. As the annealing temperature was increased above 350 °C, the diffraction peaks (100), (002) and (101) were observed clearly, which reveal polycrystalline nature of ZnO hexagonal structure [15]. Moreover, with an increase in annealing temperature, the diffraction peak (100) position was shifted to the lower diffraction angle

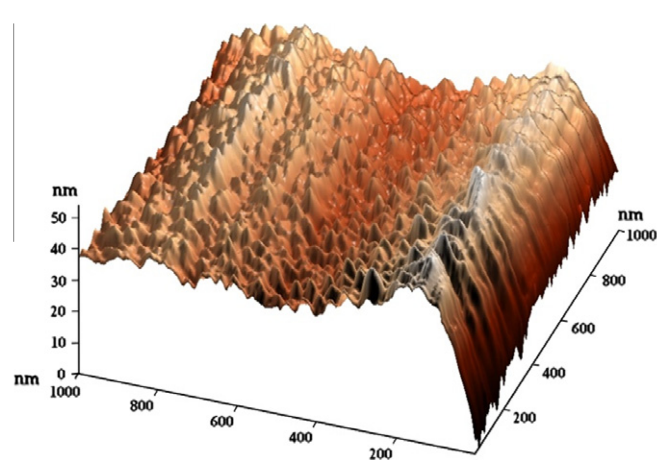

Fig. 2. AFM micrograph of indium doped ZnO films annealed at 375 °C.