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ORIGINAL ARTICLE

Characteristics of Al-doped ZnO:Ni films grown on glass by sol–gel dip coating technique

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Abstract Al-doped NiZnO thin films were fabricated by dip coating and annealed at various temperatures (250–550 °C) and their properties were evaluated. With increasing annealing temperature, the Al contents in the thin films were continually increased, because of the rapid increase in the incorporation efficiency of the Al–O layer with respect to the NiZn–O layer. Polycrystalline nature of the thin films was confirmed by the X-ray diffraction technique. All films have a perfect wurtzite structure without any recordable variation in the ZnO lattice produced by replacing Zn with Ni and Al. The absorption edge shifted to a higher wavelength (red shift) with the increase of annealing temperature indicating that the shrinkage of the optical band gap was induced. The optical band gaps of thin films decreased from 3.5 to 2.5 eV. All films showed ferromagnetic behavior. The annealing process provided a reduced resistivity due to the improved crystal structure of films.

1. Introduction

ZnO with a large band gap is considered as an important semiconductor material, showing room temperature ferromagnetic properties when doped with 3d transition metal ions such as Ni, Co, or Mn [1–3]. ZnO:Ni films co-doped with Al are important functional materials for optoelectronic and magneto-electronic applications. ZnO:Ni films have been widely investigated by many research groups [1,4–6] because they have potential applications in a variety of Opto-electronic devices such as solar cells, memory devices and sensors. A large number of studies focused on the structure, magnetism and transmittance of visible light of the ZnO:Ni films. A few researchers studied Al doped ZnO:Ni films in order to improve the conductive stability of the films [7–9].

ZnO was usually prepared by pulse laser deposition [10], radio frequency magnetron sputtering [11] and molecular beam epitaxy [12]. These techniques required complicated, high temperature deposition, and costly vacuum systems for fabrication. While, the solution growth method was an easy, low temperature and inexpensive that could produce high quality ZnO materials [13–15]. This paper reported the structural, electrical and optical properties of Al-doped ZnO:Ni films using a sol–gel technique.

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2. Experimental details

Zinc acetate di-hydrate and nickel acetate tetra hydrate were used as precursor materials and aluminum nitrate nano-hydrate was used as the doping material. At start 5 ml of diethyl amine was added to 46 ml of propanol and stirred at 80 °C for 1 h until a transparent solution was obtained. After that, 5.35 g zinc acetate di-hydrate was introduced into the solution and magnetically stirred at 80 °C for 1 h then it was cooled to room temperature. Afterward 0.468 g aluminum nitrate nano-hydrate was totally mixed into combined solution. After that 6.1 g nickel acetate tetra hydrate was fully dissolved in the prepared solution and then stirred for 1 h at 100 °C and afterward 45 ml ethanol was added to a mixed solution of zinc acetate dehydrate and nickel acetate tetra hydrate and then stirred for 2 h at 700 rpm at 100 °C and left for aging for 2 days. This sol was deposited on a pre cleaned soda lime glass substrate at a constant withdrawal speed of 250 mm/s. An average of five layers was required for each film with 100–150 nm thickness. Then these films were air dried after deposition and heated and dried at 100 °C in an oven for 15 min. For phase formation, thin films were annealed at 250, 400, 450, 500 and 550 °C for two hours at ambient conditions. Structural, optical, magnetic, electrical and surface properties of annealed thin films were studied.

Thermal analysis of the dried gels was examined by a thermo gravimetry–differential thermal analyzer (TGA–DSC; SDT Q600) heating from 27 to 1000 °C ramp at 10 °C/min. The Fourier transform infrared (FTIR) transmittance measurements were performed with a Model M 2000 Midac USA spectrophotometer in the spectral range from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. Crystallinity of Al doped MnZnO films was characterized by X-ray diffractometer (Rigaku Dmax-III A, Geiger flux instrument, Cu Kα = 1.54056 Å). The optical transmission spectra were recorded with a UV/VIS/NIR spectrophotometer (Hitachi U-2800) ranging from 200 to 900 nm in wavelength. Surface morphologies of the films were observed by field emission scanning electron microscope (SEM, S-3400N, Hitachi). Magnetic properties were measured by using Vibrating Sample magnetometer VSM (Lakeshore) 7407.

3. Results and discussion

3.1. FTIR

FTIR stands for Fourier transform infrared spectroscopy that uses the Infrared radiation to identify chemical bond in materials. To analyze the materials by FTIR, KBr pellets were prepared and then distinguished by infrared spectroscopy at 400–2000 cm^{-1} wavelength range. In FTIR, beam of light was passed through the sample, some part of the radiation was absorbed through sample and other part of the radiation was transmitted by the sample. To confirm the formation of Al doped NiZnO, FTIR spectroscopy was done and FTIR spectrum is shown in Fig. 1.

One principle dip was observed at 571 cm^{-1} which was due to the insertion of Al in ZnO lattice [16]. When precursor solution was condensed, hydrolysis and condensation or polycondensation took place. So, the stretching modes of Al and its linkages with ZnO were observed [17]. The absorption dip at

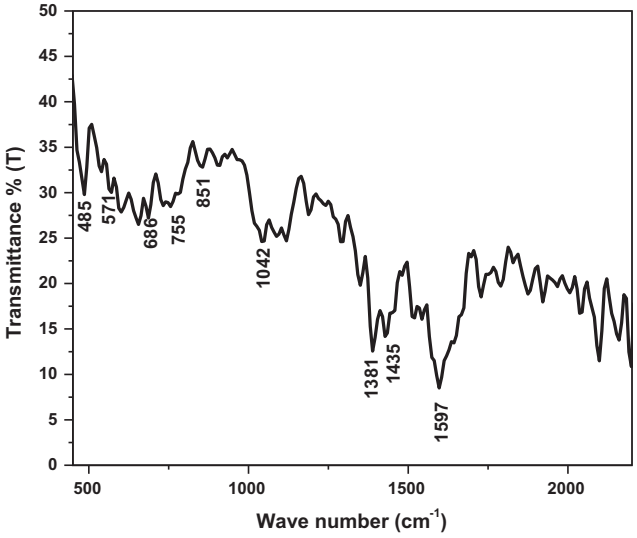

Figure 1 FTIR of Al doped NiZnO.

485 cm^{-1} was corresponding to the stretching mode of ZnO. The two dips were recorded by Wang et.al. [18] in the range 1600–1350 cm^{-1}, which acted as a fingerprint of the acetate anion group in the zinc acetate. Appearance of a sharp dip at 1597 cm^{-1} was attributed due to the OH- vibrational mode. These FTIR spectral results confirmed that the bonding force of acetate anion with zinc cations reduced with phase transformation (zinc acetate to ZnO), and OH- groups gradually replaced acetate groups and the acetate groups were removed completely forming $Zn(OH)_2$ and finally ZnO could be formed with the release of acetate anion. This formation of ZnO clearly indicated that sol–gel synthesis was complete. The bands at 1381 and 1435 cm^{-1} were assigned to the C–O and the C═O stretching modes. The dips at 686, 755 and 1042 cm^{-1} illustrated Ni occupation with ZnO [19]. FTIR confirmed that acetate cation of nickel acetate was completely removed binding nickel ion with ZnO [20].

3.2. Thermal analysis

The thermal decomposition of metal acetates and nitrates dissolved in propanol with diethanolamine (DEA) was shown in the TGA/DSC (Fig. 2) traces led toward the synthesis of pure Al doped NiZnO. It could be seen that the decomposition process consisted of three stages. In the first stage weight loss took place between 30 and 260 °C. In this stage water and organics got evaporated as well as removal of acetate groups took place [21]. In the 2nd stage there was a sharp fall in weight between 260 and 292 °C. This abrupt weight loss was due to the formation of Al doped NiZnO from its hydro-oxide and removal of diethyl amine [21]. The 3rd stage of weight loss took place between 292 and 786 °C gradually. It was due to the nucleation and crystal growth of Al doped NiZnO films. Two exothermic peaks were observed at 298 and 816 °C while one endothermic peak was observed at 774 °C. The appearance of exothermic peak at 298 °C showed evaporation of organics while other exothermic and endothermic peaks predicted crystallization of the material.