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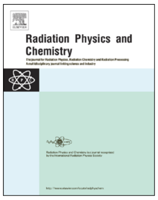

The improvement in the electrical properties of nanospherical ZnO:Al thin film exposed to irradiation using a Co-60 radioisotope

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HIGHLIGHTS

- Gamma radiation affected the nanospherical structure of film depending on the cumulative dose.
- Resistivity, carrier density and carrier mobility were improved by Co-60 radioisotope.
- There is a relation between improvement of electrical and optical properties of irradiated film.

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ABSTRACT

Al doped ZnO (ZnO:Al) thin films were prepared using a sol–gel dip coating technique and deposited on borosilicate glass substrates. The irradiation treatment, was conducted using Co-60 radioisotope, played an important role in enhancing electrical properties. The absorbed dose was a key parameter to decrease the electrical resistivity and to increase carrier density and carrier mobility of nanospherical ZnO:Al thin film. ZnO:Al thin film with the doping of Al at 0.8 at% had the lowest electrical resistivity and the highest optical transmittance after the irradiation treatment. Optical properties, such as transmittance and reflectance, were affected at an absorbed dose of 0.2 Gy. The curves of optical density were improved at ~380, 420, and 520 nm in visible range after the irradiation process. Besides, another characteristic optical density band between~900 and 1100 nm was enhanced by gamma irradiation. It has been suggested that the mechanism of absorption is related to an allowed direct transition at the irradiated ZnO:Al thin film on borosilicate glass. The optical band gap of the ZnO:Al thin films broadened with increasing doping concentration. However, there is a decrease in optical energy gap of ZnO:Al thin film along with the absorbed dose of the film.

1. Introduction

The researches of transparent conducting films have focused on the optical thin films. ZnO thin films have been used in many applications due to their advantages, such as cost effectiveness and non-toxicity (Gordillo and Calderon, 2001; Nunes et al., 2000; Hyun et al., 1996; Young-Sung Kim and Weon-Pil Tai, 2007). The doping process greatly influences the electronic and optical properties of ZnO. The fact that doped ZnO thin films have great potential for various applications such as transparent conducting electrodes makes them important in technological aspect. For the high conductivity and good optical transmittance, Al doped ZnO (ZnO:Al) films have drawn considerable attention in terms of transparent conducting electrodes (Hiramatsu et al., 1998). They are suitable for fabrication of transparent electrode of solar cells (Xue et al., 2006; Nunes et al., 2000). Transparent and conductive materials are broadly used in the terrestrial and the space applications. The ionising radiation is available especially as gamma radiation, and determination of its effect is important for the efficient usage of devices on terrestrial or space missions. Devices consisting of thin films are exposed to ionising radiation, as the cumulative dose, during their missions. Thus the changes that occur in structural properties, electrical properties, and optical behaviour, such as transmittance and reflectance, with the absorbed dose are important. The results of radiation damage in transparent materials are classified in three categories: atomic displacement by momentum and energy transfer; ionisation and charge trapping; and radiolytic or photochemical effects. These effects are associated with the energy of radiation, as well as the total dose (Badhwar et al., 1995). Trapping an electron in transition elements of optical materials prevents discoloration. These electrons contribute to new induced colours with irradiation. The ionising radiation creates bound electron–hole pairs (excitons).

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Exposure to ionising radiation results in atomic displacements or broken bonds by radiolytic or knock-on displacements (Uhlman and Kreidl, 1991; Vogel, 1994; Bishay and Maklad, 1966; Speit et al., 1992). Defect centres are formed in the transparent materials as a result of charge trapping by radiolytic electrons or holes at the end of the irradiation process. Out of the essential processes occurring during the irradiation of the samples is the formation of electron–hole pairs. The photoelectrons are trapped at structural defects or impurities such as oxygen vacancies and multivalent impurities once these free carriers move and recombine, and the holes are also self-trapped at bridging or non-bridging oxygen. These new electronic configurations affect the structural, optical, and electrical properties of the film (Baydogan and Tugrul, 2006; Zayim and Baydogan, 2006; Da Costa et al., 2006). When ZnO:Al nanocrystalline texture is subjected to several types of radiation, direct and indirect ionising radiation affects the physical properties of the nanospherical ZnO:Al structure depending on the cumulative dose (Bishay and Maklad, 1966). However, the improvement of electrical properties such as resistivity, carrier density, and carrier mobility of ZnO:Al thin films using a Co-60 radioisotope in sensor systems and electronic devices have not been reported, yet. In this respect, the purpose of this study is to examine the changes in electrical, structural, and optical properties of ZnO:Al thin film after gamma irradiation of nanocrystalline film.

2. Experiments

The thickness of the films was measured using a surface prophilometer. The final thickness of the films was within the range of 250 nm for all the samples characterised in this study. The resistivity of the ZnO:Al thin film was measured using a four point probe. *After the film thickness is measured, the electrical resistivity of the ZnO:Al thin film is determined in ohm.cm.* The AFM images were obtained using a MPP-11100 High-Resolution Tapping Mode silicon probe (tip radius < 10 nm, cantilever length 125 μ, resonance freq. 300 kHz) operated in tapping mode by 1 Hz scan rate. An X-Ray diffractometer with a Cu K_α radiation with a wavelength of 1.54 Å was used in the present study. A continuous scan mode was used to collect $2(\theta)$ data from 20° to 80°. Diffraction patterns were collected at a scan rate of 0.01° 2θ/min and a step size of 0.01°. Possible misidentification of the peak was accepted as 0.01°. Spectrophotometric measurements were performed using a double beam spectrophotometer with a 0.5% T-transmittance (0~100%T) photometric accuracy. Therefore, the estimated uncertainty is acceptable to evaluate the significance of the changes observed in optical characterisation and XRD analysis.

2.1. *Sol–gel process data*

After being cleaned with detergent and flushed with copious amounts of de-ionised water, the borosilicate glass substrates were consecutively rinsed with acetone, methanol, isopropyl alcohol, and dried in air.

The starting material was Zinc acetate dehydrate $Zn(CH_3COO)_2 \cdot H_2O$ (extra pure). Diethanolamin (DEA–$C_4H_{11}NO_2$) and absolute ethanol (C_2H_5OH–purity, 96%) were stabiliser and solvent, respectively. The dopant source of aluminium was Aluminumnitrat-Nanohydrat ($Al(NO_3)_3 \cdot 9\,H_2O$) (Merck). Once dissolved in ethanol, Diethanolamin and the dopant was added at 60 °C, Zincacetat-dihydrat was mixed thoroughly using a magnetic stirrer (Heidolph MR 3001 K) for 1 h at 60 °C in order to obtain a clear and homogeneous mixture. The molar ratio of DEA to Zincacetat-dihydrat was maintained at 1.0 M, and the concentration of Zincacetat-dihydrat was 0.5 M. The molar ratio of dopant [Al/Zn] in the solution was prepared for four different dopant levels; 0.8, 1.0, 1.2, and 1.6 at%. The solution was mixed up to room temperature. It was observed that the prepared sol showed high sensitivity for humidity, and the humidity ratio was achieved at 43% in preparation of the solution. The humidity level was controlled using a dehumidifier to maintain the solution quality during preparation of the solution, and the dip coating process in the laboratory.

ZnO:Al thin films were deposited by dip coating the stock solution on borosilicate substrates. Computer-controlled KSVLMX2 Dip Coater equipment was utilised during this process. Borosilicate glass substrates were dipped into the emulsion at a speed of 50 mm/min, and pulled off with the same speed.

The pre-heat treatment was performed in a furnace, under oxygen, at 500 °C for 10 min. The procedure from coating to drying was repeated five times. The post-heat treatment process was carried out at 700 °C under vacuum for 1 h. The pressure of the vacuum ambient was 0.003 mbar. The purpose of the pre-heat treatment, conducted to enhance crystal growth, was to increase the concentration of oxygen vacancy, and conductivity of the films. For all ZnO:Al thin films the annealing process was performed at four different Al doping levels; ranging from 0.8 at% to 1.6 at%.

2.2. *Irradiation process data*

A Co-60 radioisotope was used as an appropriate irradiation source for the optical structures with high energy gamma photons to irradiate ZnO:Al (Baydogan et al., 2007; Baydogan and Tugrul, 2006). Table 1 illustrates the properties of a Co-60 radioisotope. The cumulative dose of the material is an important parameter for the absorbed dose of irradiated material during its mission. The thin film sample was placed panaromicaly around the irradiation source and the surface of the thin film was subject to gamma rays. The absorbed dose of ZnO:Al was 0.2 Gy. The cumulative dose is the total dose resulting from the repeated exposures of ionising radiation to the same portion for a period of time. In either terrestrial or space applications, a material is exposed to uniform or non-uniform radiation fields. Radiation fields vary as per geometry or time. The use of a Co-60 radioisotope with the activity level of 0.018021 Ci was preferred to control the absorbed dose and determine the changes in optical and electrical properties at ZnO:Al nanostructure sensitively.

Placed around the source, the samples were irradiated at the same distance. Therefore, the same absorbed dose was performed under identical irradiation conditions. All irradiation tests were conducted at room temperature.

2.3. *Characterisation*

The characteristics of optical density bands are explained as of the cause of colour due to sunlight absorption at the colour centres of transition elements (Baydogan et al., 2007). Hence the determination of the transition elements in borosilicate glass is required as the substrate of ZnO:Al thin film. The transition elements on borosilicate glass substrate were examined using XRF technique and the chemical composition is presented in Table 2.

Table 1
The properties of Co-60 radioisotope.

Radioisotope	K_γ (Rm^2/Ci h)	A (Ci)	$T_{1/2}$ (y)	E_γ (MeV)	Abundance (%)	Production mode
Co-60	1.32	0.018021	5.27	1.17 1.33	99.90 99.98	Co-59(n,γ)