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Decomposition mechanism of indium oxide nanoparticles sandwiched between zinc oxide layers by energetic ions

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Abstract

Decomposition of indium oxide nanoparticles (IONPs) sandwiched between zinc oxide (ZnO) thin films by energetic ions is reported. Multilayers thin films were deposited using RF magnetron sputtering at room temperature, consisting two thin indium oxide layers sandwiched between three ZnO layers. Films exhibit very high transparency in the visible region. A sharp near band edge absorption with exciton absorption peak in the film annealed at the highest temperature was also observed. The structural and optical properties reveal that the as-deposited films show the formation of IONPs around the interface, which further grow upon increasing in annealing temperature. However, irradiation induces the decomposition of IONPs for the possible formation of single phase indium doped ZnO (IZO). The mechanism of the decomposition of IONPs is understood by the creation of ion tracks in IO. The track radius (R_e) of 5.9 nm is calculated in the framework of thermal spike model. Therefore, the IONPs with diameter $\leq 2R_e$ decomposed or amorphized between the crystalline ZnO layers; while the IONPs with diameter $> 2R_e$ show reduction in size by the electronic sputtering from the IONPs surface under the thermo-elastic effects.

Keywords: Indium oxide nanoparticles (IONPs); Energetic ions; Thermal spike model; Thermo-elastic effects

1. Introduction

In recent years, the exploration of Transparent Conducting Oxides (TCOs) is an active area of research due to their multifunctional uses for the development of various optoelectronic device applications; such as solar cells, flat panel displays, transparent electrodes, diodes, etc. [1–4]. The important properties of TCO materials like transparency and conductivity are heavily dependent on crystalline phase and lattice defects. The composition of thin multilayers or superlattices can even affects the thermal (Kaptiza) resistance of interface [5], which can be controlled by the thermal annealing in controlled environment or by energetic ion irradiation [6–9]. It may be noted that the energetic ion irradiation induced defects in similar oxides has been used for better understanding of the evolution of Raman phonon modes and even semiconductor to metal transition as reported in our previous works [10–13]. Thus, the modifications in multilayer systems are liable to develop nanocomposite materials with superior properties. The most of the nanocomposite films show the characteristic of formation of metal oxide phases and metallic clusters by the treatment of thermal annealing, which affect the physical properties of the system. In such cases, the main issue is to dissolve these secondary metal or metal oxide nanoparticles (NPs) completely in the host system and to substitute them as metal cations at the proper metal site, as required for the development of spintronic devices and/or to enhance the conductivity of the host metal oxides. Generally, the decomposition of such NPs is difficult to achieve by thermal annealing [14]. However, energetic ion irradiations have proven to be as an unique tool to dissolve the NPs inside the host matrices to develop the single phase material [9].

Role of energetic ion irradiation in various undoped, doped, bilayer and/or multilayer thin system has been reported to

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modify or control the structural, optical, and electrical properties by depositing large electronic energy via inelastic collisions [12,13,15–17]. The deposited energy is confined to a nano-cylinder along the ion trajectory. These high densities of electronic excitation in target materials are liable to perturb the atomic structure and induced various modifications such as damage creation at high electronic excitation [18–21] and track formation/sputtering [22–24]. Energetic ions can also enable mixing of bilayer or multilayer thin films around the interface by the inter-diffusion of elements across at the interface/s [25]. It is reported that the mixing of metal–semiconductor and metal–metal multilayer system increases with the increase in irradiation fluence and electronic energy loss value [26,27]. The mixing of ZnO/SiO_2 at the interface has also been reported due to inter-diffusion during transient melt phase [28]. So, the energetic ions have been proven to be as an effective tool to the decomposition of NPs for the development of stable single phase materials.

Therefore, the present study reports the experimental results on the effect of energetic ions on RF magnetron sputtering deposited multi-layer metal-oxide ($ZnO/In_2O_3/ZnO/In_2O_3/ZnO$) thin films which induces interface mixing through the decomposition of indium oxide (IO) NPs inside the ZnO thin films. The size dependence of the decomposition of IONPs with respect to the track size and their effect on the structural and optical properties are investigated under the framework of thermal spike and thermo-elastic models [20,21].

2. Experimental details

Multi-layers thin films of thickness around 350 nm consists of two thin indium oxide layers of thickness around 20 nm sandwiched between three zinc oxide layers ($ZnO/In_2O_3/ZnO/In_2O_3/ZnO$) of thickness around 100 nm were deposited using RF magnetron sputtering at room temperature. The substrates were cleaned in acetone then rinsed by hydrofluoric acid and deionized water followed by drying in nitrogen gas before loading into the deposition chamber. ZnO target with 99.99% purity and a commercially available metallic indium target of 50 mm diameter from Semi Wafer Inc., Taiwan were used as sputtering targets. The chamber was evacuated down to a base pressure of 5.5×10^{-5} mbar before introducing the gas into the chamber. Both the ZnO and In_2O_3 layers were deposited in the presence of oxygen and argon gas environment. The mixture of $Ar+O_2$ gas was kept at a constant flow of standard cubic centimeter per minute (sccm) or ratio (70%+30%), respectively using the MKS mass flow meters. During the deposition, base pressure was maintained at 50 mTorr, RF power was fixed at 150 W, substrates were at room temperature and the distance between target to substrate was kept at 5.5 cm.

Post annealing of the samples were carried out using Nabertherm (GERO) tubular furnace with alumina tube at different temperature ranging from 500 °C to 850 °C in oxygen ambient for time 1 h for improving the stoichiometry and crystalline nature of the films. The oxygen gas flow was maintained as one bubble per second and the ramp rate of temperature rise was kept at 3 °C/min. As-deposited, 500 °C and 850 °C annealed films were irradiated by 120 MeV Ag ions for fluence of 3×10^{13} ions/cm^2 using the 15 UD Pelletron Accelerator available at Inter University Accelerator Centre (IUAC), New Delhi. The structure of the films is investigated by Grazing Incidence X-ray Diffraction (GIXRD) measurements, carried out using Bruker D8 advanced diffractometer equipped with Copper anode with scan speed of 0.5° per minute and with step size of 0.02°. The elemental composition, thickness and the interfacial diffusion behavior of indium atoms in ZnO layers of as-deposited, annealed and irradiated samples were studied by Rutherford Backscattering Spectrometry (RBS) measurement using 2 MeV He^+ ions at scattering angle of 170°. The samples were tilted by 7° to avoid the channeling of He^+ ions during the backscattering measurement and the analysis of the RBS data is performed using the RUMP simulation code [29]. Field Emission Scanning Electron Microscopy (FE-SEM) along with Energy Dispersive X-ray (EDX) analysis was also carried out using MIRA\\TESCAN FE-SEM system. The UV–visible studies on films were carried out using Hitachi UV3300 double beam spectrophotometer. All the measurements were performed at room temperature (RT) using facilities at IUAC, New Delhi.

3. Results

GIXRD patterns of as-deposited and annealed multilayer thin films are shown in Fig. 1(a) and the schematic of the same is shown in Fig. 1(b). The diffraction peaks corresponding to (100), (002) and (101) planes in GI-XRD patterns indicate that the films posses polycrystalline nature with hexagonal wurtzite crystal structure of ZnO [JCPDS 79-0206]. The intensity of (002) diffraction peak is relatively more intense as compared to (100) peak, indicates a texturing along the *c*-axis perpendicular to the substrate surface. A broad peak observed at $2\theta = 30.498°$ is assigned to the (222) diffraction peak of IONPs [JCPDS 74-1990]. The (222) diffraction peak of IONPs and (002) diffraction peak of ZnO get pronounced with increase in annealing temperature. The average crystallite size of both ZnO and IONPs are calculated by using the Scherrer's formula [30,31].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where D is the average size, λ is the wavelength (1.5404 Å) of Cu Kα line, θ is the Bragg angle and β is full width at half maximum (FWHM) in radians of (002) and (222) diffraction peaks of ZnO and IONPS, respectively. The calculated average size of ZnO and IONPs are cited in Table 1. It is clearly evident from this table that the average size is growing with increase in annealing temperature. The diffraction peak position of ZnO corresponding to (002) and (101) are shifting towards the higher 2θ value and attain a value equivalent to the stress free ZnO at 500 °C and get more pronounced when the films were annealed at 850 °C. The annealing at 850 °C, induces a shift towards higher 2θ value with large increase in the size. Similar results are observed for (222) peak of IONPs, which also shifts to higher 2θ value of 30.69° from their bulk position (30.57°). The observation reveals that as-deposited films may not be highly