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Role of carrier concentration in swift heavy ion irradiation induced surface modifications

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ABSTRACT

Highly conducting SnO_2 thin films were prepared by chemical spray pyrolysis technique. One set of as-deposited films were annealed in air for 2 h at 850 °C. These as-deposited and annealed SnO_2 thin films were irradiated using gold ions with energy of 120 MeV at different fluences ranging from 1×10^{11} to 3×10^{13} ions/cm^2. Electrical measurement shows that as-deposited SnO_2 films are in conducting state with $n = 3.164 \times 10^{20}$ cm^{-3} and annealed SnO_2 films are in insulating state. The amorphized latent tracks are created only above a certain threshold value of S_e, which directly depends on the free electron concentration (n). The electronic energy loss (S_e) of 120 MeV Au^{9+} ions in SnO_2 is greater than the threshold energy loss (S_{eth}) required for the latent track/molten zone formation in annealed SnO_2 thin film, but is less than S_{eth} required for as-deposited SnO_2 film. Therefore, the latent tracks/molten zones are formed in the annealed SnO_2 film and not in the as-deposited SnO_2 film. Thermal spike model is used for the calculation of threshold energy loss and radius of melted zone. The possible mechanism of the structural changes and surface microstructure evolutions is briefly discussed in the light of ion's energy relaxation processes and target's conductivity. The atomic force microscopy (AFM) study of films shows that the morphologies of irradiated films are linked with carrier concentration of target materials.

1. Introduction

Ion beams can be used in a variety of different ways to synthesize and modify materials on the nanometer scale. By adjusting ion species, ion energy, ion fluence and irradiation geometry it is possible to tailor the ion irradiation conditions for specific needs. In ion beam irradiation process, the kinetic energy of incident ions is transferred to atomic/lattice and electronic systems of solids through elastic collision and electronic excitation/ionization, respectively. The transferred energy to the lattice system induces atomic displacements directly. In the electronic excitation/ionization process, on the other hand, atomic displacements can be caused as a result of indirect energy transfer from irradiating ions [1]. For ions at a higher energy (~ 100 keV/amu), the energy (a few keV/Å) is mainly deposited via electronic excitation and ionization processes [2,3]. In most insulators, when the highly localized energy deposited on target electrons is transferred from the electrons to the target lattice, an extended damage is induced along the ion path: the so-called latent track [3,4]. In metals, however, atomic displacements through the electronic excitation/ionization had been considered to hardly occur because of rapid energy dissipation by a large number of free electrons [4]. In the last two decades, nevertheless, atomic displacements induced by high-density electronic excitation have been found even in pure metallic targets [5,6]. The question of the transformation of the energy deposited by the incident ion during the slowing-down process into energy stored in the target as lattice defects is still to be answered. Two mechanisms have been proposed: (i) The thermal spike (TS) model in which the kinetic energy of target electrons excited by incident ions is transferred to the lattice system through electron-lattice interaction after rapid energy diffusion in the electronic system [7–28]. (ii) The Coulomb explosion (CE) model in which the electrostatic energy of the space charge created just after the ion passage is converted into coherent radial atomic movements leading to a cylindrical shock wave [29]. Both mechanisms are sensitive to the deposited energy density as well as to the rate of energy loss (dE/dx). The TS model of latent track formation is a well established approach that has been successfully applied to insulators, semiconductors, metals, intermetallic compounds and polymers [7–28]. Because of the complexity of all energy relaxation processes involved, this model is also subjected to criticism. However, the TS model seems to be the most elaborated one; furthermore, to our knowledge, currently it is the only model being able to provide at least approximate predictions on latent track formation in numerous conducting and non-conducting targets.

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For swift heavy ions (SHI), i.e., ions having velocity comparable to or larger than the orbital electron velocity of the lattice atoms, the energy dissipation in the lattice takes place mainly through ionization and electronic excitation [30–33]. The rapid energy transfer during the electronic excitation can result in a variety of effects in materials including amorphization, defect creation, defect annealing, crystallization, etc. There have been numerous studies on the effects of SHI irradiation in different varieties of targets including insulators, semiconductors and metals, where electronic energy loss ($[dE/dx]_e$) is projected as the major parameter that determines the energy relaxation processes and the resultant effects in materials [30–33]. But if a systematic analysis is done on the effects of SHI irradiation in semiconductors, it can be observed that the effects produced are determined not only by the electronic energy loss ($[dE/dx]_e$) but also by the physical properties of the target materials [34,35]. Several material properties (such as carrier concentration in the present study) that are also influenced by the synthesis conditions seem to decide the ion beam induced effects and are of extreme importance in determining the response of a material to the SHI beam [34]. In this paper we report our studies on the effect of SHI irradiation in SnO_2 polycrystalline thin films differing in their conductivity. There exist few reports in the literature discussing the effect of SHI irradiation on the structural, optical, electrical and sensing properties of SnO_2 thin films grown using different deposition techniques [36–50]. However, no systematic studies have been carried out to verify the role of material properties such as carrier concentration (n) in determining the energy relaxation processes of SHI in SnO_2 thin films.

2. Experimental details

Highly conducting SnO_2 thin films were prepared using chemical spray pyrolysis technique. Dehydrate stannous chloride $SnCl_2.2H_2O$ (Sigma Aldrich purity > 99.99%) was used for making the spray solution for SnO_2 thin films. An amount of 11.281 g of $SnCl_2.2H_2O$ (Sigma Aldrich purity > 99.99%) was dissolved in 5 ml of concentrated hydrochloric acid by heating at 90 °C for 15 min. The addition of HCl rendered the solution transparent, mostly, due to the breakdown of the intermediate polymer molecules. The transparent solution thus obtained and subsequently diluted by methyl alcohol, served as the precursor. The amount of spray solution was made together 50 ml. The spray solution was magnetically stirred for 1 h and finally was filtered by a syringe filter having 0.2 μm pore size before spraying on the substrate. Fused quartz slides (10 mm × 10 mm × 1.1 mm), cleaned with organic solvents, were used as substrates. During deposition, the substrate temperature was maintained at 425 °C. The solution flow rate was maintained at 0.2 ml/min by the nebulizer (droplet size 0.5–10 μm). One set of as-deposited films were annealed in air for 2 h at 850 °C.

To observe the effect of SHI irradiation, these as-deposited and annealed SnO_2 thin films were irradiated with 120 MeV Au ions using a 15 MV pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi. Irradiation was done at six different fluences: 1×10^{11}, 3×10^{11}, 1×10^{12}, 3×10^{12}, 1×10^{13} and 3×10^{13} ions/cm^2. The fluence values were estimated by integrating the charges of ions falling on the samples kept inside a cylindrical electron suppressor. The ions were incident perpendicular to the surface of the samples. A high vacuum of 10^{-6} Torr was maintained in the target chamber during the bombardment. Ion beam was raster scanned on the film surface by a magnetic scanner for maintaining a uniform ion flux throughout the film. Beam current was kept constant during experiments and it was around 0.5 particle nanoampere. One sample of each group was left unirradiated in the chamber and was used as the reference sample. We divided our samples into two groups, viz. group A and group B. Group A consists of films which are as-deposited and irradiated (without any post deposition annealing). On the other hand, group B consists of films which underwent post deposition annealing and were further irradiated.

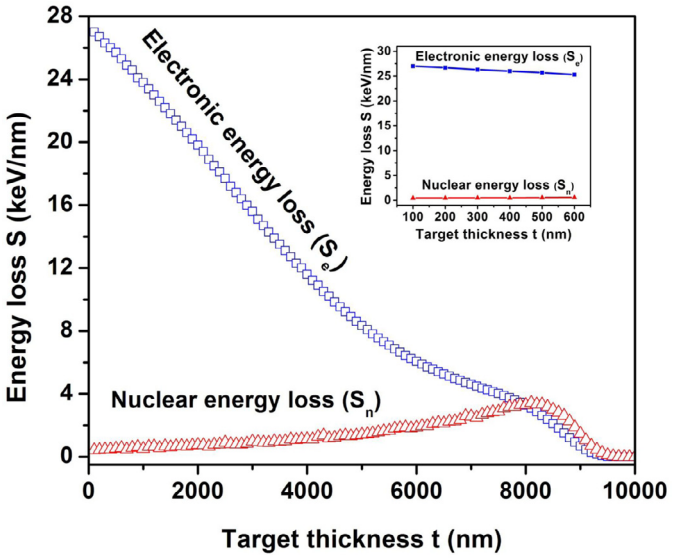

Fig. 1. Variation of nuclear energy loss S_n and electronic energy loss S_e with depth for 120 MeV Au^{9+} ions in SnO_2 matrix as determined by SRIM. Ratio of S_e/S_n is 60. The inset shows the almost constant value of S_e for even 600 nm depth from the surface of the SnO_2 film.

The gross structure and phase purity of all films were examined by X-ray diffraction (XRD) technique using a Bruker AXS, Germany X-ray diffractometer (Model D8 Advanced) operated at 40 kV and 60 mA. In the present study, XRD data of group A and group B thin films were collected in the scanning angle (2θ) range $20° - 60°$ using $Cu - K_\alpha$ radiations (λ = 1.5405 Å). The experimental peak positions were compared with the data from the database Joint Committee on Powder Diffraction Standards (JCPDS) and Miller indices were assigned to these peaks. Atomic force microscopy (AFM) was performed with Multi Mode SPM (Digital Instrument Nanoscope IIIa) in AFM mode to examine the microstructural evolution and root mean square surface roughness of the sample before and after irradiation. Hall measurements were conducted at room temperature to estimate the film resistivity (ρ), donor concentration (n) and carrier mobility (μ) by using the four-point van der Pauw geometry employing Keithley's Hall effect card and switching the main frame system. A specially designed Hall probe on a printed circuit board (PCB) was used to fix the sample of the size 10 mm × 10 mm. Silver paste was employed at the four contacts. The electrical resistivity and the sheet resistance of the films were also determined using the four probe method with spring-loaded and equally spaced pins. The probe was connected to a Keithley voltmeter constant-current source system and direct current and voltage were measured by slightly touching the tips of the probe on the surface of the films. Multiple reading of current and the corresponding voltage were recorded in order to get average values. Thickness of the deposited films was estimated by an Ambios surface profilometer and was approximately 500 nm.

3. Results and discussion

The electronic energy loss (S_e), nuclear energy loss (S_n) and maximum penetrable range (R_p) of the 120 MeV Au ions in SnO_2 are 27.19 keV nm^{-1}, 0.479 keV nm^{-1} and 8490 nm, respectively [51,52]. The variation of S_e and S_n with depth in SnO_2 matrix for 120 MeV Au ions is shown in Fig. 1. Near the surface of the film, S_e exceeds S_n by two orders of magnitude and is almost constant throughout the film thickness, as shown in the inset of Fig. 1. This reveals that the morphological and structural changes in SnO_2 thin film on irradiation by 120 MeV Au^{9+} ions are almost exclusively due to electronic energy losses.