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Band gap engineering and low temperature transport phenomenon in highly conducting antimony doped tin oxide thin films

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Abstract

A huge band gap tuning and low temperature transport phenomenon in highly transparent antimony doped tin oxide thin film (Sb:SnO_2) under the influence of swift heavy ions irradiation (SHII) is reported. Structural analysis shows an enhancement in crystallinity at initial fluence of irradiation followed by amorphization at higher fluences. Films were also well studied for their surface morphology by atomic force microscopy and scanning electron microscopy. Band gap analysis reveals a drastic band gap narrowing around 1.1 eV upon SHI irradiation. Transport measurements show that the high conductivity and the carrier concentration decrease upon increase in the fluence of irradiation. The mechanism of charge carrier transport investigated at low temperature is attributed to nearest neighbor hopping (NNH) and variable range hopping (VRH) in different temperature regimes. Origin of the band gap tuning is understood in framework of Burstein–Moss (BM) shift, Quantum Confinement (QC) effect and band-tailing states in amorphous semiconductors.

Keywords: Transparent Conducting Oxide (TCO); Burstein–Moss (BM) shift; Quantum Confinement; Amorphization; Nearest neighbour hopping (NNH) and Variable Range Hopping (VRH)

1. Introduction

Tin oxide (SnO_2) belongs to the class of wide band gap semiconductors and thus optically transparent in visible part of electromagnetic spectrum [1]. In general, optically transparent materials are insulator, but the resistivity of SnO_2 can be varied from 10^{-4}–10^{6} Ω-cm, similar to the most semiconductors [2]. Combination of these two features makes it one of the potential transparent conducting oxides (TCOs). Thus, it is suitable for a number of applications, such as solar cell electrode, light emitting diodes, flat panel display and transparent electronics [3–7]. Moreover, its applicability as an oxidation catalyst and gas sensor has also been well recognized [8,9]. Its wide range of applications in different fields of science and technology makes it an interesting material for current research. Doping of SnO_2 further enhances its capability for various technological applications [10–13]. So, there is a growing interest in modifying the structural, optical and electrical properties of SnO_2 with doping of suitable dopant. Particularly, antimony doped tin oxide (Sb:SnO_2) shows better electrical conductivity as compared to pure SnO_2 [14,15]. Hence, good electrical conductivity of Sb:SnO_2 with very high transparency makes it a promising research material for its manifold opto-electronic applications.

The modification of the properties of materials under the influence of Swift Heavy Ions (SHIs) irradiation has emerged as an exciting field of research and development. SHI can be used to modify the properties of metals, semiconductors, insulators and polymers [16–26]. Passage of SHI deposits energy in electronic excitations of the order of few keV/Å in the materials. Such large excitation energy brings out various changes in

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materials; for instance structural and transport properties in case of SnO_2 [27–32]. However, efforts toward band gap tuning and detailed understanding on low temperature transport phenomenon in Sb:SnO_2 yet to be reported. Therefore, the present manuscript reports a huge band gap tuning and low temperature transport mechanism along with their origin.

2. Experimental details

Sb:SnO_2 thin films were deposited using sol–gel spin coating technique. The sol was prepared using tin tetra chloride hydrate $SnCl_4 \cdot xH_2O$ (98%, Alfa Aesar), antimony chloride $SbCl_3$ (98.5%, CDH) and 30 ml ethanol as a starting precursor. The solution was stirred for few hours and a clear transparent solution was obtained, which was further aged for 3 days for completing the gelation process. After that, Sb:SnO_2 thin films were deposited over pre-cleaned quartz and p-type silicon (100) substrates. These B-doped silicon wafers were procured from semiconductor wafer, Inc. and exhibit resistivity of 1–10 Ω-cm. Pre-cleaning of quartz and Si substrates was performed using solution of acetone (20%) and de-ionized (DI) water (80%) for 10 min in ultrasonicator. The Si substrates were further dipped into 5% HF solution in DI water and subsequently rinsed with DI water. Films were deposited on these cleaned substrates using spin coating technique at a speed of 2800 rpm. The deposited films were pre-heated at 200 °C for 5 min and then the procedure was repeated several times for increasing the thickness of films. All the deposited thin films were post annealed at 700 °C temperature in tubular furnace in oxygen environment for 1 h. The schematic diagram of the whole process is shown in Fig. 1.

Annealed films were irradiated at room temperature (RT) with 120 MeV Ag^{+9} ion beam at different fluences: 1×10^{11}, 1×10^{12}, 2×10^{12}, 3×10^{12} and 1×10^{13} ions/cm^2 using the 15UD Pelletron Tandem accelerator at the Inter-University Accelerator centre (IUAC), New Delhi. During the irradiation process, the experimental chamber was evacuated to a high vacuum of 9.96×10^{-7} Torr. The value of electronic energy loss (S_e), nuclear energy loss (S_n) and range of 120 MeV Ag ion in SnO_2 (density – 6.95 g/cm^3) was calculated using SRIM-2008 software and found to be 2.31 keV/Å, 11.22 eV/Å and 9.01 μm, respectively. The value of S_e is thus very large as compared to S_n, therefore the modifications are mainly dominated by S_e effects. The calculated ion range suggests that ions will pass through the films, which are much smaller than the range of ions. The studies of thickness and elemental composition were carried out with Rutherford backscattering spectrometry (RBS) technique by using 2 MeV He^+ incident ions and detector was kept at back scattering angle of 165° with respect to beam direction. Structural phase identification was carried out by glancing angle x-ray diffraction (GAXRD) using Bruker D8 advanced X-ray Diffractometer equipped with copper anode. The X-ray tube angle was fixed at 2° with a scan speed of 0.5°/min in the range of 20–60°. Surface morphological investigations were done by Nanoscope III Atomic Force Microscope (AFM) in tapping mode and scanning electron microscope (SEM) techniques. Resistivity Vs temperature (ρ–T) measurements were performed in Van der Pauw four probes method using a setup equipped with Keithley constant current source meter (2182A), Nano voltmeter (6221), Lakeshore temperature controller and CTI cryogenic close cycle refrigerator (CCR). The carrier concentration and Hall mobility of all the films were measured using Van der Pauw Ecopia HMS-3000 Hall measurement system. UV–vis absorption and transmittance measurements were carried out by Hitachi UV3300 double beam spectrophotometer in the range of 200–800 nm. All the measurements were carried out at IUAC, New Delhi.

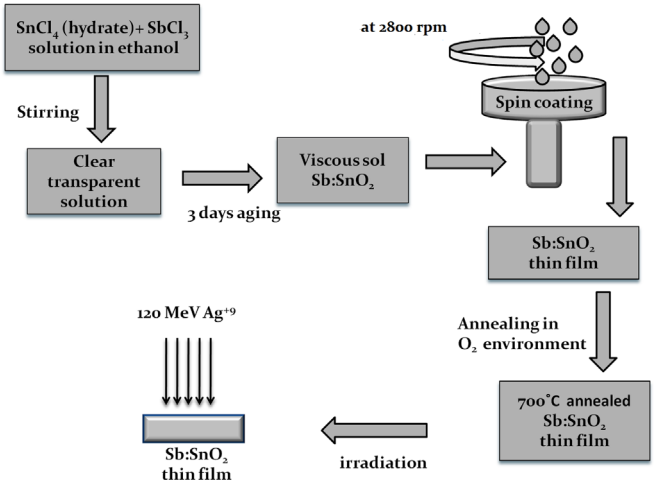

Fig. 1. Schematic of the deposition of Sb:SnO_2 thin films and their SHI irradiation.

3. Result and discussions

3.1. Film thickness and structural studies

The depth profile of elemental composition of Sb:SnO_2 thin film has been examined with RBS analysis. The Rutherford Universal Manipulation Program (RUMP) simulated and experimental RBS data of Sb:SnO_2 thin film is shown in Fig. 2. Simulation suggests the film thickness of 290 ± 10 nm with 3 at% Sb doping in SnO_2. However, it is difficult to find exact doping percentage of Sb in SnO_2 film, because the atomic weight of both Sb and Sn is almost same.

Fig. 3 shows the GAXRD pattern of pristine and Ag ion beam irradiated films. These patterns reveal that Sb:SnO_2 thin films are having all peaks corresponding to the standard rutile phase with polycrystalline structure up to a fluence of 3×10^{12} ions/cm^2 (JCPDS 041-1445). Pristine and irradiated films have a preferential orientation along (110) diffraction plane. The lattice constants 'a' and 'c' are determined using tetragonal phase structure relation:

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right), \quad (1)$$

where d, (hkl) are inter-planer distance and miller indices, respectively. The calculated values of crystallite size, lattice

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