Structural and morphological properties of Ag ion irradiated SnO$_2$ thin films

K M Abhirami$^1$, P Matheswaran$^1$, B Gokul$^1$, R Sathyamoorthy$^1$, K Asokan$^2$

$^1$PG and Research Department of Physics, Kongunadu Arts and Science College, Coimbatore, Tamil Nadu- 641 029, India.
$^2$Materials Science Division, Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi- 110 067, India.
E-mail: abhirami.km@gmail.com

Abstract. SnO$_2$ thin films of thickness 300 nm were prepared by reactive thermal evaporation and subjected to sintering at 600 °C for 2 hr. The annealed films were irradiated using silver (Ag) ions with energy of 120 MeV at different fluences ($1 \times 10^{11}$, $5 \times 10^{11}$, $1 \times 10^{12}$, $5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$). The effect of swift heavy ion (SHI) irradiation on structural, morphological and optical properties were studied using X-ray diffractometer (XRD), Scanning electron microscopy (SEM) and UV-visible spectrophotometer. XRD studies showed formation of tin oxide with tetragonal structure. Morphology analysis revealed uniform deposition of the material with increase in grain size after irradiation upto $1 \times 10^{12}$ ions/cm$^2$ and beyond that size tends to decrease. In addition, agglomeration of nanocrystalline grains was observed after Ag ion bombardment with varying fluence. The transmittance decreases from 90% to 80% as the fluence increases.

1. Introduction
Ion irradiation is a useful tool for impurity doping and defect production in materials, which helps to alter their structural, electrical, optical, and magnetic properties with a high spatial selectivity [1, 2]. The dynamic development of interest in wide band-gap semiconductors thin film and its widespread utilization in the fields of technology have led to the increased interest in the various problems of the properties of these semiconductors thin film in the recent years. Metal oxides are the best suited for wide band-gap semiconductors. Oxides are the basis of smart and functional materials. The synthesis and device fabrication using functional oxides have attracted a lot of attention due to the functionality of the physical properties of these oxides. Functional oxides have two structural characteristics: cations with mixed valence states, and anions with deficiencies (vacancies) [3]. SnO$_2$ is an n-type semiconductor with a wide band gap of approximately 3.7 eV. SnO$_2$ film shows the best thermal and chemical stabilities. It has extensive applications such as transparent conducting oxide in solar cells and other optoelectronic devices and remains active material for gas sensor.

In this paper, in an attempt to synthesize SnO$_2$ thin films with different morphology, we have made use of Ag-ion irradiation at room temperature and have studied changes in structural, optical, electrical, and morphological properties for a wide range of fluence.

2. Experimental details
SnO$_2$ thin films were prepared by means of reactive thermal evaporation of thickness 300 nm on glass substrates at 300 °C. The vacuum of the chamber during deposition was maintained at about 5x 10$^{-6}$ mbar. The as grown films were sintered at 600 °C for 2 h. The 120 MeV Ag$^{9+}$ ion beam irradiations at fluences of $1 \times 10^{11}$, $5 \times 10^{11}$, $1 \times 10^{12}$, $5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$ were first carried out for the structural phase transformation and bandgap modification. SHI irradiations were carried out with 120 MeV Ag ions using 15 UD tandem Pelletron accelerator at IUAC, New Delhi. The projected range of 120 MeV ions in the films as calculated using TRIM95 code is about 9 μm, which is greater than the total...
thickness of the film (0.2 μm). Thus, the bombarding ions pass through the entire film and come to rest in the substrate.

Irradiated and pristine films have been characterized using different techniques. Structural modifications were analyzed by X-ray diffraction (XRD) Philip PW1700 diffractometer (using Cu Kα). Surface structures were characterized by field emission-scanning electron microscopy (FE-SEM) [MIRA, TESCAN] at IUAC, New Delhi. Electron beam of energy 20 keV was used to capture the SEM images in the present experiment. UV-visible spectroscopy is performed to study the modification of band gap due to SHI irradiation. Optical absorption spectra were recorded with the conventional two-beam method using the U-3300 UV-visible spectrophotometer of Hitachi.

3. Result and discussion

Structure of the pristine and irradiated films was investigated by XRD technique. Figure 1 shows the XRD patterns of pristine and irradiated films. The diffraction patterns corresponding to irradiated films and pristine films match well with the JCPDS data [4], whereas the diffraction angle and intensity of the (101), (200) peak varies with ion fluence. No additional peaks related to other crystalline phases or metallic tin were observed. The grain size was calculated using Debye–Scherrer’s formula and the estimated grain size for the as-grown film is about 17.3 nm. The full width of half maximum (FWHM) of this peak found to dwindle up to 1 x 10^{12} ions/cm^2, implying that irradiation at low fluence increases the grain size. Thus, the crystallinity and quality of the film were getting improved with ion irradiation at low fluence. While at higher ion fluence beyond 1x10^{12} ions/cm^2, the FWHM of the peak seems to be augmented, implying that the size of coherent domains decreased. The irradiation results to an increase in the grain size and a maximum grain size of 27.3 nm was estimated for film irradiated at a fluence of 1 × 10^{12} ions/cm^2. At higher ion fluence of 1×10^{13} ions/cm^2 the grain size decreased to a value of about 11.7 nm. The increase in grain size might be due to the annealing effect of SHI below the threshold \( S_e \) value and the growth of small crystalline inclusions present in the film, leading to local crystallization. Similar grain growth was observed in SHI irradiated thin films [5, 6]. However, the observed decrease in the apparent grain size at higher fluences could be due to an increase of the micro-strains generated by irradiation-induced lattice defects.

![Figure 1. XRD pattern of pristine and irradiated SnO\(_2\) thin films](image-url)
Surface morphology of the pristine and irradiated films has been characterized by FE-SEM. The SEM image of the pristine sample (figure 2), contains tetragonal shaped structures grown perpendicular to the surface. As the fluence increases the grains melt due to irradiation induced annealing and form bigger grains. At higher fluence of about $1 \times 10^{12}$ ions/cm$^2$, the tetragonal like structure gradually disappears and grains were observed to be agglomerated under disorder induced by swift heavy ions.

![SEM image of pristine and irradiated SnO$_2$ thin films](image)

**Figure 2.** SEM image of pristine and irradiated SnO$_2$ thin films

UV–Visible spectroscopy provides useful information about the optical band gap of the semiconductors. Transmittance spectrum is shown in figure 3. The optical absorption study of the irradiated and pristine films was carried out and the band gap of the films has been calculated using Tauc's plot by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ and extrapolating the linear portion of the absorption edge to find the intercept with energy axis. The structural transformation (upto $1 \times 10^{12}$) generally leads to the formation of larger grains, which results in the reduction of band gap of the semiconductors. We also notice an increase in optical bandgap (beyond $1 \times 10^{12}$) in the irradiated film, which may be due to the irradiation provoked defect creation like anti-site oxygen and oxygen vacancies in the film. The calculated values of $E_g$ are 3.55, 3.40, 3.62 and 3.84 eV for films irradiated at fluences of 0, $1 \times 10^{11}$, $1 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$, respectively. This shows a consistent decrease of $E_g$ with an increase in ion fluence up to $1 \times 10^{12}$ ions/cm$^2$, and at higher fluence ($1 \times 10^{13}$ ions/cm$^2$) a definite increase in the band gap was observed. The shift in $E_g$ upon irradiation can be attributed to several reasons. The variation in the optical band gap can be candidly related to the change in the grain size because; we
have observed a consistent increase of grain size up to $1\times10^{12}$ ions/cm$^2$ and a sudden decrease at $1 \times 10^{13}$ ions/cm$^2$. The drop off in the energy gap with increasing ions fluences is due to creation of midway energy levels [7] and quantum confinement effect [8, 9].

Figure 3. Transmittance graph of pristine and irradiated SnO$_2$ thin films

4. Conclusion
The experimental data show that Ag ion irradiation (at lower fluences) induces formation of crystalline phase, whereas at higher fluence the crystallinity declines. In addition, we find that irradiation at higher fluences gives rise to inhomogeneous strain due to fluctuations in size and shape of individual grains. The grain size increases upto $1\times10^{12}$ and decreases beyond that forming agglomerated structures at high fluence. The value of bandgap at $1\times10^{12}$ is 3.62 eV which is very near to the bulk bandgap value. The change in optical band gap follows the change in grain size and hence the observed effect could be results of irradiation persuade modifications in the grain size.

5. Reference
[1] Cogan S F, Andersson E J, Plante T D, and Rauh R D 1985 Appl. Optics 24 2282
[2] Isidorsson J and Granqvist C G 1996 Sol. Energ. Mat. Sol. C 44 375
[3] Wang Z L and Kang Z C 1998 Functional and Smart Materials, Plenum, New York
[4] JCPDS No. 721147
[5] Sreekumar R et al.  2008 J. Appl. Phys. 103 023709
[6] Agarwal D C et al. 2006 Nucl. Instrum. Meth. B 244 136
[7] Chandramohan S et al. 2007 Nucl. Instrum. Meth. B 254 236
[8] Chaudhary Y S et al 2004 Nucl. Instrum. Meth. B 225 291
[9] Mohanta D, Mishra N C and Choudhury A 2004 Mater. Lett. 58 3694

Acknowledgement
The author (KMA) sincerely thanks IUAC, New Delhi for the project and the help during experiment and characterization.