www.amlett.com, www.amlett.org, DOI: 10.5185/amlett.2012.ib.108
"Nanostructuring by electrons, photons and ions" Special Issue Published online by the VBRI press in 2013

Modification of nanocrystalline RF sputtered tin oxide thin film using SHI irradiation

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Received: 16 March 2012, Revised: 22 July 2012 and Accepted: 26 July 2012

ABSTRACT

Nano crystalline tin oxide thin films were deposited on Si and quartz substrates using R. F. magnetron sputtering technique. A set of films was annealed in oxygen environment. These as-deposited and annealed films were irradiated using 100 MeV Ag ions at different fluences ranging from 3×10^{11} to 3×10^{13} ions/cm^2. The structural, optical and surface morphological properties of films were studied using X-ray diffraction (XRD), UV-Vis spectroscopy, and atomic force microscopy (AFM) techniques. As deposited films showed the polycrystalline nature and annealing enhances the crystallinity along a particular plane. Upon irradiation at lower fluences up to 3×10^{12} ions/cm^2, reduction in crystallinity is observed but at highest fluence 1×10^{13} ions/cm^2 a small increase in crystallinity occurs as inferred from XRD spectra. UV-Vis study showed red shift at the lower fluences and blue shift at higher fluences. The pristine film, as observed in AFM micrograph, has randomly distributed surface nano structures with broader size distribution. Irradiation induces the formation of regular shape structures with narrow size distribution. These results may be attributed to the energy deposited by swift heavy ions in the film. Copyright © 2013 VBRI press.

Keywords: Tin oxide thin film; nanostructures; nanocrystals; RF sputtering; annealing; swift heavy ion irradiation.

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Introduction

The nanostructured materials (NSMs) of metal oxides with ultra-fine grain size exhibit a number of improved properties as compared with conventional coarse-grain sizes and thus have considerable attraction for engineering applications [**1**]. High strength, superior chemical stability and wear resistance can make the use of NSMs as part of the high-temperature devices. Grain diameter and significant volume of the atoms at the defect sites, mainly at interfaces, are two main factors which determine the properties of NSMs. Thus, the atomic structure of interfaces is crucial for the properties of these materials. Hence, nanocrystalline thin films play a significant role in improving the performance and reliability of nanoscale devices [**2,3**].

Tin oxide (SnO_2) is a wide band gap (3.6 eV at 300 K) material with up to 97% optical transparency in the visible spectrum (for 0.1 to 1.0 µm thick films) having wide variation in electrical resistivity (10^{-4} to 10^6 Ω-cm) [**4**]. High chemical stability and stable large band gap make thin films of tin oxide very attractive to be used in device fabrication. Thus, tin oxide is a versatile material having wide range of fascinating applications due to its remarkably suitable physical properties [**5, 6**]. Its applications can be broadly classified into three major areas namely gas-sensing, transparent conductor (as contact electrode) and oxidation catalyst. Being highly reflective for IR radiation, it is extensively used in smart windows-an energy conserving device [**7-10**]. Amorphous tin oxide thin films, in addition to the nanocrystalline films, have gained considerable attention to be used in a new area of electronics called transparent electronics and/or giant micro-electronics [**11-13**]. The uses of nanostructured metal oxides in biosensors are newly developing fields. It is believed that the sensible application of nanostructured metal oxides can lead to the fabrication of novel biosensing devices [**14-15**].

In view of large number of applications, a variety of deposition methods have been employed for the fabrication of amorphous and nanocrystalline tin oxide thin films. Thermal evaporation, e-beam evaporation, pulsed laser deposition, magnetron sputtering, chemical vapor deposition, sol-gel, swift heavy ion (SHI) irradiation etc. are used successfully for the fabrication and development of tin oxide thin films [**16-24**]. Among these techniques, rf magnetron sputtering is considered to be advantageous because one can deposit uniform films on a larger area easily and economically [**25**].

SHI irradiation is a unique technique for the modification of materials. Such modifications in matters, caused by SHI irradiation, have mostly been explained in the frame work of thermal spike model [**26**]. When SHI passes through a material, it deposits an enormous amount of energy to the electronic sub-system of the lattice in a very short span of time which leads to lattice modification, i.e. either it gets disordered or amorphised or recrystalized, consequently modifying the material. The uniqueness of modifications induced by SHI in comparison to other techniques is its spatial selectivity and precise control over the modifications by changing the ion species, ion's energy, fluence, angle of incidence, irradiation temperature etc. [**27-30**]. The earlier studies on SHI irradiation of tin oxide were performed on the nanopowder deducing the fact that tin oxide is Se sensitive to SHI irradiation [**31-32**]. Recently, Mohanty *et al.* [**18**] showed the effect of 100 MeV Ag ions on amorphous tin oxide films deposited on different substrates using e-beam evaporation. They observed formation of SHI induced nanocrystals in amorphous films and induction of crystallinity is better on crystalline substrates rather than amorphous substrates. In this way they have fabricated tin oxide nanocrystals using SHI irradiation. Rani *et al.* [**17**] irradiated sol-gel prepared tin oxide film by 75 MeV Ni ions and explained the effect of SHI on structural, optical and surface properties. However, there is a lack of understanding on SHI induced modifications or effects in nanocrystalline tin oxide films. In the present study, we have prepared nanocrystalline tin oxide thin films using rf magnetron sputtering technique. These films were irradiated by 100 MeV Ag ions at different fluences and further measurements were carried out to study modifications in structural, optical and surface morphological properties. The changes occurred due to irradiation are explained in the frame work of thermal spike model.

Experimental

Thin films of tin oxide (SnO_2) were deposited on Si and quartz substrates using rf magnetron sputtering technique. A pellet was prepared using commercially available powder of tin oxide (purity 99.99%, Sigma-Aldrich). The diameter and thickness of this pellet was ~2 inches and ~2.5 mm, respectively. Before employing the pellet as the sputter target, it was sintered at 1200 ºC for 12 h. Thoroughly cleaned substrates were mounted on the substrate holder and the deposition chamber was evacuated to a base pressure of 9×10^{-5} Torr. Argon (Ar) and oxygen (O_2) gasses were allowed to flow in the deposition chamber at the rate of 5.0 and 2.0 sccm respectively. The pressure during deposition was 10 mTorr. The net rf power supplied to the target was 160 W. The substrates were heated up to 325 ºC during film deposition. The target to substrate distance was maintained at ~7 cm. The thickness of the film was measured (using Rutherford backscattering spectrometry (RBS) technique) to be ~210 nm. The atomic concentrations of Sn and O, obtained from RBS data, confirm the film composition to be SnO_2. The phase identification was performed by X-Ray diffraction (XRD) technique. One set of as-deposited films were further annealed in oxygen environment for one h at 800 ºC to study the modifications in structural, optical, and surface morphological properties.

We divided our samples into two groups, viz. Group A and Group B. Group A consists of films which were 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.

The as-deposited and annealed films were irradiated by 100 MeV Ag ions at different fluences ranging from 3×10^{11} to 3×10^{13} ions/cm^2 using the 15 UD tandem Pelletron accelerator at Inter-University Accelerator Centre (IUAC), New Delhi. Irradiations were performed in a high vacuum chamber at room temperature and at a normal incidence to the surface of films. Ion flux was kept to a low level in order to minimize the charging effects and sample heating. The electronic energy loss (S_e) and the nuclear energy loss (S_n) values, corresponding to 100 MeV Ag ions, are 21.96 and 0.13 keV/nm, respectively which shows the dominance of S_e over S_n. Hence, the modifications in the films are expected to be caused mainly by S_e related processes. The projected range of the energetic ions was calculated to be 8.11 µm (using the SRIM software) [**33**]. As the projected range is much higher than the film thickness, the ions would pass through the film and get implanted deep into the substrate. As-deposited, annealed and irradiated samples were characterized by using XRD (for structural analysis), atomic force microscopy (AFM) (for surface morphological study), and UV-Vis spectroscopy (for optical properties) to study the respective modifications. XRD patterns were recorded using a Brukar D8 Advanced AXS diffractometer at a grazing incidence of 2º with CuK$_\alpha$ (λ=1.54184 Å) radiation. AFM images were captured using a Nanoscope IIIA atomic force microscope in tapping mode. UV-Vis spectra were recorded using a Hitachi U-3300 spectrophotometer. All these characterizations were performed at IUAC, New Delhi.

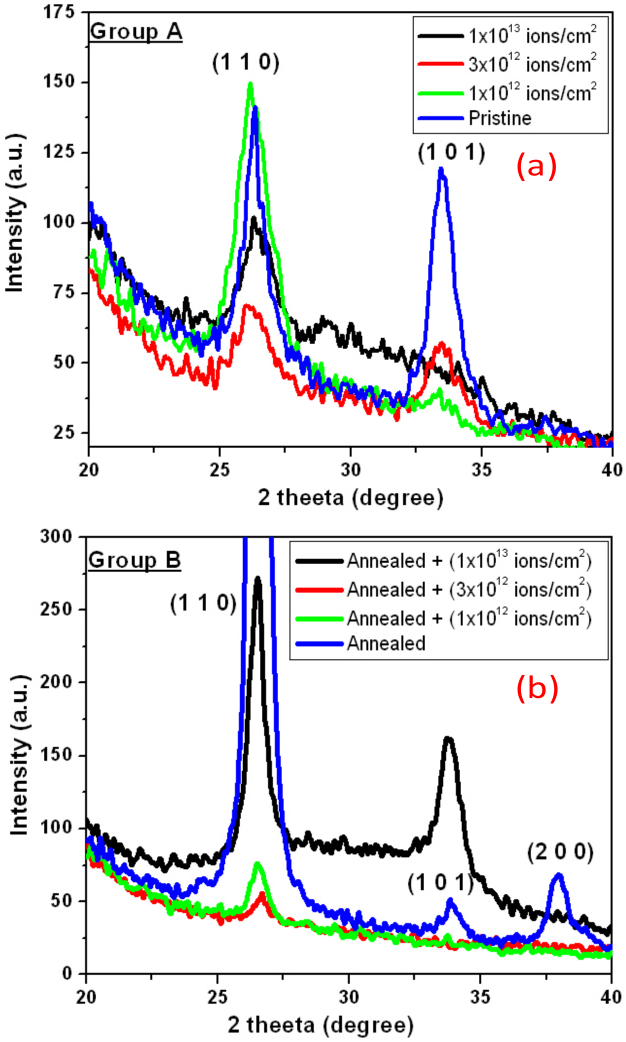

Fig. 1. (a) XRD spectra of as-deposited and irradiated (group A) films and (b) XRD spectra of annealed and irradiated (group B) films.

Results and discussion

XRD analysis

Fig. 1 (a) shows the XRD patterns for Group A films. The as-deposited films turn out to be polycrystalline in nature with (1 1 0) and (1 0 1) planes of tetragonal rutile tin oxide at 26.29° and 33.49º, respectively. The average crystallite size was obtained 8.9 nm (calculated from the Scherrer's formula) [**34**]. Irradiation at the lowest fluence (i.e. 1×10^{12} ions/cm^2) gives rise to an increase in the full width of half maxima (FWHM) of the (1 1 0) peak with a little shift towards the lower 2θ value, while the other peak almost diminishes and the average crystallite size became 5.2 nm. Irradiation at the intermediate fluence (3×10^{12} ions/cm^2) also causes a slight increase in the FWHM value corresponding to the (1 1 0) plane and the (1 0 1) peak reappears. On the other hand, irradiation at the highest fluence (1×10^{13} ions/cm^2) leads to a decrease in the FWHM value and the (1 0 1) peak disappears. The average crystallite size became 5.1 and 5.4 nm corresponding to the intermediate and the highest fluence, respectively.

Fig. 1(b) presents the XRD patterns of Group B films. It is observed that annealing enhances the crystallinity in a significant manner (the average crystallite size became 13.1 nm) and the films have a preferential growth along the (1 1 0) orientation. In addition, a new peak along the (2 0 0) direction appears. The growth of tin oxide nanocrystals and thus improvement in crystallinity after annealing (in the temperature range of 600 to 1000 ºC) is a common phenomenon [**35**]. The intensification of crystallinity along the (1 1 0) plane is highly favourable from the gas-sensing application point of view [**36**]. The growth of the (2 0 0) plane may be due to its lower surface energy. In this case, irradiations performed at the lowest and the intermediate fluences show a reduction in crystallinity along the (1 1 0) direction, while other peaks disappear. Regain in the crystallinity occurs for irradiation performed at the highest fluence and the average crystal size becomes 11.2 nm. Such a reduction in crystallinity at the lower fluences may be attributed to ion-beam induced amorphization or disordering of crystals whereas irradiation at the highest fluence may cause recrystallization and thus the improved crystallinity.

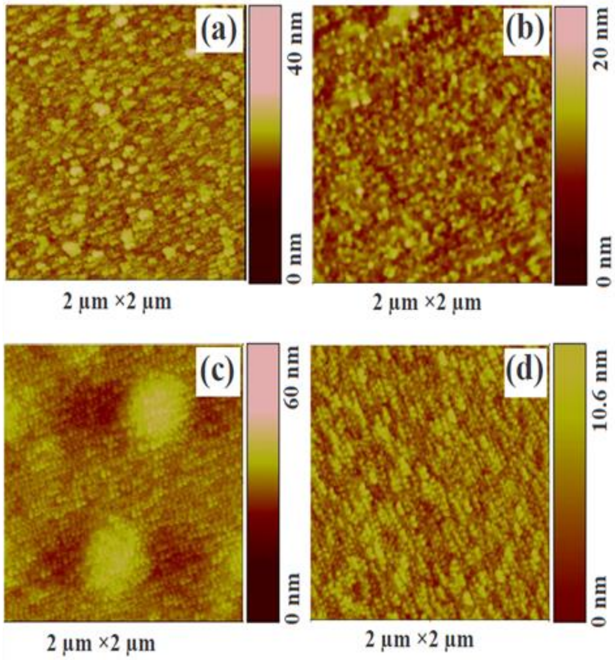

Fig. 2. AFM images of (a) as-deposited, (b) irradiated at 1×10^{13} ions/cm^2 (Group A), (c) annealed, and (d) irradiated at 1×10^{13} ions/cm^2 (Group B) films.

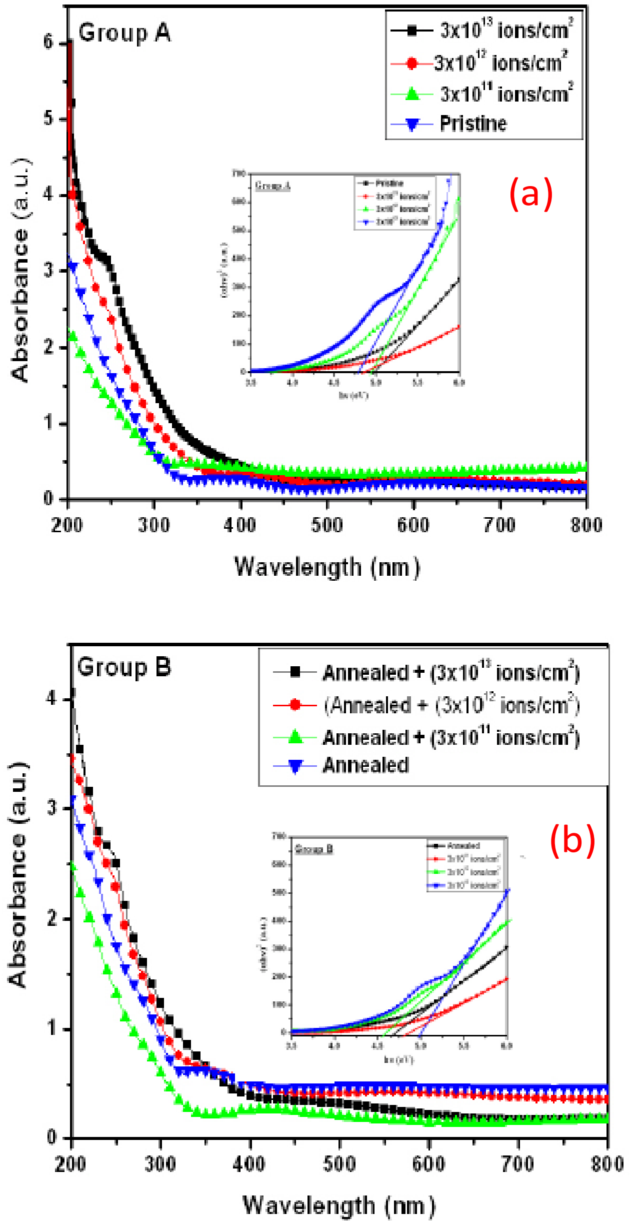

Fig. 3. (a) Absorption and tauc's (inset) spectra of group A films and (b) Absorption and tauc's (inset) spectra of group B films.

Surface morphological analysis

Fig. 2 shows the AFM micrographs of as-deposited, annealed, and irradiated samples on Si substrates. **Fig. 2**(a) shows the morphology of the as-deposited film which has nanostructures with broader size distribution in the range from 30 to 80 nm. The root mean square (rms) surface roughness is 1.6 nm. When this as-deposited film is irradiated with 1×10^{13} ions/cm^2 (**Fig. 2**(b)), there is an insignificant increment in rms roughness (1.8 nm) and the bigger structures break. On the other hand, the smaller structures retain their size and shape. The dimension of nanostructures becomes 30 to 65 nm. **Fig. 2**(c) shows the surface morphology of an annealed film. After annealing, the nanostructures become almost spherical in shape with size in the range of 30 to 55 nm and rms roughness of 3.6 nm. The increment in rms roughness is caused due to the thermal heating induced growth in crystallinity. These crystals are aligned in a particular direction leading to increment in rms roughness [**37**]. **Fig. 2**(d) shows the surface of the film annealed and then irradiated at 1×10^{13} ions/cm^2. At this fluence nanostructures are arranged in a particular direction and start to form nanobead like structures with size in the range of 30-65 nm (having 1.6 nm rms roughness). This arrangement of structures, in a particular direction, may be occurring due to SHI induced surface diffusion [**27**].

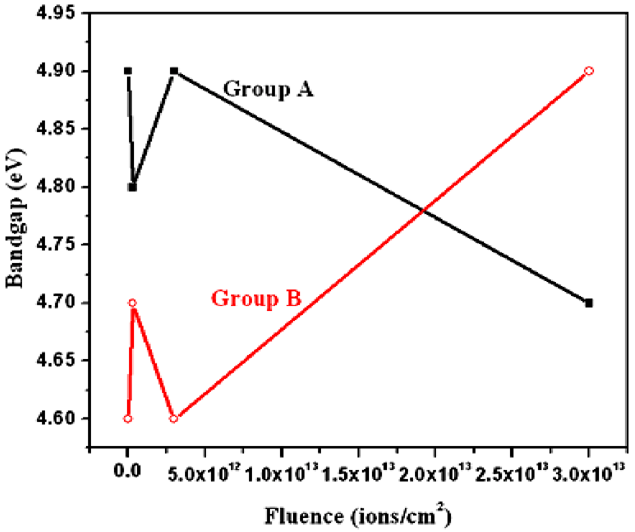

Fig. 4. Variation in band gap of group A and B films with fluence.

Optical properties analysis

Figs. 3(a) and (b) show the absorption spectra of group A and B samples, respectively on quartz substrates. The band gap has been estimated using Tauc's procedure [**27**]. The band gap of the as-deposited film is found to be 4.9 eV which is significantly higher from its generally accepted value (3.6 eV at 300 K) [**4**]. Researchers have reported that the band gap of tin oxide nanostructures shows a noticeable blueshift as compared to the bulk value. In nanoregime, surface to volume ratio increases which causes self equilibrium state of nanostructures. The excess energy of surface atoms influences the band structure [**37, 38**]. Irradiation at the lowest fluence of 3×10^{11} ions/cm^2 causes a little shift in absorption in the visible region and the band edge is shifted towards higher wavelength indicating a lowering in the bandgap to 4.8 eV. Irradiation at 3×10^{12} ions/cm^2 and 3×10^{13} ions/cm^2 fluences cause reduction in absorption in the visible range up to its initial value and the band gap becomes 4.9 and 4.7 eV, respectively.

For Group B, annealing decreases the bandgap to 4.6 eV from 4.9 eV (as-deposited film). This may be due to the fact that oxygen environment decreases oxygen vacancies and consequently the number of carrier concentration decreases in the conduction band. Hence, the Fermi level gets down and the band gap decreases. Annealing also reduces stress and/or strain in the films which may help to improve crystallinity and surface roughness. These facts together may lead to the reduction in band gap [**39**]. The variation in the band gap in Group A and B films with fluence is shown in **Fig. 4**. Change in the band gap, due to irradiation, is explained in terms of loss of oxygen atoms and creation of defect states near the conduction band. Ion irradiation can produce defect levels (band tailing effect) below the conduction band which are responsible for the reduction in band gap. Increament in band gap may be due to the Burstein-Moss effect [**40**].

Conclusion

Polycrystalline thin films were prepared using rf magnetron sputtering and irradiated using 100 MeV Ag ions. Irradiation at lower fluences decreases the crystallinity whereas at the highest fluence, there is a small increament. Hence, lower fluences causes amorphization and highest fluence recrystallizes the material. At the highest fluence irradiation the bigger nanostructures break while the smaller structures retain the shape and size. Also, irradiation at different fluences change the band gap in dramatic manner.

Acknowledgements

Authors are highly thankful to DST, New Delhi for providing financial support under the project. We are grateful to Dr. D.K. Avasthi for the useful discussions and encouragement. We express our thanks to Sunil Ojha for helping in RBS measurements. We are also thankful to the reviewer for his helpful comments which have been used in revising the manuscript.

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