## 5.2.44 Control of Size Distribution of $SnO_2$ nanoparticles by ion beam

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Tin dioxide ($SnO_2$) is one of the most widely used semiconductor oxide gas sensors for its high sensitivity to $H_2$ and CO gases [1]. In the present work nanocrystalline $SnO_2$ thin films are grown on fused silica substrate using RF sputtering technique. To study the effect of ion beam on size distribution, these nanophase films were bombarded with 250 KeV $Xe^+$ ion beam at high fluences. The as grown films as well as ion bombarded films were characterized by UV-Visible absorption spectroscopy, photoluminescence spectropscopy, and atomic force microscopy (AFM) techniques.

Optical absorption spectrum of as grown films as well as bombarded films are shown in figure1. The band edge is shifted towards red from 350 nm to 400 nm for nanocrystalline $SnO_2$ thin films bombarded with Xenon ion beam.

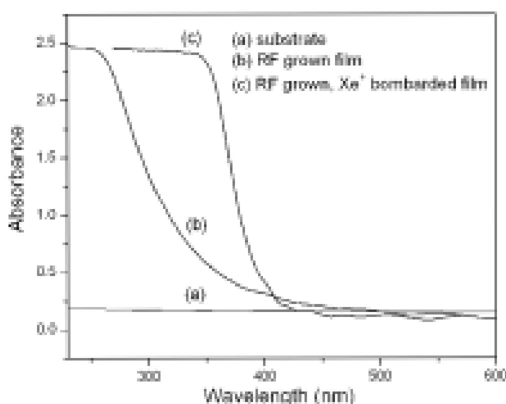


Fig. 1 : UV-VIS absorption spectra of $SnO_2$ thin films

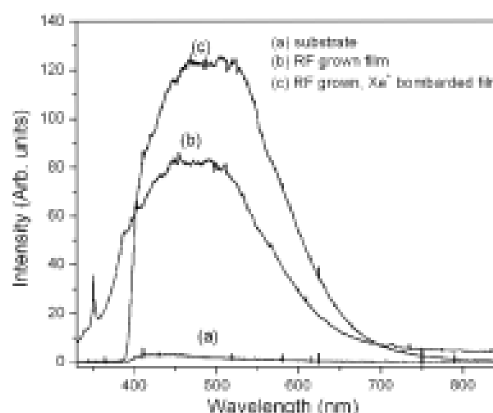


Fig. 2 : PL spectra $SnO_2$ thin films

Band edge shifting towards lower energy (350nm to 400nm) implies that the size of nanoparticles increases after ion bombardment [2]. Figure 2 gives the PL spectra of as grown films as well as ion bombarded films. PL peak is shifted towards higher wavelength at 495 nm for ion-bombarded films. But the FWHM of PL peak decreases for ion bombarded films which indicate that the size increases but the distribution decreases.

The topography of RF grown films and ion bombarded films are shown in figures 3 and 4.

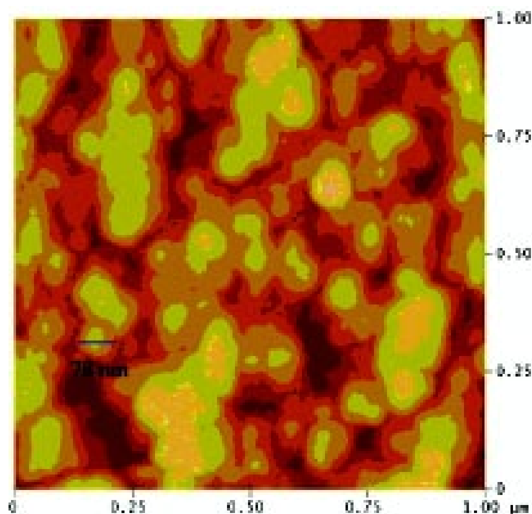


**Fig. 3 : AFM picture of RF grown $SnO_2$ thin films**

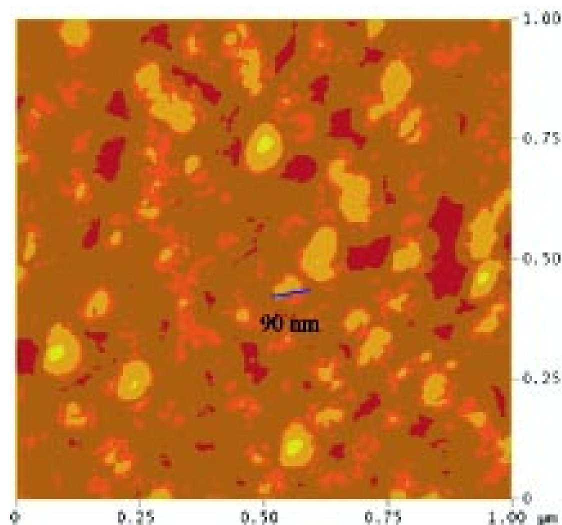


**Fig. 4 : AFM picture of RF grown $Xe^+$ ion bombarded $SnO_2$ thin film**

In case of RF grown films the topography shows that the size of grains are 40±5 nm having some aggregated lumps. The morphology of the RF grown $SnO_2$ films, bombarded by $Xe^+$ ions shows the size of the grains is 45±1 nm. Due to increase in size of the particles (~5nm) and decrease in their initial concentration the rate of agglomeration process decreases thus leading to formation of narrow size distribution of particles (~1nm) [3]. The results of imaging studies support the result of optical studies.

During ion bombardment process, the local heat generated due to energy loss leads to melting of the films. When beam is stopped, the supersaturation solution of $SnO_2$ is formed in the matrix. Tin dioxide nanoparticles are expected to be nucleated around this large number of vacancies created in matrix as well as in thin films and grow uniformly with time [4]. As nucleation and growth processes are separated, uniform size distribution of nanoparticles occurs.

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## 5.2.45 Barrier height modification of Au/n-Si Schottky diode by energetic argon ion bombardment

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N-type Si (100) sample of resistivity 1Ω–cm were used to fabricate Au/n-Si Schottky diodes. Aluminium (Al) was selected to make ohmic contact. The I-V measurement in both forward and reverse bias contacts show ohmic behavior. Schottky diodes were created by deposition of Au on the sample having ohmic contact by thermal resistive heating technique in an ultra high vacuum chamber. A 100 nm Au layer was deposited through a stainless steel mask having contact diameter 2 mm at a base pressure in $10^{-8}$ m bar region. The thickness of the metal layer was monitored with quartz crystal thickness monitor. The contacts were used to determine the forward and reverse current-voltage characteristics between -4 V to +4 V. The Schottky contact were bombarded by 1 MeV Ar ion beam to a total doses of $5x10^{10}$ and $5x10^{11}$ ions $cm^{-2}$.

As deposited metal-semiconductor contacts usually exhibit non-ideal current-voltage characteristics. The experimental data is best fitted by the non-ideal diode equation

$$I = I_s \exp [q (V–IR) INKT]–1 \quad \text{.......................................} \quad (1)$$

where $I_s$ is the saturation current and n is the ideality factor . R is the semiconductor series resistance. The saturation current $I_s$ is given by

$$I_s = A^* A T^2 \exp (–\Phi_b IkT), \quad \text{..........................................} \quad (2)$$

where $A^*$ , A, and $\Phi_b$ represents the Richardson constant, the contact area ,Schottky barrier height respectively. The other symbols in the above equations have their usual meaning. By using a least square fitting procedure $I_{s,}$ n and $\Phi_b$ are calculated from I-V data , which provide a basis for comparison of electrical characteristics before and after irradiation.

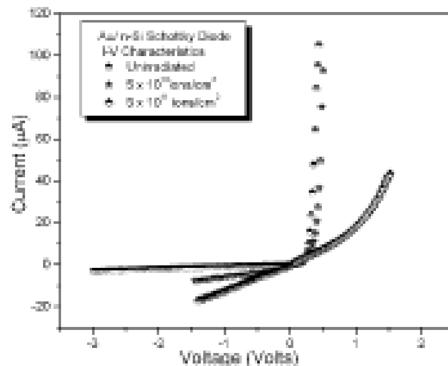


**Fig. 1 : Forward I-V Characteristics of Au/n-Si diode before and after irradiation**

Figure 1 shows the I-V characteristics for pristine as well as irradiated Schottky diode . For pristine Schottky diode the ideality factor, n, is equal to 2.3. After irradiation with a fluence of $5x10^{10}$ ions $cm^{-2}$, the value of ideality factor increases to 4.8. According to the Fermi level pinning model of Bardeen [1], when the interface state density increases from the Schottky limit to Bardeen limit, the Schottky barrier height decreases. In our case from the I-V characteristics

for pristine diode we have calculated the Schottky barrier height as 0.794 eV. This means there is a finite density of interface states existing at Au/n-Si interface for the unirradiated samples. The Schottky barrier height decrease to a value of 0.63 when diode is irradiated at a fluence of $5x10^{10}$ ions $cm^{-2}$. In this case ideality factor increases to a value 4.8 which according to this theory shows an increase in density of interface states. Au/Si is one of the systems having highest mixing rate[4]. In our case when the fluence increases to $5x10^{11}$ ions $cm^{-2}$, the rectification properties get highly degraded and Au contacts do not show any rectifying property,. This behavior comes due to large electronic energy loss as compared to nuclear energy loss at higher fluences. So as the fluence increase, contribution of energy loss to the system increases , which results in ion beam mixing of Au/n-Si layers at the interface and Schottky diode shows Ohmic behavior after 1 MeV Ar ion irradiation at fluence of $5x10^{11}$ ions $cm^{-2}$.

Thus initially irradiation causes an increase in interface state density leading to a decrease in Schottky barrier height at an irradiation fluence of $5\times10^{10}$ ions $cm^{-2}$ . As the fluence increases ion beam mixing of gold and silicon layers increases and at a fluence of $5\times10^{11}$ ions $cm^{-2}$ Au/n-Si Schottky diode does not show any rectifying property and the contacts become Ohmic in nature.

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## 5.2.46 Formation of nanostructures of ZnO


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Zinc oxide is a II-VI n-type direct band gap semiconductor, having a hexagonal wurtzite structure. It has a wide band gap of 3.37eV and an exciton binding energy of 60 meV[1]. It is nontoxic, inexpensive, and abundant material. The bulk crystals usually have a high impurity content which lead to unwanted deep radiative and nonradiative recombinations[2]. Thin film on insulating substrate is suitable for better opto-electronic device formation. Vacuum evaporation is a suitable technique for preparing ZnO films[3].

ZnO films of 400 nm were deposited on fused silica at room temperature by e-beam evaporation technique at a pressure of 23.4 mbar and at a growth rate of 0.8 nm/s. Zinc oxide powder made into a pellet was used as target. The base pressure of the growth chamber was of the order of $10^{-6}$ mbar. The thickness of the deposited ZnO film was 400 nm. After deposition, the films were annealed in oxygen ambience in a tubular furnace in steps so as to optimize the time and temperature. Annealing was done first at 450°C for 4 hrs and 8 hrs and

subsequently at 800°C for 1 hr. At each step UV-Visible absorption spectroscopy was done using HITACHI U-3300, spectrophotometer. X-ray diffraction studies were carried out for analysis of films. The films on quartz substrates were bombarded with 15 keV $Ar^+$ ions with a fluence of $5 \times 10^{15}$ ions/$cm^2$. Surface modifications were studied using Nanoscope III A scanning probe microscope in tapping atomic force microscope (AFM) mode.

The X-ray diffraction spectrum of ZnO film on quartz (Fig.1) shows that good quality films were developed by this technique. Peaks at 34.58°, 36.43°, 47.72°, 63.05°, 68.13° correspond to hexagonal zinc oxide.

Room temperature absorption spectroscopy was carried out for pristine quartz, as deposited and annealed ZnO films under different annealing conditions. As deposited film which was dark brown in color shows a broad featureless spectrum. The annealed samples which became transparent after annealing show prominent absorption features at 376 nm which corresponds to 3.32 eV. Films which were annealed at 450°C for 4 hrs and 8 hrs show two broad peaks at 416 nm and 507 nm which is due to zinc interstitials and oxygen vacancies. Clean tailing spectrum for the sample annealed at 800°C for 1 hr indicates that the defects were annealed out at higher temperature.

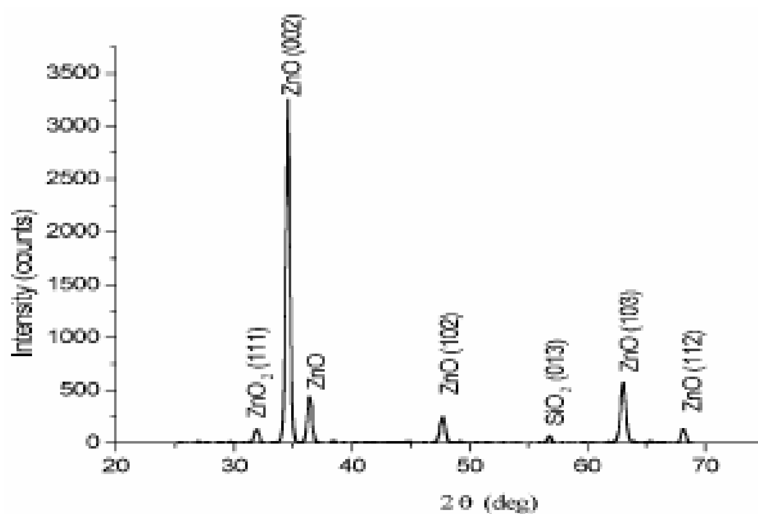


**Fig. 1: XRD spectrum of ZnO film on quartz**

Absorption spectroscopy was also carried out for the pristine and sputtered films of ZnO . For the sputtered sample the absorbance has decreased. The decrease in the absorbance is attributed to the removal of grain boundaries and strain due to large $S_{n.}$ The slight increase in heights of the peaks at 416 nm and 526 nm could be attributed to the introduction of some oxygen vacancies in the host material by ion beam.

In order to determine the change in the surface morphology of the films after sputtering we performed AFM (Fig.2 and Fig.3). The roughness of the film decreased from 26 nm to 15 nm after sputtering. Average grain size also decreased from 150 nm to 40 nm. Tuning of surface

morphology on nanometric scale by inert ion sputtering can be achieved by driving a competition between ion erosion and surface diffusion.

Thus good quality ZnO films were prepared by e-beam evaporation and subsequent thermal annealing with optimized time and temperature. Sputtering with 15 keV $Ar^+$ led to the formation of nanostructures on the surface predominantly due to elastic energy loss without degrading the quality of the base films.

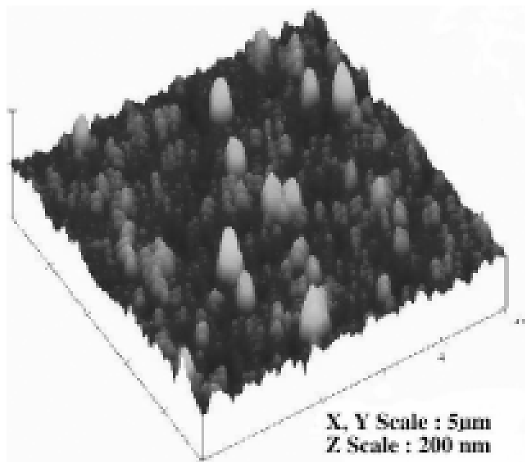


**Fig. 2 : Pristine**

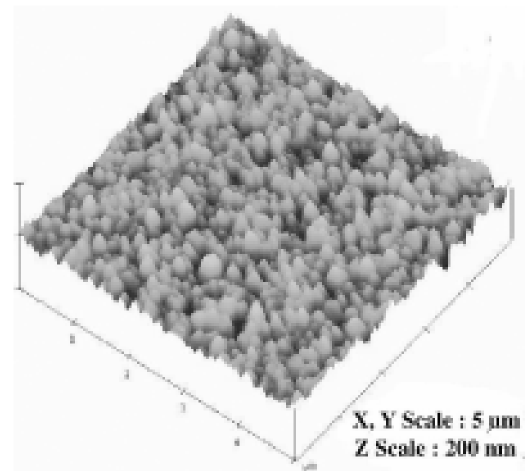


**Fig. 3 : Sputtered**

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