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# Copper Ion Beam Irradiation-Induced Effects on Structural, Morphological and Optical Properties of Tin Dioxide Nanowires *

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*The 0.8 MeV copper (Cu) ion beam irradiation-induced effects on structural, morphological and optical properties of tin dioxide nanowires ($SnO_2$ NWs) are investigated. The samples are irradiated at three different doses $5 \times 10^{12}$ ions/cm$^2$, $1 \times 10^{13}$ ions/cm$^2$ and $5 \times 10^{13}$ ions/cm$^2$ at room temperature. The XRD analysis shows that the tetragonal phase of $SnO_2$ NWs remains stable after Cu ion irradiation, but with increasing irradiation dose level the crystal size increases due to ion beam induced coalescence of NWs. The FTIR spectra of pristine $SnO_2$ NWs exhibit the chemical composition of $SnO_2$ while the Cu–O bond is also observed in the FTIR spectra after Cu ion beam irradiation. The presence of Cu impurity in $SnO_2$ is further confirmed by calculating the stopping range of Cu ions by using TRM/SRIM code. Optical properties of $SnO_2$ NWs are studied before and after Cu ion irradiation. Band gap analysis reveals that the band gap of irradiated samples is found to decrease compared with the pristine sample. Therefore, ion beam irradiation is a promising technology for nanoengineering and band gap tailoring.*

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Recent studies have shown that numerous fascinating characteristics have been proposed by semiconductor nanomaterials. These include, good conductivity, superior hardness,[1] higher luminescence efficiency,[2] enhanced thermoelectric merit,[3] and reduced lasing threshold.[4] One-dimensional nanomaterials have attracted much attention recently due to their potential applications as building blocks for nanostructure devices.[5] Among them, metal oxide nanostructures, due to their novel characteristics, have significant space in electronic and optical technology. These materials are widely synthesized with several techniques.[6]

$SnO_2$ is a wide band gap n-type semiconductor material with a direct band gap of 3.6 eV,[7] where inherent oxygen vacancies act as an n-type dopant.[8] It is a versatile material and has a wide usage as the most attractive material for gas sensors, photosensors, transparent conductive electrodes and photovoltaic applications.[9] In such applications, reducing the band gap down to a few electron volts is of particular interest due to the fact that the electrical conduction can be greatly enhanced by tailoring the band gap of materials. Most of the modern scientific applications demand special engineering of morphology, structure, magnetic and electronic properties of materials. Ion beam irradiation may cause a huge stress on the surface of nanomaterials. The change in surface configuration has a great effect on the properties of the materials. Recently, it was reported[10] that the sensing properties of $SnO_2$ NWs have been enhanced significantly due to the change in surface configuration. In addition, ion implantation has been widely used to improve the mechanical and tribological properties of nanowires.[11–13] In this context, the ion beam has proven to be a very useful tool to obtain desired properties of nanomaterials.[14] Ion beam irradiation is also a famous issue of interest in the field of nanoengineering.[14,15] Nowadays it is used for desired modification in the electrical, structural and optical properties of nanomaterials.[14–16] However, little effort has been made to studying the effect of ion beam irradiation on the properties of $SnO_2$ NWs.[17] Thus a further study is mandatory to make a database regarding the effect of different ion species and ion beam energy on the properties of $SnO_2$ NWs which will be useful for the scientific community to design $SnO_2$ NWs-based devices for working in a harsh environment (upper space) as well as a clean environment.

In the present study, Cu ion beam irradiation effects on the structural, morphological and optical properties of $SnO_2$ NWs are investigated. XRD, SEM, FTIR and UV-vis spectroscopy are used to characterize the samples before and after Cu ion beam irradia-

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tion.

To synthesize tin dioxide nanowires, 1.05 g $SnCl_4.5H_2O$, 1.40 g of NaOH and 40 ml DI water and ethanol were used. All the chemicals used in the study were highly pure. $SnO_2$ nanowires were synthesized by chemical route. To perform the chemical reaction, 1.05 g $SnCl_4.5H_2O$ and 1.40 g of NaOH were dissolved in a solution containing 40 ml of each of DI water and ethanol. The synthesized mixture is then transferred into a Teflon lined autoclave in which it was heated at 180℃ for 18 h. A grey white powder obtained after heating was washed repeatedly with ethanol and then dried again at 60℃ in a vacuum oven.

A homogenous solution of the powder in ethanol was achieved after continuous stirring for 50 min. This solution is then dripped on a glass substrate to form films of tin dioxide. Four samples were prepared with tag samples 1–4. Among them, samples 2–4 were irradiated with a copper ion beam at the dose level of $5\times10^{12}$, $1\times10^{13}$ and $5\times10^{13}$ ions/cm$^2$, respectively, in a 5UDH-pelletron accelerator at room temperature at National Centre for Physics, Islamabad, whereas sample 1 was kept pristine. The morphological analysis of the samples were carried out by a Jeol JSM-6510 LV scanning electron microscope. The FTIR spectra were conducted with a Perkin Elmer spectrum 100 series FTIR spectrometer. Optical properties were carried out by using a Perkin Elmer LAMBDA 950 UV-vis spectrometer. For x-ray diffraction study, a Bruker D8-ADVANCE diffractometer was used.

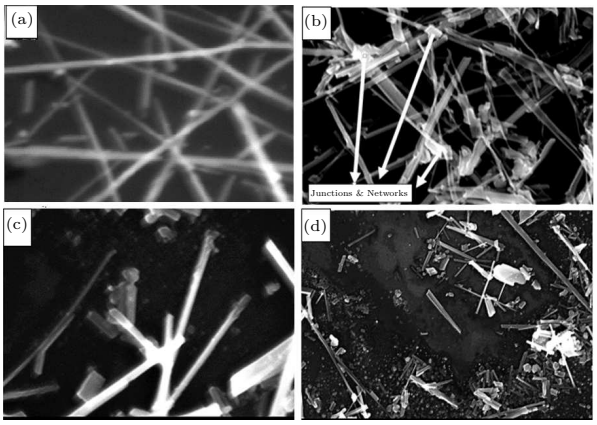


**Fig. 1.** (a) SEM image of pristine sample 1. (b) SEM image of sample 2 (irradiated at $5\times10^{12}$ ions/cm$^2$) showing formation of various networks and joints. (c) SEM image of sample 3 (irradiated at $1\times10^{13}$ ions/cm$^2$). (d) SEM image of sample 4 (irradiated at $5\times10^{13}$ ions/cm$^2$)

The SEM images of the samples are taken and analyzed to study the effects of Cu ion beam irradiation on the morphology of samples. The SEM image of the pristine sample (Fig. 1(a)) shows the formation of $SnO_2$ NWs of varying diameter. Figures 1(b)–1(d) show the SEM images of the irradiated samples. These figures clearly indicate the coalescence of $SnO_2$ NWs at the junction points. The fusion or coalescence of $SnO_2$ NWs is due to the local heating produced by Cu ion irradiation and collision cascade effect.[14] To understand the coalescence phenomenon, we have simulated 0.8 MeV Cu ions in $SnO_2$ to calculate electronic energy loss $S_e$, nuclear energy loss $S_n$ using TRM/SRIM,[15] which are found to be $8.13\times10^1$, $9.7\times10^1$ eV/Å, respectively. It is shown that both $S_e$ and $S_n$ are almost equally responsible to deposit energy. This confirms our experimental results that Cu-ion-irradiation-induced local heating and collision cascade effect are the main causes to fuse nanowires each other. Recently, we reported the coalescence of silver nanowires under proton beam irradiation.[14]

XRD patterns of all the samples have been analyzed to identify the crystalline phases and to determine the grain size by using Cu $K_\alpha(\lambda = 1.5418\,\text{Å})$. The XRD patterns show prominent peaks at $2\theta = 25.77°$, $33.90°$, $37.38°$, $51.21°$ and $53.86°$. All these peaks correspond to $SnO_2$ tetragonal structure as per JCPDS 41-1445 standards. Peaks along (110), (101), (200), (211) and (220) planes confirm the crystallinity of the samples. The peak at $33.90°$ shows the most preferred crystal orientation in (101) plane indicating the growth of the sample in that direction. There is no extra peak appearing in the graph, which confirms the absence of impurities. However, when these NWs are treated with copper ions at the dose of $5\times10^{12}$ ions/cm$^2$, an extra peak at $45.57°$ is found to appear, which corresponds to elemental tin along (201) plane. When the ion-beam dose is increased, the extra peak becomes more and more prominent as depicted in Fig. 2. A similar type of behavior is also reported by Iqbal *et al.*[18]

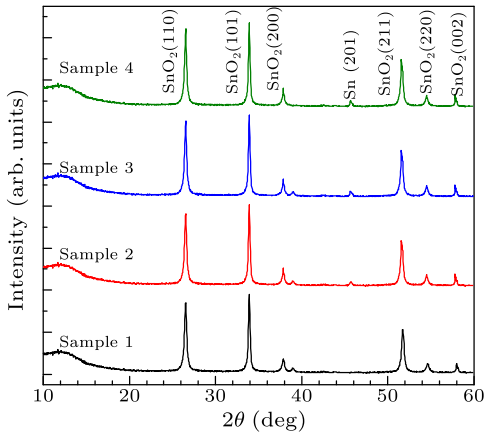


**Fig. 2.** XRD patterns of pristine (sample 1) and the copper irradiated samples (samples 2–4 irradiated with copper ion beam at the dose level of $5\times10^{12}$, $1\times10^{13}$ and $5\times10^{13}$ ions/cm$^2$, respectively).

From XRD analysis it has been verified that $SnO_2$ NWs have the tetragonal crystal structure with the lattice constants $a = b = 4.538$ Å and $c = 3.188$ Å. The grain size is calculated with the help of Debye–Scherrer's formula, $D = k\lambda/\beta\cos\theta$, where $k$ is a con-

stant, and $\lambda$ is the wavelength of x-ray (0.1541 nm). The estimated grain size for sample 1 is found to be 11.88 nm while the grain size increases with the Cu ion beam irradiation. This increase in grain size is due to the ion beam induced coalescence of NWs, which is consistent with the SEM results. Similar results were also observed in our ion beam irradiation effects on silver nanowires.[14,15]

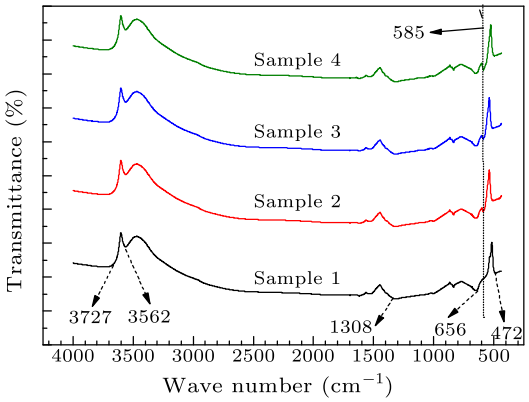


**Fig. 3.** FTIR spectra of all samples.

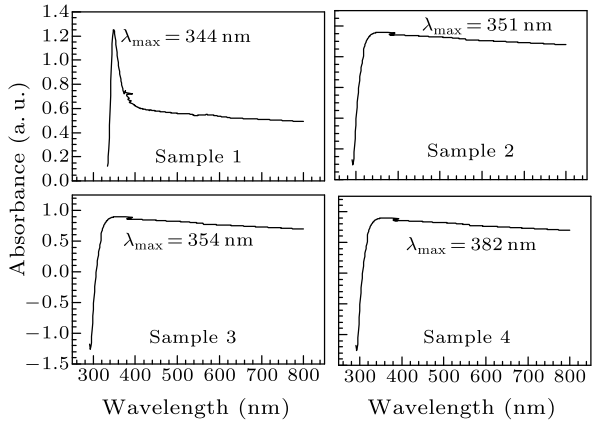


**Fig. 4.** Absorption versus wavelength characteristics of the $SnO_2$ samples.

The FTIR spectra explored important features of $SnO_2$ NWs at 470 cm$^{-1}$ and 656 cm$^{-1}$, which correspond to O–Sn–O and Sn–O stretching vibration,[19] respectively, as shown in Fig. 3. The bands around 1300 cm$^{-1}$ are assigned to bending modes of Sn-OH.[20] The symmetric stretching of H–O–H bond is also observed in the range of 3400–3700 cm$^{-1}$.[21] In Fig. 3, the most important feature is observed at 585 cm$^{-1}$, which corresponds to the vibration of the Cu–O bonds.[20] This feature is only observed in the irradiated samples. The appearance of this band confirms the presence of copper impurity in all the irradiated samples. To further confirm the presence of Cu impurity in $SnO_2$, we have simulated 0.8 MeV Cu ions in $SnO_2$ to calculate the stopping range using the TRM/SRIM[15] code, which is found to be 345.5 nm. It shows that most of the Cu ions are implanted into $SnO_2$.

The optical characterization is carried out by using a Perkin–Elmer, LAMBDA 950 spectrometer in the wavelength ranging from 200 nm to 800 nm. Figure 4 shows the absorption versus wavelength plot of pristine and irradiated samples. From Fig. 4 it can be seen that when the nanowires are irradiated by the copper ion beam, the absorption tendency of nanowires is shifted towards the region of high wavelengths. This band edge shifting towards lower energy implies that the size of the nanoparticles increases after ion beam irradiation.[14] This phenomenon can be explained by the fact that ion beam irradiation results in coalescence of nanowires owing to local heating. Thus NWs fuse together to form joints which consequently results in the increase of the particle size. It has been reported[22] that if the absorption edge is shifting towards the higher wavelengths, it essentially shows that the size of the nanoparticles is increasing.

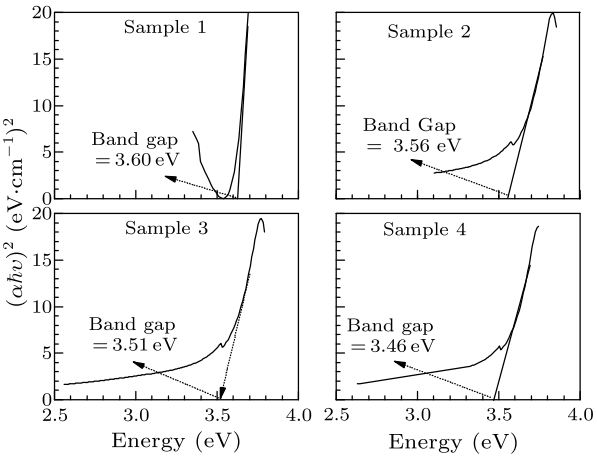


**Fig. 5.** Tauc's plots of the pristine (sample 1) and the irradiated (samples 2–4) samples.

The optical band gap values were calculated from the optical absorption spectra by using Tauc's relation

$$\alpha h\nu = A(h\nu - E_g)^n,$$

where $\alpha$ is the linear absorption coefficient of the sample, $h\nu$ is the incident photon energy, $A$ is the energy independent constant, $E_g$ is the optical band gap energy, and $n$ is a constant which determines the type of transition. We use $n = 1/2$ due to the fact that $SnO_2$ is a direct band gap semiconductor. Tauc's plots of the samples are illustrated in Fig. 5. A decrease in optical band gap of the samples has been observed with the increase of the ion beam dose. For example, the band gap of sample 1 is found to be 3.60 eV, which is in good agreement with the reported values. The band gap of sample 2 is reduced to 3.56 eV. For samples 3 and 4 it is further reduced to 3.51 eV and 3.46 eV, respectively. The dose level versus band gap plot is shown in Fig. 6. It clearly indicates that the band gap

is decreasing with the increasing dose level. For instance, at zero dose level (sample 1), the band gap is 3.6 eV. For a dose level of $5 \times 10^{12}$ ions/cm$^2$ (sample 2), the band gap is decreased to 3.56 eV. Figure 6 reveals that the band gap is decreasing linearly with increasing the dose level, and at relatively high dose level ($5 \times 10^{13}$ ions/cm$^2$) the band gap is decreased to 3.46 eV. This reduction in the optical band gap may be attributed to the irradiation-induced defects in our samples. It can be explained by the fact that during the ion implantation, Cu impurity is introduced in all irradiated samples. This is confirmed by the FTIR spectra as well as the stopping range of Cu ions in $SnO_2$ (345.5 nm). Thus we may conclude that the reduction in the band gap in our samples is due to the presence of Cu impurity which can create defect levels within the band gap of material, resulting in the reduction of band gap.[17,23]

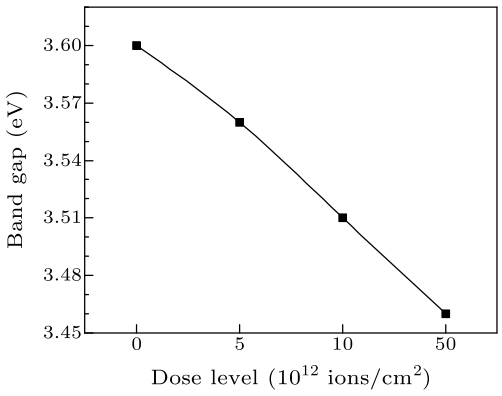


**Fig. 6.** Dose level versus band gap of the pristine (sample 1) and the irradiated samples (samples 2–4).

In conclusion, copper ion beam irradiation of $SnO_2$ NWs has been investigated in this work. The samples are irradiated at different doses ($5 \times 10^{12}$, $1 \times 10^{13}$ and $5 \times 10^{13}$ ions/cm$^2$). The irradiated samples show the coalescence of nanowires as examined using SEM. XRD patterns confirm the tetragonal phase of $SnO_2$. FTIR spectroscopy has been utilized to study the vibrational modes of the samples. The FTIR spectra have shown the appearance of new band (Cu–O) in all irradiated samples. UV-vis spectroscopy is employed to examine the optical properties of the samples. A red shift in the absorption edge along with a decrease in the band gap due to irradiation is observed. Thus irradiation is a reliable tool for nanoengineering and band gap tailoring.

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