



# Lithium ion beam impact on selenium nanowires

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## ARTICLE INFO

### Keywords:

Ion irradiation  
Selenium nanowires  
Texture analysis  
Electrical properties  
Impedance

## ABSTRACT

This study is structured on  $\text{Li}^{3+}$  ion irradiation effect on the different properties of selenium (Se) nanowires (NW's) (80 nm). Template technique was employed for the synthesis of Se nanowires. Exploration of the effect of 10 MeV  $\text{Li}^{3+}$  ions on Se NW's was done for structural and electrical analysis with the help of characterization tools. X-ray diffraction revealed the variation in peak intensity only, with no peak shifting. The grain size and texture coefficients of various planes were also found to vary. Current-Voltage characteristics (IVC) show an increment in the conductivity up to a fluence of  $1 \times 10^{12}$  ions/cm<sup>2</sup> and a decrease at the next two fluences. The effects of irradiation are presented in this paper and possible reasons for the variation in properties are also discussed in this study.

## 1. Introduction

In the recent years, a great deal of interest has been found in the synthesis of nanomaterials and nanodevices because of their unique properties. A development in semiconducting based nano-devices of small dimension and uniformity is a necessary stair toward developing the next generation technology. Apart from 2D or 3D materials, 1D nanostructures holds different properties. These are the smallest dimensional structure that can efficiently transport electrical carriers, and thus can be used as bases for the construction of new generation integrated nanoscale electronic and photonic devices. Semiconducting nanowires possess massive application in nano-electronics and photoelectric elements like solar cells, photo detectors, lasers and sensors [1–4].

Selenium is an important VI group p-type semiconductor, having energy band gap of the order of 1.6 eV. Due to high catalytically activity, high photoconductivity ( $8 \times 10^4 \text{ scm}^{-1}$ ) and functional properties in superconductivity [5,6] one dimensional selenium nanowires have been studied extensively. Selenium nanowires find utility in the area of solar batteries, photoelectric cells, light-measuring devices, xerography and their spectral response to entire visible range is much needed characteristic required for photoconductor. Synthesis of 1D nanostructures can be achieved by various techniques like, sonochemical approach, self-seeding process, hydrothermal method, vapor phase growth, template based method and many more. Among these, template assisted electro-deposition is a versatile and efficient technique for the growth of nanowires with controlled diameter, length and shape [7].

Irradiation of nanomaterial with swift heavy ions (SHI) is a unique tool for engineering the properties of nanostructures and involved a lot of attention in last few years. Modification in nanostructures can be achieved by low or high energy ions. SHI irradiation can be used to enhance the structural, photo electronic and optical properties of the materials. Energy of SHI in target material imparted through two mechanisms: (a) nuclear energy loss ( $S_n$ ), which involves transfer of energy to target atom through elastic collision and dominates at low energy ( $< 1 \text{ MeV}$ ) and (b) electronic energy loss ( $S_e$ ) which is inelastic collision between incident ion and electron of target atom and dominate at higher energy ( $> 1 \text{ MeV}$ ) [8]. In case of swift heavy ions irradiation, electronic energy loss ( $S_e$ ) is dominating process due to inelastic collision. Energetic ion piercing crystal lattice creates excitation and ionization process which leads to creation of wide variety of defects like; defect clusters, vacancies and dislocations which affect the energy levels and changes their physical properties in controlled way [9–11]. The creation of defects mainly depends upon mass, energy and fluence of the incident ion [12]. In the performance of the devices like, solar cells, sensors, schottky diodes etc. these defects play an important part with trapping and recombination of current carriers. Distributions of defects in material are mainly responsible for modification of the electrical and optical properties of the material [13,14]. A number of studies on irradiation of bulk and thin films were reported, but only a few papers in literature were found which provides much information about the irradiation induced modification in the properties of semiconducting nanowires [15–18]. But not so much work had done on the irradiation of selenium nanowires [19,20], which motivate us to move forward in this direction so that we gain much more information

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about effect of irradiation on selenium nanowires properties.

Present study deals with the study of modification in structural, electrical and optical properties of 10 MeV  $\text{Li}^{3+}$  ion irradiated selenium nanowires (80 nm) synthesized via template assisted electro-deposition.

## 2. Experimental details

### 2.1. Synthesis

All the chemicals used for synthesis purpose are of AR grade and used without any further purification. Se nanowires used in the present study were synthesized by electro deposition with a three electrode set up using electrolyte, containing selenium dioxide ( $\text{SeO}_2$ ) and boric acid ( $\text{H}_2\text{BO}_3$ ) having pH around 2. Ion track etched polycarbonate membrane (whatman make) having pore diameter 80 nm, coated with thin layer of gold-palladium alloy, were used for deposition of selenium nanowires. Deposition was carried out at room temperature ( $30 \pm 2^\circ\text{C}$ ) in a Perspex cell having a hole (1 cm diameter) at the bottom for 7 min. Deposition voltage was optimized using cyclic voltammetry. Deposition was carried with the help of SP-240 Biologic Potentiostat via chrono-ampereometry technique. All the potentials were applied with respect to Ag/AgCl reference electrode. A thin platinum wire of diameter around 5 mm served as counter electrode and a copper substrate on which template was placed acted as working electrode and filling of pores took place during electro chemical deposition. After completion of deposition electrolyte was poured off and sample was removed carefully from working electrode.

### 2.2. SRIM calculations

The range of  $\text{Li}^{3+}$  ion in selenium nanowires was calculated with the help of SRIM software and was found to be  $21.75\ \mu\text{m}$  which is larger than length of nanowires ( $10\ \mu\text{m}$ ), so probability of implantation is negligible. 10 MeV  $\text{Li}^{3+}$  ions in selenium nanowires have electronic stopping power  $37.733\ \text{eV}/\text{\AA}$  whereas nuclear stopping power was  $30.061 \times 10^{-3}\ \text{eV}/\text{\AA}$ . So in present case, modifications in target material were mainly due to electronic excitation.

Inside targeted material, the trajectories of incident ions strongly depends upon their energy. At low energy, the trajectories follow zigzag pattern showing large random deviation from initial direction and a significant straggling. On the other hand, at high energy where electronic stopping dominates, the trajectories basically remain straight with small straggling and well simulated by SRIM 2008 programmer shown in Fig. 1. TRIM calculation for damage inside Se material during Li ion bombardment are shown in Fig. 1, which confirms that mostly lithium ions ionizes the target material with only a few amount of target vacancies. Some restrictions are also there with TRIM calculation as it calculates only for smooth surface and no consideration was made on damages produced by previous incident ion.

### 2.3. Irradiation parameters

Selenium nanowires were irradiated with 10 MeV  $\text{Li}^{3+}$  ions from Inter University Accelerator Centre (IUAC), New Delhi, India for different fluences ranging from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The samples were mounted on a copper ladder having four faces perpendicular to the ion beam flux. The samples were irradiated in vacuum chamber ( $6 \times 10^{-6}$  Torr) by ion beam magnetically scanned over an area of  $1 \times 1\ \text{cm}^2$ . Ion beam current was maintained constant at 1 pA (particle nano Ampere) at the time of experiment. The reason of using such low current was to avoid burning of polycarbonate membrane due to rise of temperature.

### 2.4. Characterization

Rigaku Mini-Flex diffractometer equipped with  $\text{CuK}_\alpha$  radiation ( $\lambda=1.54\ \text{\AA}$ ) was used for structural analysis of pristine and irradiated samples at a scan speed of  $2^\circ/\text{min}$ . Estimation of crystal size was made from peak broadening by Scherrer method. SEM image provide morphological information and were recorded by using JEOL JSM-6390 LV. Before morphological analysis, template was dispersed using dichloromethane, ethanol and de-ionised water. To make sample surface conducting, sample was coated with gold platinum alloy in JEOL JFC-1600 Auto Fine coater unit. I-V measurements were carried out with the help of Keithley-2400 series source meter and Ecopia Probe station using two probes.

## 3. Results and discussion

### 3.1. Morphological analysis

Surface morphology of pristine samples was investigated by SEM as shown in Fig. 2. The length of wires was estimated around  $10\ \mu\text{m}$  which confirms the complete and uniform deposition of pores. Dissolution of membrane affects the wires like wires gets slanted or may be breaking can takes place.

### 3.2. Structural analysis

For structural analysis XRD spectra of irradiated nanowires was compared with pristine, as shown in Fig. 3. The presence of a number of peaks from different family suggests the polycrystalline nature of pre- and post-irradiated samples. The observed XRD spectra closely match with the JCPDS card no. 020677 which confirms the Hexagonal structures of as prepared nanowires with lattice constants  $a=0.443\ \text{nm}$  and  $c=0.511\ \text{nm}$ , which are in the range of the standard values given in the JCPDS card. On comparing the XRD spectra of pre- and post-irradiated samples, no shifting in the “2 $\theta$ ” position was observed but variation in the peak intensity was noticeable. This variation in the peak intensity is a directly reflection of the crystallographic orientations of the planes [21].

Estimation of preferred orientations can be done on the basis of texture coefficients (T.C.) [22] of the peaks given by

$$T.C. = \frac{I(hkl)/I(hkl)}{\frac{1}{n} \sum I(hkl)/I(hkl)}$$

where  $I(hkl)$  is the relative peak intensity as observed in XRD spectra,  $I_s(hkl)$  is the relative intensity of peaks as given in the standard JCPDS card and  $n$  stands for number of miller planes. The value of T.C. for different peaks is as shown in Table 1.

The maximum value of T.C. never exceed  $n$  and a value of texture coefficient greater than one for any peak indicate the preferred orientation of grains in the sample [23]. T.C. values mentioned in bold (Table 1) illustrated the preferred orientation of the crystal planes. Mentioned values of T.C. shows that the ion fluence affects the crystallographic orientation. Energy imparted by incident ions also affects the strain and reflection (R) of the material [24]. In pristine case, planes (110) and (400) show preferred orientation but after irradiation there is a decrease in the T.C. of these planes and a significant increase in the value of T.C. of (213) plane was observed. As the radiation passes through material, it imparts its energy to the target material which results in the form of planes movement, variation in the average grain size and strain. From X-Ray line broadening, the average grain size of pre- and post-irradiated samples was determined from Scherrer's formula [25],

$$D = \frac{k\lambda}{\beta \cos\theta}$$

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