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Effect of Gamma Rays Exposure on Cu-Se Heterojunction Nanowires

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Metal-semiconductor hetero-junction nanowires are a new class of material created by combining metallic and semiconducting materials. These materials exhibit unique features that could not be seen in the separate components at the nanoscale. With the development of technology, nanowire-based semiconducting elements play a significant part in the generation of new devices that are currently expanding quickly. Pre and post gamma exposed Cu-Se heterojunctioned nanowires were characterised to recognize the impact of gamma exposure. I-V measurements of heterojunction nanowires reveal an increase in current with the gamma dose. XRD of Cu-Se nanowires before and after irradiation showed no change in peak positions, but there were a variation in grain size and the texture coefficient. UV-Vis spectroscopy demonstrates that the optical band gap decreases with dose rate.[1]

Keywords: Heterojunction, Gamma Irradiation, Structural properties, Optical properties, Electrical properties

1 Introduction

Since their invention, heterostructures remain potential candidates for novel device applications. Now a days, low dimensional heterostructures especially 1D heterostructures, attracts the interest of the research community. A novel miniaturized semiconductor device can have a unique metal-semiconductor contact made at the nanoscale by connecting a metallic nanowire to a semiconductor nanowire.

Due to promising advantage of confinement effect and their applicability in different applications like, nanoscale electronics, photonis and sensors, 1D heterostructures are attracting the attention of different researchers[1]. Hetrojunctions serve as fundamental components in nanodevices and other applications, such as electromechanical, electrochemical, and optoelectronic ones.[2- 4]

Only a few reports have been published so far regarding the successful fabrication of heterostructures within a specific 1D nanostructure. However, in order to construct nanoscale devices, various nanostructures with distinct sections such as semiconductor, metal or insulators must be brought together to generate junctions with specific features. Only a few papers have been published on the effective fabrication of heterostructures inside a particular 1D nanostructure. Copper-Selenium heterojunction nanowires were made using a step-electrochemical technique with template confinement. A brief description of devices based on Cu-Se hetero-junction nanowires addresses the important issue of gamma irradiation effects. The irradiation of materials with gamma rays has proven to be an efficient method for modifying their physical, optical, and electrical properties because of its strong penetrating ability.[5, 6] Gamma exposures can have both short-term and long-lasting effects on the heterojunction properties, depending as a function of radiation dose.[7] Gamma irradiation produces modifications within the structure, optical and electrical properties of semiconductor material. However, a few research work, have been conducted to look at the electrical, optical, and microstructural properties of gamma-irradiated heterojunctions.[8- 12] Gamma exposure effect on various properties of Cu-Se heterojunction nanowires are the subject of the current research.

2 Materials and Methods

2.1 Synthesis

Chemicals used for synthesis of Cu-Se nanowires are copper sulphate, selenium dioxide and boric acid (Aldrich Company - AR grade). Electrical deposition was performed in the pores of a grooved

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*Corresponding author (E-mail:sony.spanchal@gmail.com) polycarbonate membrane, manufactured by Whatman with a pore diameter of 100 nm. Before electro deposition of heterojunction nanowires, membrane was coated with gold-palladium alloy to achieve adequate electrical connection prior to deposition on one side of the film. This coated template, which is capable of making good contact after placing on copper substrate, serves as working electrode for electrodeposition. Working electrode is placed inside electrolyte in such a way that open side of pores is facing up. For the deposition of required heterojunction between copper and selenium part a two-step procedure is adopted. The deposition of the copper fraction up to half the pore length is performed in the first step, followed by the deposition of the selenium fraction in second step.

All depositions were performed at room temperature (32 ± 2) °C. Electrochemical deposition of heterojunctioned nanowires (selenium and copper), a three-electrode configuration was used. The reaction was controlled by chrono-amperometer the SP-240 biological potentiometer.

For the deposition of Cu- segment, an electrolytic solution of 1M $CuSO_4$ is used along with Cu metal road as an anode. The deposition potential during Cu deposition is maintained at 0.4 V. To deposit Se nanowire section, an electrolyte consisting of 0.4 M SeO_2 and 0.4 M H_2BO_3 was used with a pH value of approximately 2. A potential of - 1 V was applied against reference electrode (Ag/AgCl). Deposition of Cu and Se nanowire segments was performed in the Perspex chamber for 5 and 7 minutes, respectively. For counter electrode a thin platinum wire having diameter 0.5 mm is used.

2.2 Gamma irradiation parameters

Electrodeposited Cu-Se heterojunction nanowires were exposed with doses of 50, 100, 150 and 200 KGy of gamma rays using Co^{60} source in the gamma chamber 1200 BNT of IUAC, New Delhi, India. Dose can be controlled by adjusting exposure time. During the time of irradiation process the activity of the Co^{60} is found to be 4.533 KGy/hour.

2.3 Characterization

XRD, SEM, UV-visible, and PL studies were performed to examine the gamma-irradiation-induced variation on various properties of Cu-Se heterojunction nanowires. Structural analysis of pristine and irradiated nanowires was performed on a Rigaku Mini-Flex II XRD using CuKα radiation (λ=1.54 A°) at a scanning rate of 2°/min. Microscopic images of specimens taken with a JEOL JSM-6390LV Scanning Electron Microscope (SEM). A double-beam UV-Vis spectrometer was used to study the optical properties. A two probe method was used to study the current voltage characteristic of pre- and post-irradiated samples. An arrangement of Keithley source meter (model- 2400) and two tip made of tungsten tip (diameter 10 µm) was used to study the I-V behaviour of Cu-Se nanowires at room temperature

3 Results and Discussion

3.1 Morphological analysis

The template method was used to directly deposit the Cu–Se heterostructure nanowires within the membrane pores on the copper substrate. SEM analysis was performed after template dissolution. The synthesis of intensity and uniform nanowires with nearly identical diameters of 100 nm (pore diameter) and length of 10 mm (membrane thickness) is depicted in figures 1a and 1b. However, the bending and breaking of wires occurs at some locations as a result of the membranes dissolution's with dichloromethane and ethanol.

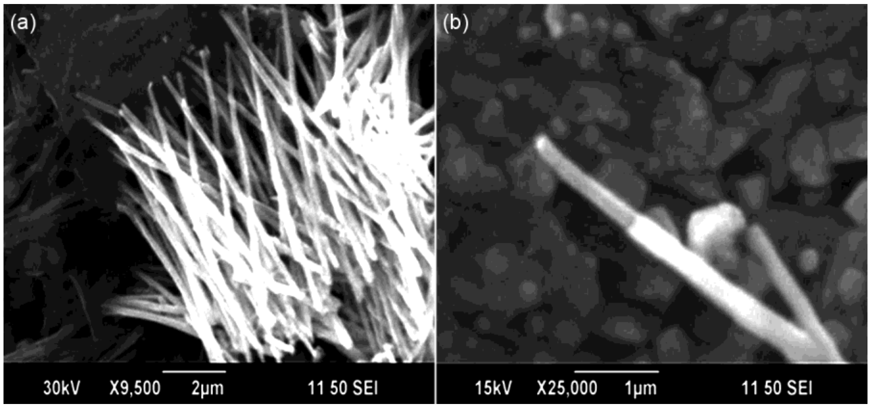

Fig. 1 — (a) SEM image of Cu–Se nanowires and (b) showing the heterojunction.

3.2 X-ray diffraction study

To investigate the effect on structure of nanowires XRD of pre and post irradiated samples were performed. The X-ray diffraction spectra of nanowires before and after gamma irradiation are depicted in Fig. 2. The irradiated and untreated samples were all examined by XRD, and the results showed that all of the samples had a single phase and were polycrystalline. Because there was no additional peak or peak shifting after gamma exposure, thus irradiation had no effect on the crystal structure of the sample. The JCPDS Card No. 24-0714 and 03-1005 was in good agreement with observed diffraction peaks for Selenium and Copper segments respectively, which demonstrate that copper and selenium have cubic and monoclinic structures, respectively. Both the pristine sample and the irradiated sample were subjected to XRD analysis, although the peak position did not change significantly, the intensity change was clearly visible. The preferred orientation results in a variation in the peak's intensities. A change in the magnitude of the plane height is a concern of the favored alignment. The intensity of a plane will increase in proportion to the number of planes facing that direction. The intensity of a plane is proportional to the number of planes facing in that particular direction. The XRD spectrum of pristine specimen reveals that the intensity of the reflected planes Se (002) and Cu (311) is highest. Clearly as the dose rate increases, the intensity Se (002) plane rises until a dosage of 100 kGy reached, after that a decline in intensity was seen. Yet the Se (231) plane's intensity rises as the dosage rate does. The Cu (311) plane, also exhibits intensity variation, but it continues to be dominate for copper segment. Several strains are released between the various grains by the gamma ray energy. Induced lattice vibration is causes reorientation of these regions. When high-energy gamma rays hit the target material, secondary electrons are expected to form. On interacting with atomic electron clouds, these high-energy secondary electrons can cause lattice displacement. The secondary electrons lose a significant amount of energy, allowing the nanostructures to reorganize and as a result of which altering the relative intensities of distinct peaks. An increment in the average crystallite size is confirmed from table 1 with dose rate. A decrease in the number of micro strains, dislocations, and increased calculated average crystallite sizes can result from the annihilation of structural defects caused by an increased gamma dose.[13-17] Calculation of average crystallite size (D), strain (ε), and dislocation (δ) density is already discussed in our previous study.[10]

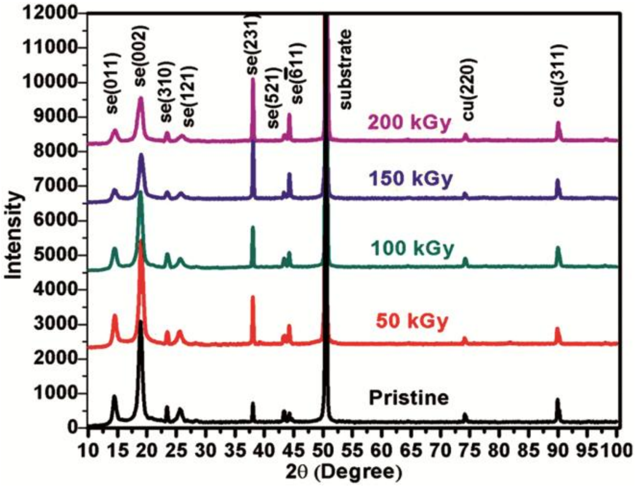

Fig. 2 — XRD Spectrum of pre- and post- Gamma exposed Cu-Se heterojunction nanowires at various Doses.

3.3 UV–visible absorption spectroscopy

To study the optical characteristic of heterojunction nanowires a room temperature UV-Visible spectroscopy was performed for all the samples. Figure 3 depicts the UV-Visible spectroscopy of Cu-Se hetro-junction nanowires at room temperature. UV absorption study shows with increase in dose rate absorption edge shifts toward wavelength from 683 nm (for pristine) to 745 nm (for samples irradiated with 200kGy). Tauc's plot, Fig. 3, was used to estimate the energy band gap of pristine and irradiated samples and a decrease in band gap was

Table 1 — Average crystallite size, strain and dislocation density

Dose Rate	Crystallite Size (D)		Strain		Dislocation Density (× 10^{15})	
	Selenium	Copper	Selenium	Copper	Selenium	Copper
Pristine	26.28	28.42	0.010	0.0023	1.45	1.24
50 kGy	26.96	30.05	0.010	0.0021	1.38	1.11
100 kGy	28.36	31.63	0.010	0.0020	1.24	1.00
150 kGy	29.55	32.17	0.009	0.0019	1.14	0.97
200 kGy	30.27	34.98	0.009	0.0019	1.09	0.82

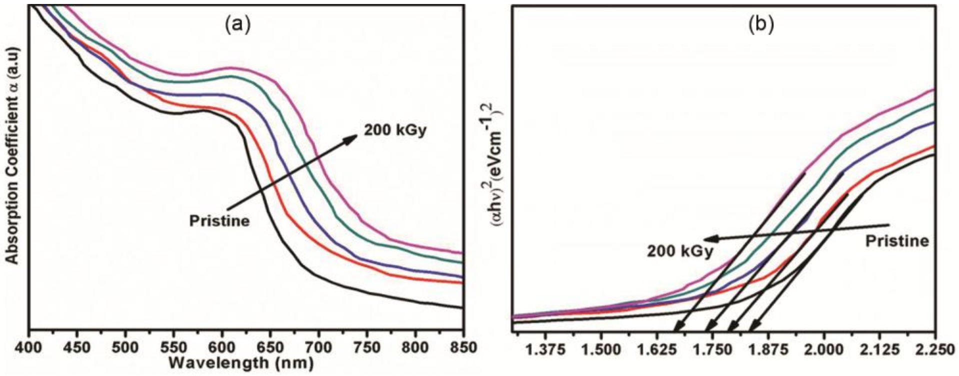

Fig. 3 — (a) Absorption spectra for pritine and irradiated samples, & (b) Tauc plot for pristine and irradiated samples.

found to be from 1.82 eV (pristine) to 1.66 eV (200 kGy). This decrease may be due to the growth of defects like, point defects (vacancy), dislocation, grain boundary generation, and rise in defect levels. When gamma rays interact with target material it may cause both defects creation and defect annihilation simultaneously. In the present study, perhaps, defect creation is dominating which results in mid gap localized states states in between the band gap on account of which a shifting of absorption edge toward longer wavelength takes place. Recent studies regarding irradiation also points toward an optical band gap reduction.[16-18]

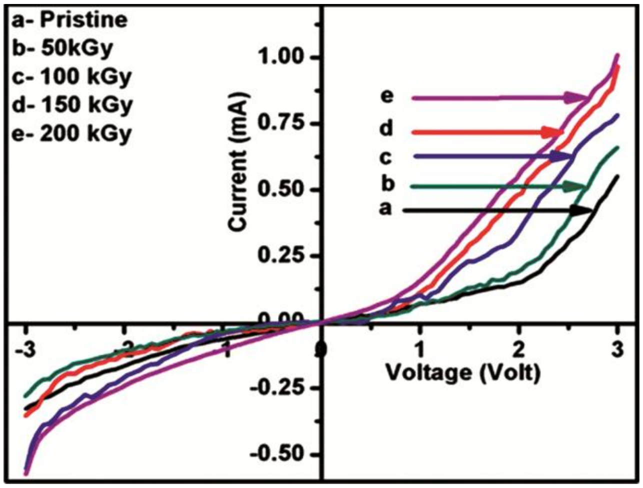

Fig. 4 — I-V characteristic of pristine and irradiated Cu-Se nanowires.

3.4 Electrical properties

Figure 4 shows (I–V) characteristic of heterojunctioned nanowires at varying gamma dose. The resultant current voltage characteristics in positive and negative bias regions are a consequence of hetero – interface nature. A rectifying behaviour is clearly visible from non-linear curves of I-V graph and is a consequence of rectifying behaviour of metal–semiconductor interface.[19-21] After gamma exposure, threshold voltage (V_{th}), the voltage at which current begins to rise in the positive and negative voltage region clearly decreases with dose in other words the conductivity of hetero-junction nanowires increases with dose rate. The primary Compton electrons receive more energy from high-energy gamma ray photons. After that, the primary electron makes secondary electrons, which can hold as much energy as the primary photon. This energy is then released as kinetic energy, which causes the material's atoms to ionize and become excited. As a result of the gamma-rays' initial ionization and damage, numerous electron-hole pairs are formed. Therefore, for post gamma irradiation, a large number of electron-hole pairs are produced due to the ionization effect of secondary electrons. The junction width narrows as a result of this enhancement in the current carrier density, lowering the potential barrier height of the selenium sement. The rectification behavior is also improved by interface smoothing and surface defect states reduced by irradiation defect annealing.[22-24] Therefore, the current-voltage behavior of heterostructured nanowires is improved by smoothing of interface and increase in conductivity of the semiconductor and metallic parts of the heterostructure. Additionally, as confirmed from XRD analysis, crystallite size increases after irradiation and consequently the quantity of grain boundaries decreases. Scattering of current carriers from grain boundaries contributes toward resistance of material, which affect the current voltage behaviour. But, after irradiation a decrease in quantity of grain boundaries results in a decrease in number of scattering and hence an increase in current voltage behaviour.

4. Conclusion

The influence of gamma irradiation on the electrical, structural, and optical properties of Cu-Se nanowires synthesized using template assisted electrodeposition was investigated. Uniform, homogeneous growth of Cu-Se heterojunction nanowires is confirmed by SEM images. No shift in the peak position is confirmed from XRD analysis along with increase in crystallite size and plane orientation. Furthermore, IV measurement and UV-visible analysis reveal variation in current-voltage characteristics and decrease in optical band gap respectively.

From present study we can conclude that gamma irradiation can utilized to increase crystal quality and hence rectified optical properties and electrical properties.

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