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Study of Fe Ion-Implant Doping on Structural, Optical and Electrical Properties of Electrochemically Synthesized CdS Nanowires

Jaskiran K* and Singh RC

Department of Physics, Guru Nanak Dev University, Amritsar, India

***Corresponding author:** Jaskiran K, Department of Physics, Guru Nanak Dev Amritsar, University, India, Tel: +91-9779167670; E-mail: kaur.jaskiran@gmail.com

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Abstract

Present paper shows the effect of Fe implantation on structural, optical and morphological properties of cadmium sulfide CdS nanowires. Nanowires of diameter around 100nm were synthesized using track etched method homemade electrochemical cell. Later CdS nanowitres were implanted with 80KeV Fe+ ion at room temperature with a fluence ranging from E14 TO 5E16 ions cm-2. Properties of the structures were investigated using XRD, UV, PL and electrical characterizations. X ray diffraction study shows that Fe ions are occupying the substitutional sites instead of forming any metallic clusters or secondary phase. There are changes in optical band gap and the PL intensity owing to the increased implantation fluence. Although the structure shows non-ohmic behavior there is noticeable change in saturation current.

Keywords Ion implantation; Nanowires; SEM; XRD; Uv-Visible spectroscopy; PL; IV characterization

Introduction

Recently there has been wide focus on promising spin-transport electronic (spintronic) devices such as spin-polarized light-emitting diodes, lasers, and field-effect transistors, nonvolatile memory, and magneto-optical switches leading to the research in the area of transition metal (Mn, Co, Fe, etc.) doped semiconductors. Cadmium sulfide (CdS) has an wide band gap of 2.42 eV (at room temperature) because of which it has been used in various optoelectronic devices [1-4]. Further doping in CdS nanowires can make them more useful in the field of room temperature (RT) ferromagnetism and tunneling magnetoresistance [5,6]. Transition metal doping of CdS can demonstrate wide variation in their intrinsic properties [7]. Although, there are different methods available for the doping, including pre and post synthesis, like co-evaporation, electrodeposition, chemical vapor deposition, spray pyrolysis etc yet ion implantation is more fast and controlled [6,7]. Ion implantation produces lattice disorder and extended defects but still the advantage of introducing controlled amount of impurities into a target material which is independent of the solubility limit of the impurity overweights the disadvantage. In the present study we attempt to study the effect of ion implantation induced Fe doping in CdS nanowires, grown *via* electrodposition in polymeric templates. It has been found that the Fe ion does not cause any phase transformation or forms any cluster. But it does effects the optical band.

Experimental

Thin polycarbonate films (thickness 10um) were irradiated at room temperature with 80 MeV Ag ions at a fluence of 8E7 using the ion beam facility at 15UD Pelletron accelerator IUAC, New Delhi, India. During irradiation, the samples were kept at room temperature and in vacuum of the order of 5E-6 mbar. Irradiated samples were then exposed to UV (365 nm, 150 W/cm2) so as to increase the selectivity of the chemical etching. Later etching was carried out with 6N NaOH solution at room temperature for 25 mins in a homemade one-compartment cell. Electrolytic solutions were prepared with ion-exchanged water containing CdS Bath: CdCl2.H2O (200mM) and Na2S2O3 (10mM), and H2SO4 98 g/L (1.0 mol/L) [8-9]. Deposition was carries out in an electrochemical cell at room temperature for 60 min. Thereafter samples were properly washed using double distilled water. To revel the nanostructures the nano-porous template was dissolved using DCM, leaving behind free standing CdS nanowires.

Later these free standing wires were impalanted with 80keV Fe+ ions at room temperature for a fluences ranging from E14to 5E16 ions cm-1. The nanostructure of the Fe-ion implanted CdS nanowires were studied using glancing angle X-ray diffraction (GAXRD) technique, UV-visible spectroscopy and Photoluminescence spectra.

Results and Discussion

Morphological and structural analysis

According to Monte Carlo SRIM2008 simulation projected range of 80 keV Fe+ ions in CdS is around 46.0 nm [10]. Figure 1 shows the SEM image of nanowires used for implantation of Fe ions. Image shows nanowires with uniform and cylindrical structure standing perpendicular to the surface. Using the Cu-Kα radiation (λ=0.154 nm) x ray diffraction studies were carried at a glancing angle of 2◦. Figure 2 shows the GAXRD patterns of the CdS nanowires before and after Fe implantation induced doping. Graph shows the polycrystalline nature of the wires and the peak positions observed matches well with the Simple Cubic structure of CdS [11]. As the fluence increases a systematic decrease in the peak intensity has been observed. These changes may be attributed to the effect of Fe doping-induced lattice disorder and related effects caused during implantation [12]. Among the different types of ion implantation modification in materials, lattice disorder is the most undesirable one. The mass and the energy of the implanted ion decide the extent and range of the disorder. Sometimes these disorders makes the material completely amorphize. But in the present study medium preserves its morphology and stays in its preferred orientation along (111) (311) and (220), even after the high implantation fluence of 5E16. Although as the fluence increases peak intensity decreases, but the peak position remains the same. Along with that no new peak appears and no formation of metallic clusters or secondary phase has been observed. This could occur because of the supersaturation of embedded particles into the

substitutional cationic locales. This shows that the material is resistant to the energy and the fluence range of Fe implantation.

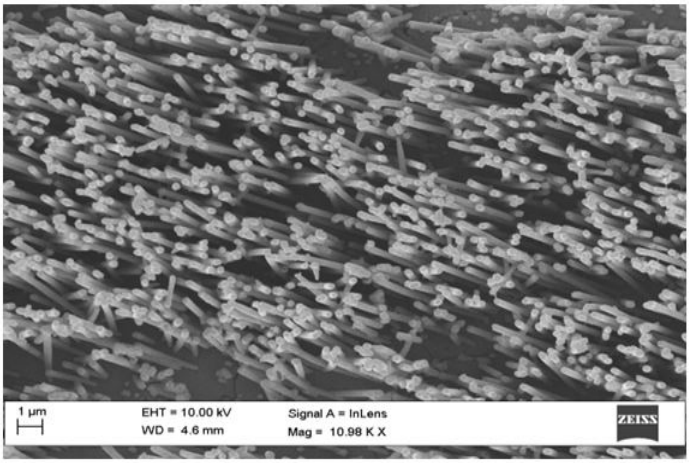

Figure 1: SEM iamge of CdS nanowires synthesized *via* electrochemical template method.

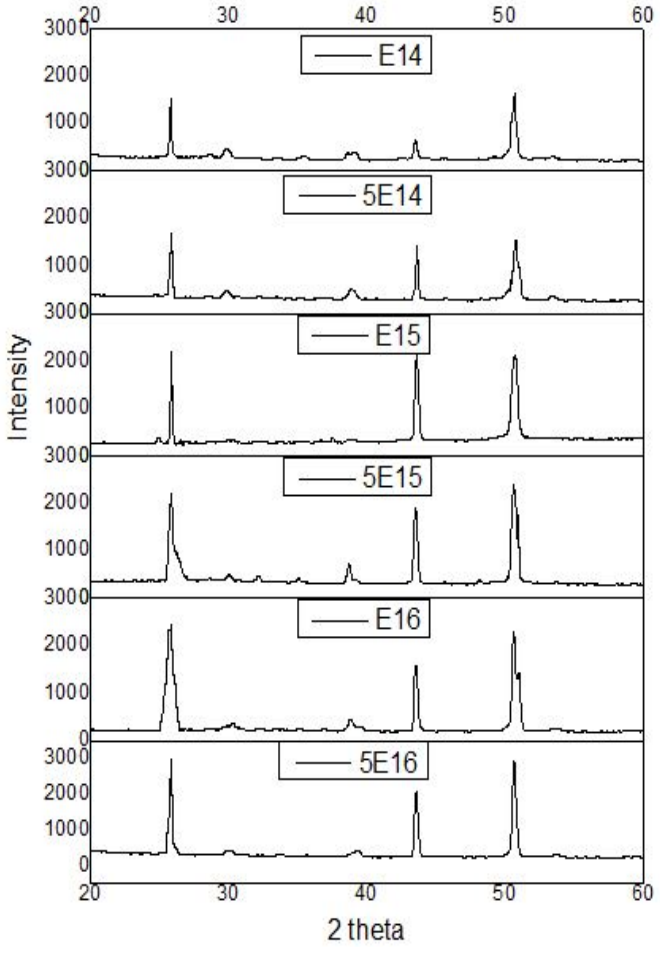

Figure 2: GAXRD patterns of the Fe+-implanted CdS nanowires for different ion fluences.

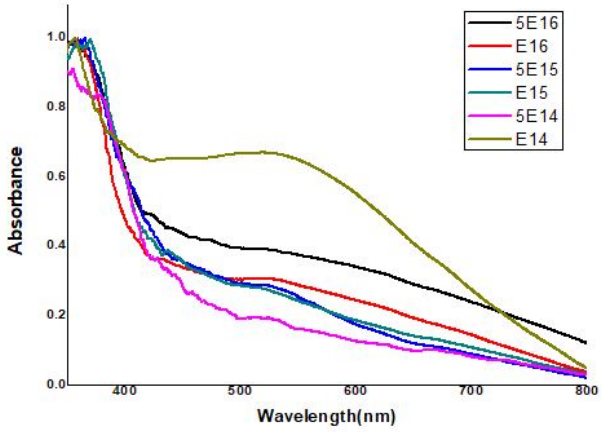

Figure 3: UV patterns of the Fe+-implanted CdS nanowires for different ion fluences.

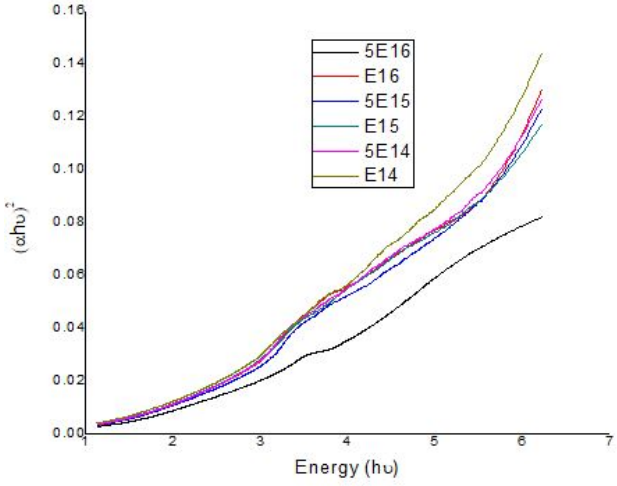

Figure 4: GAXRD patterns of the Fe-implanted CdS nanowires for different ion fluences.

Optical characterization

The threshold energy required for charge transition between the highest nearly filled band and the lowest nearly empty band corresponds to the absorption edges of semiconductors. According to the interband absorption theory, the optical band gap (Eg) of a semiconductor can be calculated using the Tauc relation [13].

$$\alpha h\upsilon = A(h\upsilon - Eg)n \quad (1)$$

Where A is the probability parameter for the transition, hυ is the incident photon energy, and n is the transition coefficient for a direct allowed transition, n is equal to 1/2. The optical absorption measurements were carried out by using UV1800 Spectrophotometer. The optical absorption spectra of as deposited and Fe implanted CdS nanowires in the wavelength range 300–800 nm are shown in the Fig. 3. The strong absorption edge appeared at 410, 413, 423,437,460 and 495 nm, respectively, which indicate slight blue shift. The optical absorption is observed to be increased with increase in implantation

fluence. By extrapolating the linear part of the absorption curves (fig 4)to intercept the energy axis (αhυ=0), the value of Eg is obtained. The estimated band gap value of un-doped CdS nanowires were found to be 3.04eV, which decreases to 2.50eV with increasing Fe ion fluence. This reduction in the Eg can be attributed to several factors like induced defect/disorder, creation of impurity states, and grain size. When low energy ion interact with matter the dominate cause of energy loss is nuclear energy loss, which results in a dense collision cascade in the matter. Due to the increase in the temperature in the region it results into the thermal motion of all the atoms near the ion path. Further by heat conduction this high temperature spreads and reduces within the matter, known as thermal spike. Both the thermal spike and binary collisions may result into atomic displacements. Although most of the vacancies get annihilated by annealing process but a large number of defects like vacancies, interstitials etc are expected to say during implantation. Which in return act as trap centers to effect the optical absorption. therefore the observed decrease in band gap is due to the band tailoring caused by the creation of localized energy band near the band edges [14].

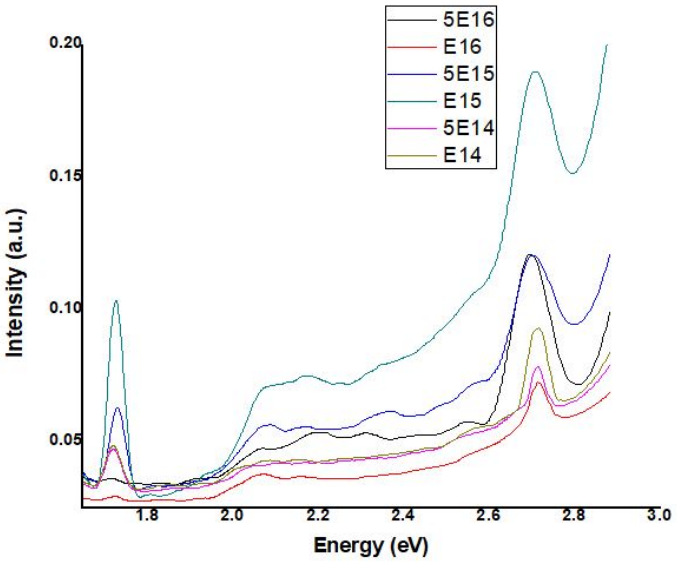

Figure 5: PL spectra of the Fe-implanted CdS nanowires for different ion fluences.

PL spectra of CdS nanostructures at different fluences were analyzed under the excitation wavelength of 420 nm.

The broad green emission band observed at 2.286 eV is attributed to the radiative transition from localized acceptor states generated by the sulfur interstitials to the conduction band.

Weak band centered at 1.72 eV, known as red emission band, which can be attributed to complex defects such as ICd-VCd Frenkel pairs. Incorporation of Fe ions into the CdS lattice changes the luminescence properties and a new peak at 2.7eV appears.

The 573 nm emission obtained assumes the involvement of impurity sub-band due to doping of Fe in CdS [15]. There are clear changes in the intensity of emission with increasing fluence which may be attributed to the presence of Fe ions.

Electrical study

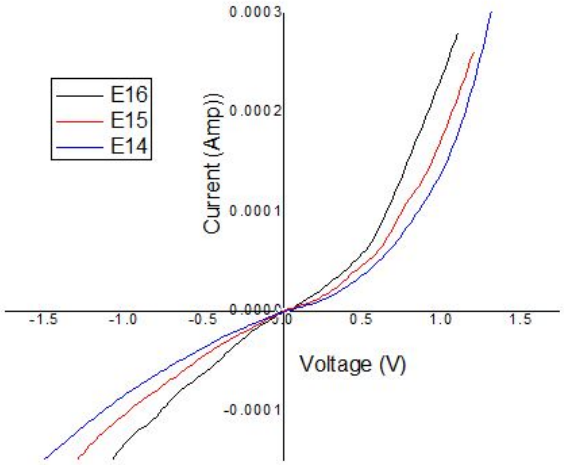

Figure 6: IV characteristics of Fe-implanted CdS nanowires for different ion fluences.

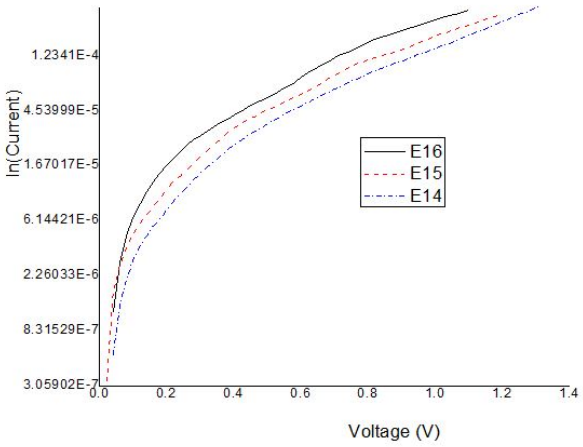

Figure 7: ln (I) vs V graph for Fe-implanted CdS nanowires for different ion fluences.

The I-V characteristics of in situ nano/micro structures were measured at room temperature by leaving the structures embedded in the insulating template membrane. A schematic view of measurement is shown in figure. A KEITHLEY 617 programmable electrometer having gold-coated base was used for the measurement. Although it is two points measurement system, the voltage drop however is minimized by making the voltage-contact nearer to the sample than the current-contact. The Fig 6 shows the voltage vs current characteristics for the nano structures implanted with ion ions at fluencies ranging. It is the collective behavior of nanowires lying parallel to each other.

Under the forward biased V at a fixed temperature

$I = I0 [\exp\{(q(V-IRs)/nkT)-1\}]$

N is the ideality factor, I0 is the saturation current and Rs is the diode series resistance. For a pure thermionic emission n=1. Fit of linear region of the forward biased semi-log IV curve (fig 7) (where V>3kBt and Rs is negligible) the value of ideality factor and Schottky

barrier height can be determined. Extrapolation of straight line portion of the plot to V=0 gives I0 and the slope S=d(lnI)/dV gives n.

Using I0 barrier height may also be calculated using the equation

ΦB=(kT/q)(AA*T2/I0)

Where A* is the Richardson constant and A is the electrical contact area [16]

From these plots we can have the values of identity factor and saturation current for iron doped nano structures as presented in Table 1.

Fluence	Slope mA/Volts	Intercept (Amp)
E16	3.84	9.68E-6
E15	3.75	6.94E-6
E14	3.67	5.38E-6

Table 1: Iron doped nano structures.

As the plots shows, the measured log I-V curve is not linear. Sze stated that if thermionic emanation is predominant, which is the significant current stream system for low impurity concentration, the curve should be linear [16]. Padovani and Stratton reported that even if thermionic-field emission is dominant, which occurs at a highly doped metal semiconductor interface, the log I-V curve is approximately linear [17]. While Lepselter and Andrews wrote that if direct tunneling is dominant, the current is directly proportional to applied bias which implies that the contact is ohmic [18]. However our results in fig 6-7 indicate that the contact does not follow any of the three models, but there is shift in plot showing the increase in current with doping which may attributed to increase in concentration of Fe ions.

Conclusion

In Conclusion, the present study shows the effect of low energy Fe ions doping on CdS nanowires with reference to the changes in structural, optical, morphological and electrical properties. The results show substitution incorporation of Fe ions into the CdS lattice, which in return causes changes in optical and electrical properties. Although the magnitude of change increases with the increase in ion fluencies, but there is no structural phase transformations or formation of any metallic clusters. Results shows decrease in the optical band gap of CdS nanowires (from 3.04 to 2.50 eV) following Fe doping, caused by disorder-induced band tailing effect. In addition there is an increase in conductivity with fluene as reflected from the IV graph.

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