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Green growth of CdSe nanostructures for application in Schottky type solar cell

ABSTRACT

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CdSe nanostructures were synthesized by using green chemical route as starch was used as capping agent. XRD, HR-TEM, SEAD, UV and PL studies were made for structural and optical properties of the prepared sample. Film morphology and the thickness measurement of n-CdSe were carried out with AFM analysis. I-V characteristics curve of this junction confirmed the formation of Schottky contact between silver (Ag) and CdSe nanostructures. Intrinsic and contact behaviors such as saturation current, barrier height, effective Richardson constant, electron affinity and ideality factor were calculated from the current-voltage characterization.

Keywords: *Green synthesis; CdSe nanostructure; Schottky cell; Optoelectronic characterization; Energy Band Diagram.*

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INTRODUCTION

The study of nanostructures had received much attention due to unique properties that are strongly dependent on the spatial dimension of the particles [1]. When the radius of nanostructures becomes smaller than the Bohr exciton of the material, quantum confinement effects dominate the optical and electronic properties of these particles [2]. Blue shift in the band gap of this material with decreasing grain size, has lead to many applied investigation [3,4]. Semiconductor nanostructures could offer good efficiency, longer life and cost advantages over the conventional semiconductor photovoltaic devices. Depending on the characteristics of the M-S interface, they can behave either as a Schottky barrier or an ohmic contact [5, 6]. The optical study of n-CdSe shown that they can be spanned the whole visible solar spectrum by tuning their shape and size. A green chemical route was used to utilize these properties CdSe nanostructures for fabrication of Schottky type cell.

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The electrical studies have been made for the Ag/CdSe//ITO junction and analysis of current-voltage characteristics allowed to understand different aspects of current transport mechanism of the device.

EXPERIMENTAL

Nanostructures of CdSe have been prepared by chemical method at 300K for 0.1M concentration in starch solution using cadmium acetate and sodium selenosulphate in equimolecular proportion. The pH value of the reaction system is of prime importance for the chemical deposition of CdSe film maintained at 8-9. The precursor of selenide ions, sodium selenosulphate used in the form of solution which has been obtained by adding selenium powder to a hot solution of sodium sulphite, magnetically stirring for 6-8 hours at 80°C.

RESULTS AND DISCUSSION

The structural characterization and average grain size of the nanostructures were done by X-Ray powder diffraction. The diffraction peaks for CdSe was observed at $2\theta = 25.5^\circ$ (111), 42.2° (220) and 49.5° (311) as in Figure 1. The highest intensity reflection peak was at 25.5° corresponding to (111) plane. The standard data indicated that the deposited film was having cubic zinc blende type structures. The strain and the particle size were calculated from the full width half maximum (FWHMs) of the diffraction peak using W-H plots. The linear combination of the contribution from the strain (ϵ) and particle size (L) can be expressed in terms of FWHMs (β) as given below

$$\beta \cos\theta/\lambda = 1/L + \epsilon \sin\theta/\lambda \quad (1)$$

The plot of $\beta \cos\theta/\lambda$ versus $\sin\theta/\lambda$ for CdSe nanostructures in the Figure 2 was straight line and the slope of the plot gives the amount of residual strain. The strain find out in this case was -7.3×10^{-2} for n-CdSe film. The negative value of residual strain for the thin film indicated the compressive strain. Again, the average particle

sizes of the nanostructures were calculated from the reciprocal of intercept on the $\beta \cos\theta/\lambda$ axis. The particle sizes were estimated 5.5 nm [7].

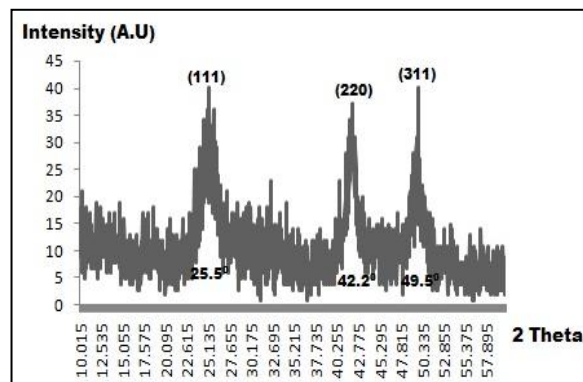


Fig. 1. XRD pattern of starch capped CdSe film

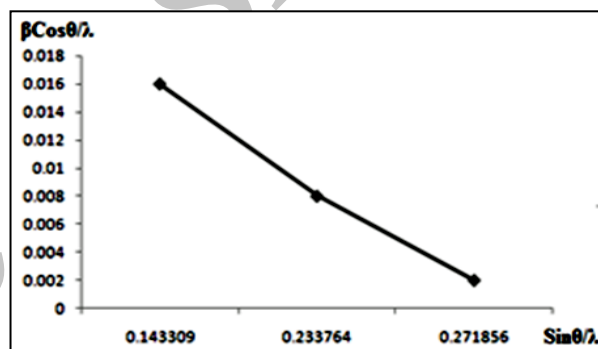


Fig. 2. Plot of $\sin\theta/\lambda$ versus $\beta \cos\theta/\lambda$ of film

A typical high resolution TEM image obtained for the sample as shown in Figure 3. The nanostructures were uniformly distributed with spherical shape. From the high resolution, the average sizes of the nanostructures were found to be 6-8 nm. The particle sizes obtain from TEM were slightly larger than that was calculated from XRD, may be due to some intrinsic defect of the sample [8]. Selected area electron diffraction (SAED) was taken for CdSe nanostructures as shown in Figure 4. The SAED pattern completely supported the result obtained from XRD. The (111), (220) and (311) planes were clearly observed in the SEAD from the diameter of the concentric rings. The elongated spots of the diffraction pattern were originated from the spherical nanostructures which intersects the Edward's sphere of reflection for different spots.

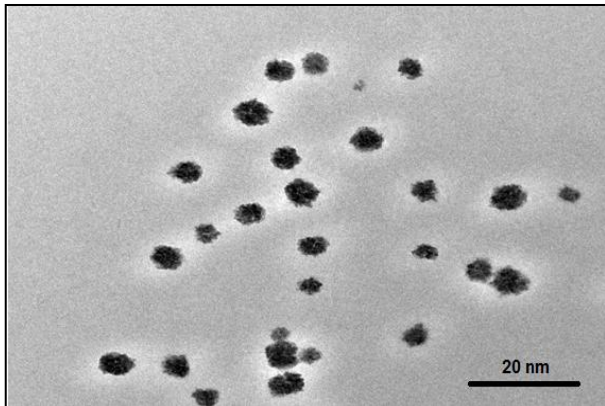


Fig. 3. HR-TEM image of CdSe nanostructures

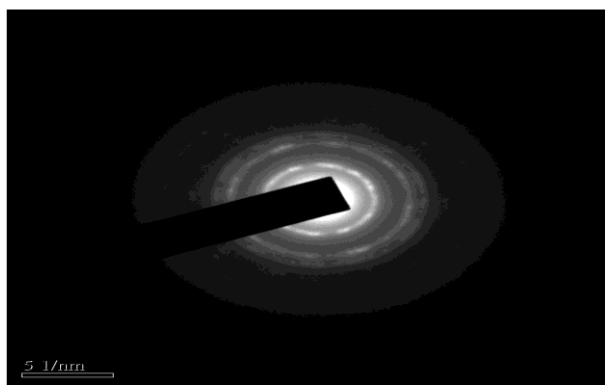


Fig. 4. SEAD image of CdSe nanostructures

The UV absorption spectra recorded for CdSe nanostructures is shown in Figure 5. There was an apparently absorption peak at around 480 nm, indicating a sufficiently narrow size of the prepared sample. The band gap calculated for the nanostructures was 2.5eV confirming the large blue shift of it. A decreased in the crystalline size was the cause of enhanced band gap. Optical excitation of electron across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the gap energy. The PL spectrum of the sample was found at 540 nm in Figure 6 and indicated the effect of quantum confinement. The narrow and high photoluminescence peak was a good sign of the efficient surface passivation of the crystallites. The capping groups were also protected the individual crystallites from chemical degradation to yield robust system [9].

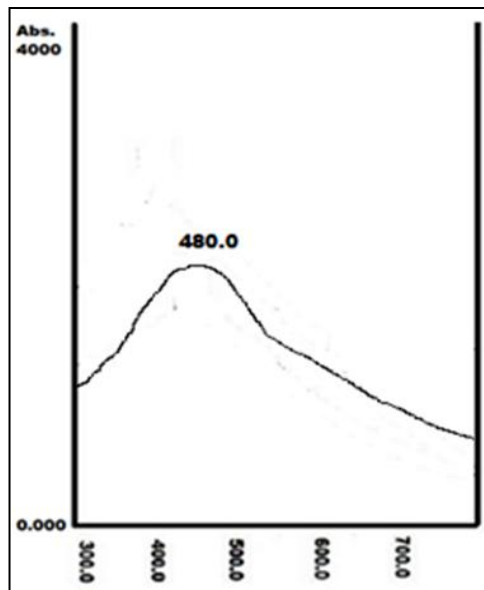


Fig. 5. UV Absorption Spectra of CdSe

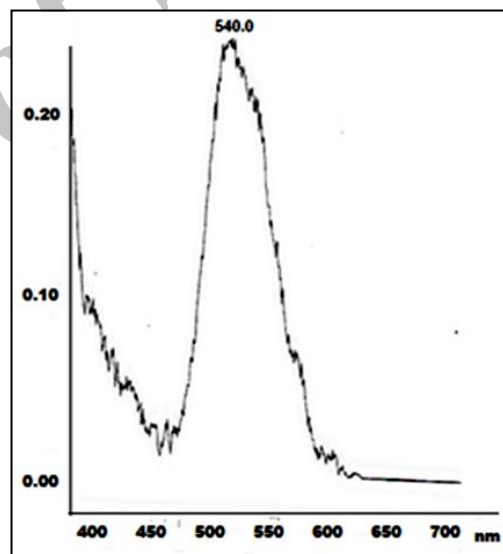


Fig. 6. PL Spectra of CdSe

A thin film of CdSe of area 2.89 cm² was prepared on ITO (Indium Tin Oxide) coated glass purchased from Sigma-Aldrich. The CBD (Chemical bath deposition) method was used for deposition of the CdSe thin film at room temperature. ITO and the Ag were utilized as front and back contact respectively. The silver (99.99% pure, purchased from Sigma Aldrich) film was deposited over CdSe by using vacuum coating unit, maintaining the pressure at 10⁻⁵ torr. The device structure of the Schottky type Solar cell is shown in

Figure 7. The thickness of the deposited film is of prime importance for the performance of the cell; therefore it was measured by AFM analysis. The graphical method was employed to measure the distance between the surface of ITO and the uppermost surface of CdSe film. The thickness measured for CdSe from **Figure 8** was 17 nm and therefore confirming the formation of thin film device.



Fig. 7. Ag/CdSe/ITO Schottky Type Cell

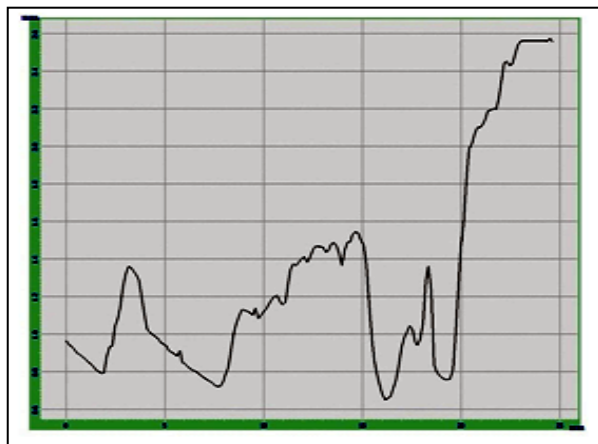


Fig. 8. Thickness measurement graph of CdSe from AFM

The size distribution of the deposited CdSe film was observed by AFM measurement in the **Figure 9**. The sizes of the nanostructures were found to be 10 nm to 90 nm for the film. The surface morphology and the quality of the CdSe film was observed by direct 3D AFM image. A good quality film but of non epitaxial manner was seen in the **Figure 10**.

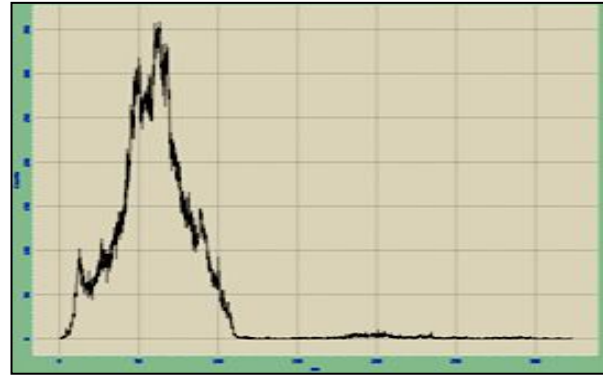


Fig. 9. Size distribution of nanostructures in the film

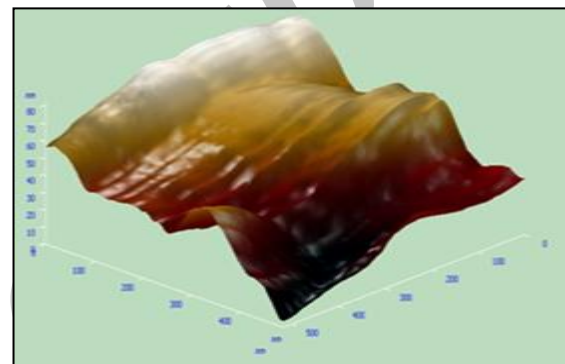


Fig. 10. 3D AFM image of CdSe film

The dark current and photocurrent characteristics of the Ag/CdSe junction verified the formation of Schottky barrier between metal and semiconductor interfaces. The I-V characteristics of the cell were done by Keithley Electrometer as shown in **Figure 11**. At low voltages, the V versus $\ln I$ graph shown in the **Figure 12** indicated the exponential variation of current with respect the corresponding voltages and suggested the current conduction by thermionic emission [10]. The analysis reveals that the current transportation equation at low voltage can be written as

$$I = I_S [\exp(eV/nK_B T) - 1] \quad (2)$$

And

$$I_S = A^* T^2 \exp(-q\phi_b / K_B T) \quad (3)$$

Here q is the charge on the electron, V is the applied voltage, n is the diode ideality factor, K_B is the Boltzmann constant, T is the temperature,

ϕ_b is the effective barrier height, A^* is the effective Richardson constant and I_s is the reverse saturation current. The effective Richardson constant was calculated by the relation

$$A^* = (4\pi q m^* K_B^2) / h^3 \tag{4}$$

In the equation m^* is the reduced mass of exciton (e-h) and h be the Planck's constant. The reduced mass of exciton can be calculated from effective mass of electron (m_e^*) and hole (m_h^*) as given below

$$m^* = (m_e^* m_h^*) / (m_e^* + m_h^*) \tag{5}$$

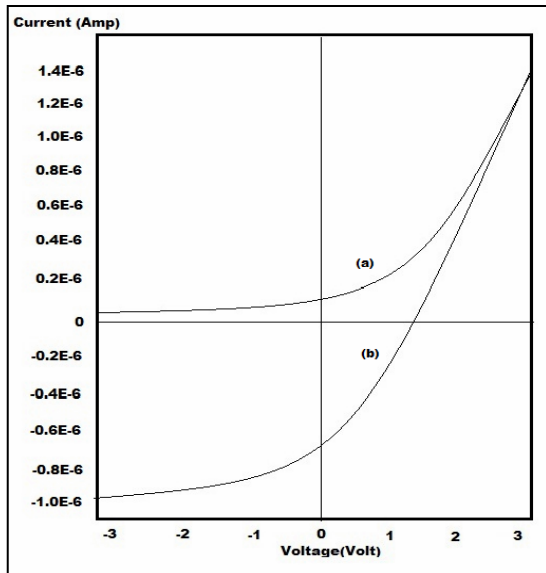


Fig. 11. I-V Characterization of Ag/CdSe Schottky cell (a) dark current (b) photo current

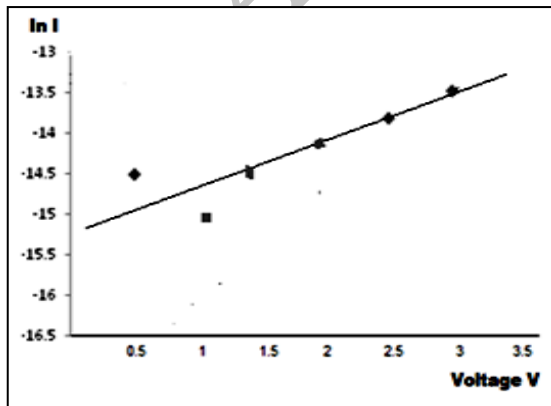


Fig. 12. ln I versus V curve at lower voltages

The effective mass of electron and hole of CdSe were $0.13m_0$ and $0.45m_0$ respectively. The calculated values of m^* and A^* were (0.9178×10^{-31}) kg and $12.11 \text{ Ak}^{-2}\text{cm}^{-2}$, using rest mass of electron as $m_0 = 9.1 \times 10^{-31}$ kg. The reverse saturation current (I_s) was determined by interpolation of exponential slope of I at $V=0$, was found as 2.5×10^{-7} Amp. The barrier height and ideality factor were calculated using equation (2) and (3) found that $\phi_b = 0.15$ eV and $n = 1.6$ respectively. An ideality factor greater than unity, was already reported by other worker [11] and generally attributed to the presence of a bias dependent Schottky barrier height. The interfacial oxide layer may be another cause for the higher value of ideal factor. A non-ohmic relation I proportional to V^2 for higher voltages fits the curve at Figure 13. Clearly, in this region the current was controlled by space charge limited conduction (SCLC) [12].

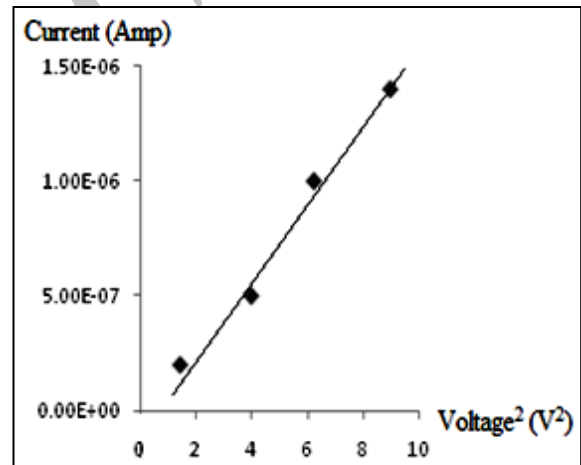


Fig. 13. I versus V^2 curve at higher voltages

The observed behavior of Ag/n-CdSe junction explained the existence of an electric dipole at the interface of the junction [13, 14]. The tunneling induced dipole effect is shown by the proposed band diagram of the junction in Figure 14.

In the band diagram the work function of silver (ϕ_m) 4.7 eV was considered as standard value and the electron affinity (Z) of CdSe was determined 4.55 eV using the relation $(Z) = (\phi_m - \phi_b)$. The energy band gap of CdSe was taken as 2.5 eV from optical measurement for the

nanostructures sample. Due to the higher value of work function of metal than the electron affinity of the semiconductor, the Fermi level of metal is in the upper position than that of the CdSe nanostructures as shown the Figure 14. It was possible that some electrons just below the Fermi level in the metal can tunnel through the interface into the interface into the forbidden gap of semiconductor leaving behind a positive charge on the metal side nearer to the metal semiconductor interface. These electrons penetrate a short distance in the semiconductor forbidden band before the reflection from the interface. On the other hand during this process CdSe received a numbers of electrons and as a result an upward bending of energy (E_g) in it was observed in the junction. The rectification occurred because the barrier for electron going from the semiconductor to metal is different from the barrier height for electrons coming out from the metal to the semiconductor.

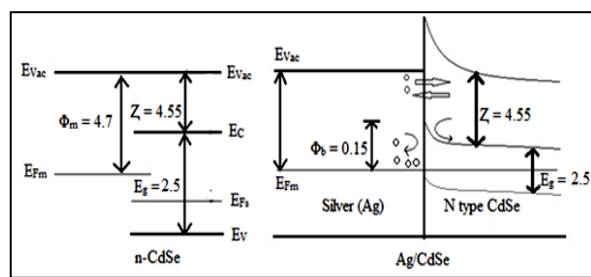


Fig. 14. Proposed band diagram of Ag/CdSe Schottky junction

CONCLUSIONS

The work explained an economically viable and easy chemical method for the synthesis of CdSe nanostructures. Though the synthesis of Cadmium Selenide is much difficult than the other II-VI semiconductor nanostructures, but low dimensional CdSe can be produced by using this simple method using Starch as a capping agent. The W-H plots were employed to calculate to calculate the particle size and strain of the prepared sample. The strains and the particle sizes were 7.3×10^{-2} and 5.5 nm respectively. Again the average particle sizes of CdSe were 6 nm to 8 nm as obtained by HRTEM. The orientation of the nanostructures were in (111), (220) and (311) planes as shown in the XRD analysis and SAED pattern. The optical observations were made by UV and PL spectra

showing a large blue shift of the sample. The most interesting part of the work is the application of prepared CdSe nanostructures for fabrication of Schottky type cell. Silver made the Schottky contact with n-CdSe at barrier height of 0.15 eV. At lower bias voltages, the conduction of current was because of thermionic emission where as SCLC (Space charge limited conduction) theory controlled the current transport mechanism at higher voltages. A band diagram of Ag/CdSe junction is proposed using tunneling-induced dipole effect at the interface of metal and semiconductor.

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