Chalcogenide Letters Vol. 14, No. 10, October 2017, p. 457 - 464

EFFECT OF SUBSTRATE TEMPERATURE ON THE STRUCTURE AND OPTICAL PROPERTIES OF PVP:n-CdSe NANOCOMPOSITE THIN FILMS AND ITS SCHOTTKY DIODES PERFORMANCE

A. AL- ZAHRA, A.Q. ABDULLAH, A. S. AL-KABBI[*]
Department of Physics, College of Science, Basrah University, Basrah, Iraq

CdSe/PVP nanocomposite material was prepared by a chemical bath deposition method at room temperature. Studies of the structure and optical properties of deposited thin film on the glass substrates at 300 and 400 K temperatures were carried out. X-ray diffraction studies showed that the crystallinity of the CdSe films was improved in the thin film prepared at higher temperature and grain sizes increased. Direct transitions have been observed in the optical measurements of the two samples and the energy gap decreases with increasing substrate temperature.The prepared material has been deposited on aluminum sheet substrates at 300 and 400 K temperatures to fabricate of Ag/n-CdSe:PVP Schottky diode. Characterization of the Ag/n-CdSe:PVP Schottky diode has been done at room temperature.The diode parameter as the ideality factor (n), the effective barrier height (Φ_b), the Richardson constant (A*) has been calculated. Cheung's method are used to calculate the series resistance.Considerable changes has been observed in diode parameters and the series resistance for the two samples.

(Received August 31, 2017; Accepted October 31, 2017)

*Keywords:*Thin films; Vapour deposition; Electrical Properties; Transport properties

1. Introduction

In recent years, Attention has been attracted to the semiconductor nanomaterials due to their controllable properties.The capability to alter the structural , optical and electrical properties of semiconductor nanoparticle by changingtheir size will be useful in many application like optoelectronic and solar cell devices[1-2]. These nanoparticles materials can be syntheses, in the ambient laboratory conditions, by building a composite material composed of nanoparticles dispersed in a host material (such as polymer)[3].When injection of their precursors into a solution of polymer the polymer chains well be restricts the growth of these materials to the nanoscale by prevent these nanoparticles to aggregate in solution [4].Thus, researchers have been employed awater soluble polymers as stabilizing materials for the composite fabrication [5- 6].Here, we used the Polyvinypyrrolidone (PVP) as stabilizing materials in the composite fabrication due to its aqueous solubility, good thermo-stability, easy processability and transparency.

Cadmium selenide (CdSe)is one of II-VI compound semiconductors with direct band gap (1.74 eV) in a bulk material. due to the unique optical and electronic properties of CdSe nanoparticle, this material has been subjected to many researches for the possibility of using it in various technological applications such as photoelectron chemical solar cell (PEC), optoelectronic devices, gamma ray detectors, light emitting diodes, solar cells, photo detectors, electro photography and in lase[7-9]. However, the improve of these different potential applications requires a homogeneous dispersion of the CdSe particles in the polymer matrix which can produced polymer/CdSe nanocomposites materials have advantages of low cost processing and appropriate for production of large area devices[10].

In present work, we have reported the simple and environmentally friendly method to synthesis of Polyvinypyrrolidone (PVP) capped CdSe nanoparticles in aqueous medium at room temperature. The effect of substrate temperature on the structure and optical properties of n-

---

[*] Corresponding author: as.alkabbi@yahoo.com

CdSe:PVP nanocomposite thin films have been investigated. The Shotticky diode of Ag/n-CdSe:PVP thin films have been fabricated. The I-V measurements have been carried out to find out the detail of junction properties such as series resistance (R_S), the ideality factor (n), the effective barrier height (φ_b).

2. Experimental Methods

2.1. Materials

CdSe nanocomposites are prepared by using Cadmium Acetate ($Cd(CH_3COO)_2$) which have been used as a cadmium source, Sodium sulphite (Na_2SO_3), Selenium Powder as a source of selenium Ions, PVP $(C_6H_9NO)_n$ with average MW~40,000 was used as a stabilizer And Ammonia liquid. Deionized water was used though the experiment and all the chemical materials are used as the method of the work.

2.2.Synthesis of CdSe/PVP nanoparticle

CdSe/PVP nanocomposites are synthesisby using sodium selenosulphate (Na2SeSO3)as the selenium source. (0.50M) of Na_2SeSO_3 solution precursor was prepared by adding 3.15g of sodium sulfate and 0.98g of selenium powder in 50 ml of water and stirring several hours untilthe selenium dissolve completely. Solution of Cadmium acetate was prepared by adding 3.15g of cadmium acetate in to 50ml of water. Cadmium acetate and Sodium selenosulfate solutions were added to 3g of PVP dissolving in 100ml of water and stirred at room temperature for up to 7 hour. The Ph of the end solution was kept about 11 by liquid Ammonia.

The thin films of Ag/n-CdSe:PVPhave been prepared by drop casting of solution on the substrate (glass or Aluminum) at two different substrate temperature (T_S = 300 and 400 K). The obtained films adhere well to the substrates. To construct Schottky junction we have deposited n-CdSe:PVPmaterial on the aluminum sheet by casting method after washing of the aluminum sheet with NaOHto remove native alumina layer and other soluble salts on it. Silver metal film has been deposited by vacuum deposition system using room temperature on the surface of n-CdSe:PVP thin films. The vacuum chamber is evacuated to 10^{-4} Pa during the evaporation. The diode is kept in the deposition chamber in the dark for 24 h before measurements. The effective area of diode is 2.5×10^{-2} cm^2.

2.3. Characterization

The properties of prepared thin films have been studied by different measurements technique. X-ray diffraction measurements have been used to examine the structural properties of thin films using a (X ' Pert Pro MPD- Philips, filtered CuKα radiation λ = 1.5405 A°).The optical properties of the thin films on the glass substrate were measured by a UV/VIS/NIR computer controlled spectrophotometer Perkin Elmer LAMBDA 750 in the range 300–900 nm at room temperature. The I-V characteristics have been made by using a Keithley 2400 electrometer.

3. Results and discussion

3.1. Structural Properties

Fig.1 shows the X-ray diffraction pattern of pure PVP thin film where broad diffraction peak appeared at $2\theta= 21.08^o$ confirms the amorphous nature of PVP. Fig (2) shows the XRD pattern of n-CdSe:PVP nanocomposite thin films at different substrate temperature. The tow films shows tow broad diffraction peaks at $2\theta=25.23^o$ and 41.9^o, corresponds to the (111) and (220) cubic crystal planes. For the films prepared at 400 K, newpeak was observed at $2\theta= 49.01^o$ with broad and low intensity corresponding to (311) plane. This improves the crystalline structure of this film and is consistent with a number of studies have prepared this material at higher preparation temperatures [11-12].The two additional peaks at $2\theta = 31.82^o$ and 34.03^o are due to the impure phase of CdSe [13]. The intensity of these two peaks decreases as the substrate temperature increases.

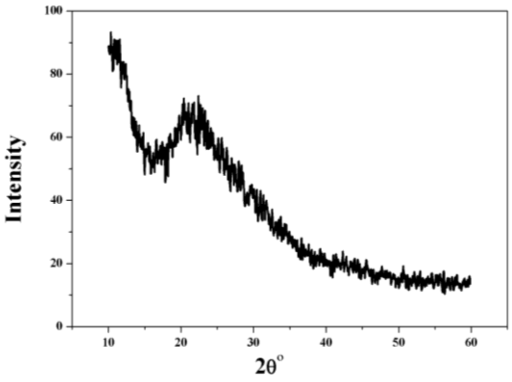

Fig.1. XRD spectra of pure PVP

The lattice parameter "a" has been evaluated from the relation [14]:

$$\frac{1}{d^2} = \frac{(h^2+k^2+l^2}{a^2} \qquad (1)$$

wher d is the interplanar distancesfor different (h k l) plans is calculated using Bragg's Law.

The diffraction pattern shown in Fig. 2 has broad peaks indicating that the prepared thin films consist of small crystallite size. The grain size (D) of the n-CdSe:PVP nanocomposite thin films are calculate by Scherrer's equation [15]:

$$D = \frac{K\lambda}{\beta COS(\theta)} \qquad (2)$$

Where β is the full width at half maxima (FWHM), k is the X-ray wavelength, θ is the diffraction angle and k is the Scherrer's constant of the order of unity.

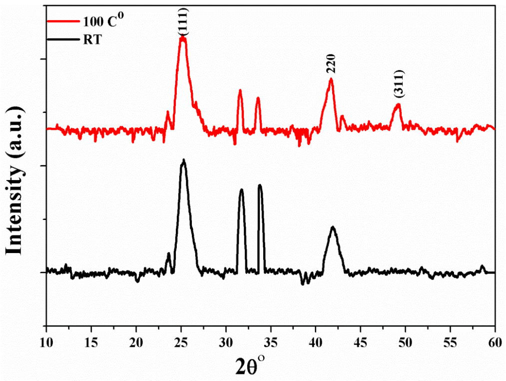

Fig.2. XRD spectra of n-CdSe:PVPthin films at 300 and 400 K

The structural parameters of the tow samples are given in Table 1.The grain size slightly increase with the increase in the substrate temperature may be due to the assemblage of small crystals.

Table 1. The structural parameters extracted from XRD spectra

Sub.Temp.	2θ°	d spacing (Å)	Plane (hkl)	D (nm)	a (Å)	ε ($x10^{-3}$)	δ($x10^{16}m^{-2}$)
300 K	25.23	3.52	111	5.87	6.09	5.9	2.8
	41.9	2.15	220	6.74	6.08	5.1	2.1
400 K	25.23	3.54	111	6.21	6.13	5.5	2.5
	41.81	2.15	220	7.86	6.1	4.4	1.6
	49.34	1.81	311	9.04	5.92	3.8	1.2

3.2. Optical Properties

Fig (3) shows the absorption spectra of n-CdSe:PVP thin films at different substrate temperature,it was measured in the range of wave lengths (300 -900)nm. The figure shows one peak at 462 nm and 492 nm for the film deposited at 300 K and 400 K, respectively.The absorption of n-CdSe:PVP thin films have been decreased with increasing of substrate temperature. The absorption peak of the film deposited at 400 K is shifted to longer wavelength side whereas it is shifted to the shorter wavelengthas compared to that of the film deposited at 300 K.

The absorption coefficient (α) is calculated from absorption data at the fundamental absorption edge by use the formula:

$$\alpha = \frac{2.303}{d} A \qquad (3)$$

Where A and d are the absorption and thickness of n-CdSe:PVP thin films respectively. The value of α as a function of photon energy is shown in Fig.3 which shows that α increases with increase in photon energy.

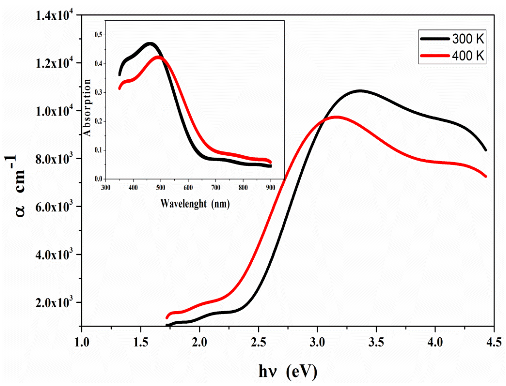

Fig. 3.Optical absorption coefficient (α) with photon energy (hν), Inset show UV–VIS spectra of n-CdSe:PVPat room temperature.

The optical absorption edge was analyzed by the flowing equation [16]:

$$\alpha h\nu = A(h\nu - E_g)^{m} \qquad (4)$$

Where A is a constant, m values are 1/2 and 2 for direct and indirect transition respectively.

The variation of $(\alpha h\nu)^2$ with photon energy for n-CdSe:PVP samples is shown in fig (4). It has been observed that the plots of $(\alpha h\nu)^2$ versus hν are linear over a wide range of photon energies indicating the direct type of transition. The intercept of these plots on the energy axis give the energy band gap whose be (2.15 eV) and(1.98 eV) of the films prepared at 300 and 400 K substrate temperature, respectively.

The obtained values of energy gap are high as compared to the it values of bulk CdSe (1.74 eV) and this may due to the effect of quantum confinement [17]. The decrease in the energy band gap value of the thin film at 400 K may be due to the increase in particle size which is confirmed by X-ray analysis.

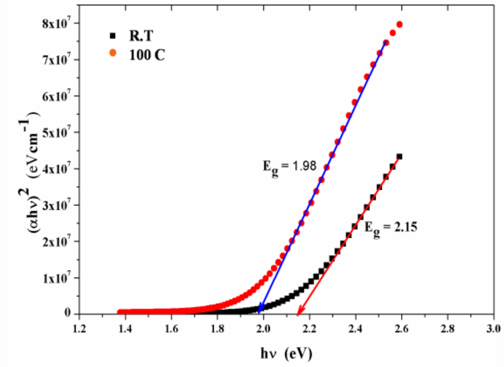

Fig. 4.The energy gap of n-CdSe:PVPfilms at different substrate temperature

3.3 Schottky diode

According to the thermionic emission model, the I –V characteristics for Schottky diode for V> 3kt/q aregiven by [18]

$$\mathrm{I}= \mathrm{I_s}\left\{\exp\left(\frac{\mathrm{qV}}{\mathrm{nKT}}\right) - 1\right\} \qquad (5)$$

Where , I is current , I_S the saturation current, n is the ideality factor ,V is thevoltage cross the diode ,q is the electron charge, T the absolute temperature, and k is the Boltzmann constant (8.62 x 10^{-5} eV/k).

This method fails when the influence of the series resistance is already significant at medium or small forward voltages or even at reverse bias. When The effect of the R_s is considered, the relation in eq.(5) is expressed as.

$$I = I_S \left\{exp\left(\frac{q(V-IR_S)}{KT}\right) - 1\right\} \qquad (6)$$

The saturation current is given by:

$$I_S = AA^* T^2 \ exp\left(\frac{-q\emptyset_b}{KT}\right) \qquad (7)$$

Where Φ_b is theSchottky barrier height,A is the diode area, A* is the effective Richardson constant that can be given a theoretical way according to:

$$A^* = \frac{4\pi q m^* k^2}{h^3} \qquad (8)$$

Where m^*=0.12 m_o, and h is Planck’s constant (h = 6.6261 $10x^{-34}$ J.s).From eq.(8) the value of the A*is equal to 14 A/cm^{2}K^2[19].

Fig. (5) shows the experimental I vs V plots of CdSe/PVP thin films at different substrate temperature, these two curves shows good diode characteristics.The prepared sample with high substrate temperature improves of the diode characteristics.Symmetry is observed in I–V in the forward and reverse bias conditions indicating a narrow depletion layer width in the junction [20].

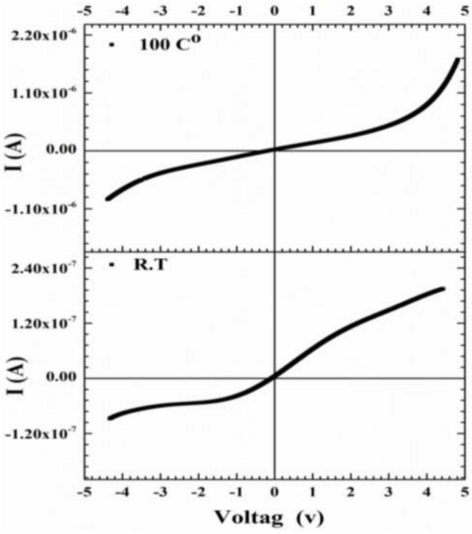

Fig.5.Current versus voltage characteristics of the Ag/PVP:n–CdSeSchottkydiode in 300 and 400 K substrate temperature

Rs is an important parameter which is responsible for the deviation of I–V characteristics from linearity of shotticky diode. The series resistance R_s, ideality factor n, and barrier height φ_b values for both samples by using Cheung's function method. According to this method, Equ. (6) can be turn into the new form [21]:

$$\frac{dV}{dlnI} = \frac{nkt}{q} + IR_s \qquad (9)$$

As shown in fig.6 and fig.7, the plot of dV/dln I vs I are give a straight line where the slope of this line will give the Rs value and the intercept of this line with y-axis will give the values. Using n values which are found from fig.6, Cheung's define H(I) functions which can be use to evaluate the $\varphi_b$values:

$$H(I) = V - \frac{nkt}{q}\ln(\frac{I}{AA^*T^2}) \qquad (10)$$

$$H(I) = IR_s + n\varphi_b \qquad (11)$$

The H(I) dependence of I have been plotted in fig. 6 and fig.7 for tow samples. It is clear from the figures that, H(I) versus I curves are nearly straight lines. The slope of this plot also provides a second determination of *R*s which can be used to check the consistency of this approach. The intercept of the straight lines with y-axes are equal to $n\varphi_b$.

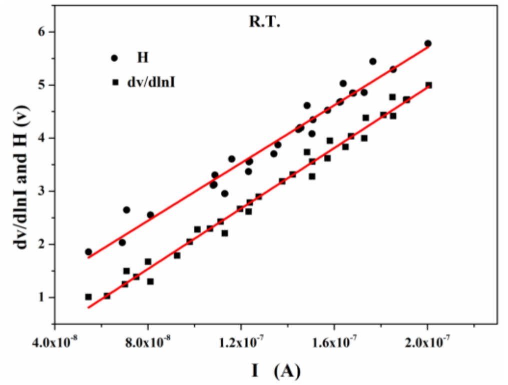

Fig. 6. Plot of dV/dlnI and Hversus I under dark conditions for Ag/PVP:n–CdSe Schottky diode in 300 K of substrate temperature

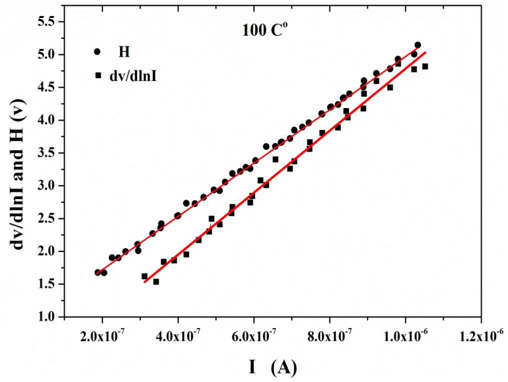

Fig. 7. Plot of dV/dlnand H versus I under dark conditions for Ag/PVP:n–CdSeSchottkydiode in 400 K substrate temperature

The calculated values of all diode parameters are given in Table 2. The R_S values obtained from both plots are in close agreement with each other. As seen in the table, the Rs value of the resistance in the sample prepared at a higher substrate temperature is less than in the sample prepared at room temperature. The increase of current can be attributed to this reduction in R_S.

We can also note that the value of R_S is large for both samples, which may be due to the presence of PVP polymer, which has a low mobility and electrical conductivity compared to CdSe semiconductor. The same results were obtained by several researchers of samples consisting of semi-conductive composite materials with polymers [22,23].The deviation of the calculated ideality factor values from unity are may due to exist of trap states in an interfacing layer which can act as localized generation-recombination centers. Also, the disorder in structure of the nanocomposite thin films may effect on the ideality factors values too.

Table 2.Schottky diode parameters

Sub.Temp.	n	I_s	φ (eV)	R_s (Ω)	
				dv/dlnI vs I	H vs I
300 K	1.92	$5.54*10^{-8}$	0.77	$2.7*10^{7}$	$2.87*10^{7}$
400 K	1.88	$1.06*10^{-7}$	0.75	$4.76*10^{6}$	$4.75*10^{6}$

4. Conclusions

XRD studies of PVP:n–CdSe thin films deposited at various substrate temperatures confirmed the cubic crystal structure and the film deposited at 400 K shows relatively better crystallinity. The variation in the direct optical band gap observed for the PVP:n–CdSe thin films, prepared at various deposition temperatures, may be attributed to the variation in crystallite size.

The I-V characteristics forAg/PVP:n–CdSeSchottky diode is measured at room temperature.Cheung's method has been used to find the ideality factor (n) effective barrier height (Φ_b) and series resistance (R_S) of the tow diodes.These parameters are less in values to the diode prepared at high substrate temperature.

References

[1] T. Lu, S. Dong, Ch. Zhang, L. Zhang, G. Cui, Coordin. Chem. Rev. **332**, **75** (2017)
[2] X.Dong,J. Xu. S. Shi. .X. Zhang. L. Li. .S. Yin, J. Phys. Chem. Solids**104**,133 (2017).
[3] N. M Saadatabadi, M. R. Nategh, M.B. Zarandi, Polym Sci. Ser A **57**,480 (2015).
[4] Gary Hodes, Phys. Chem. Chem. Phys. **9**, 2181(2007) 2181.
[5]H. Zhang, Z. Cui,Y. Wang, K. Zhang, X. Ji, C. Lü, B. Yang, M. Gao, Adv. Mate. **15**, 777(2003).
[6] R.K.Layek, A.K.Nandi, Polymer**54**, 5087 (2013).
[7] L.J. Zhao, L.F. Hu, X.S. Fang, J. Adv. Funct. Mater.**22**, 1551 (2012).
[8] O.I. Olusola, O.K. Echendu and I.M. Dharmadasa, J. Mater. Sci. Mater. Electron., **26,**1066(2015).
[9] Q. Wang, S. Li, J. Qiao, R. Jin, Y. Yu, S. Gao, Sol. Energy Mater. Sol. Cells **132**, 650(2015).
[10] M. Sharma, S.K. Tripathi, J. Lumin. **135**, 327 (2013).
[11]H. Etxeberria, G. Kortaberria, I. Zalakain, A. Larran˜aga, I. Mondragon, J. Mater Sci. **47**, 7167 (2012).
[12] A.M. Al-Amri, S.J. Yaghmour, W. E. Mahmoud, J. Crys. Grow.**334** (2011) 76-79.
[13] P.K. Khanna , K. Dhanabalan, P. More, S. Viswanathan, V. Renugopalakrishnan, In l J. Green Nanotechnology**4**, 62(2012).
[14] C. Kittel, Introduction to solid state physics,.Wiley, New York; (chapter 2) 1996.
[15] S. Sarangi, S. Sahu, Physica E Low Dimens. Syst. Nanostruc., **23**, 159 (2004).
[16] J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi A 15, 627 (1966).
[17] K. Sharma, A. S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi, Mate. Rese. Bull. 47, 1400 (2012).
[18] S. M. Sze, Physics of Semiconductor Devices, Wiley, 2nd edn New York, p.255,1981.
[19]M. Sharma, S. K. Tripathi, Optoelectronics. Advanced Materials **6**, 200 (2012).
[20] M. Das, S. Middya, J. Datta, A. Dey, R. Jana, A. Layek, P. P. Ray, J. Electron. Mater.**45**, 4293(2016).
[21] S. K. Cheung, N. W. Cheung, Appl. Phys. Lett. **49**, 85 (1986).
[22] S. K. Tripathia, M. Sharma, J. Appl. Phys. **111,** 074513 (2012).
[23] M. Gokcen, T. Tunc¸, S. Altindal, I. Uslu, Current Appl. Phys. **12**, 525(2012).