Study the structural and electrical properties of CdSe nanoparticles

M.A.Batal, Kaesar Alyamani*

Department of Physics, College of Science, Aleppo University, (SYRIA)

E-mail : alyamani.k@gmail.com

ABSTRACT

CdSe nanoparticles were prepared in aqueous medium using chemical method.XRFspectrum reveal both Cd and Se. XRD spectrum shows that CdSe nanoparticles have hexagonal structure, From XRD, Crystallization size85.6 nm, lattice constant C7.28Aæ%, effective strain2.*10^{-4}(lin^{-2}m^{-4})between the nano crystals and dislocation (irregular)2.85*10^{-4} $(lin m^{-4})$ were determined. FTIR spectrum shows some toxicity in CdSe nanoparticles suchO-H. From Impedance Spectrum of CdSe,activation energy 0.0275 eV and the density ofcarriers charge were determined. From C-V characteristic type of semiconductor and it was found to be n- type. CdSe hastwo donors levels ($N_{d1=}$3.06*10^{22} cm^{-3} $N_{d2=}$6.12*10^{22} cm^{-3}). Finally,the derivation of capacitance respect in function of temperature, from its graph energy diagram of CdSe nanoparticles was plotted. © 2015 Trade Science Inc. - INDIA

INTRODUCTION

Cadmium selenide (CdSe) is solid hexagonal or cubic crystal. It is a direct band gap n-type semiconducting material with a band gap of 1.74 eV at 300K. Its molecular weight is 191.37 g/molWhere Cd is 58.74% and Se is 41.26%. Its appearance is dark red color. CdSe in the bulk form is not very interesting. The most interesting form of CdSe is nanoparticles. Much current research on CdSe has focused on nanoparticles. Researchers are concentrating on developing controlled synthesis of CdSe nanoparticles. It has useful properties for optoelectronic devices, laser diodes,nanosensing, biomedical imaging and high efficiency solar cells[1]. The nanoparticles ofCdSe high quality may be identical in distribution, size, and that took attention increasingly in industry. The smaller size of nanoparticles of CdSe from 1nm to 10nm, the surface atoms number increases from 20% to 100%, where theatomssurface are often unsaturated linkages surface or the presence of peripheral links where these atoms have a large free energy to be active most of the atoms in the bulk materials[2]. CdSe Belongs to component ofII-VI, which like the other compounds of this group, isdimorph at ordinary pressures and this depends on the method of preparation. Wheresingle crystal of CdSe crystallize either insphalerite (cubic, zinc blende)structure. Sphalerite is the stable low temperature phase and the cubic-to-hexagonal transition occurs atcritical temperature T_c=(95 ± 5) Cæ%. Theenergy difference between the phases is a few meV when preparing samples at temperatures higher than the critical temperature where the

wurtzite structure remains presentat room temperature. CdSe Single crystals have a specific density of 5.816 g/cm^{3}and melting pointof 1541 K. Hardness of these crystals is about 4M&! and their thermal conductivity is3.49 W m^{-1} K^{-1}. As these belong to the crystal semiconductor n-type electrical conductivity ranging where these initial crystallization without alloy between 10^{-1} - 10^{-7}CdSe single crystals exhibits n-type electrical conduction without doping intentionally and their conductivity ranges changes between 10^{-7}-10^{-1}(&!-cm(. Hall mobility of CdSe single crystals has been measured to be between 325-1050 (cm^2/Vs). CdSe single crystals with 2mm thickness transmit the lightwith wavelength between 0.53-15μm. Their refraction index is 2.55 for incident light at900nm[3]. In these work,The CdSe nanocrystalline samples were prepared and characterized by XRD,FTIR spectrum,XRF spectrum DC,AC Measurement.

MATERIALS

Metallic selenium powder, sodium sulûte (Na$_2$SO3), Cadmium chloride (CdCl$_2$.H$_2$O) Ethylene glycol,N$_2$H$_2$, NaOH, deionized water ;all chemical from Mirck.

SYNTHESIS OF CDSE QD

Nanocystals of CdSe were prepared by chemical solutions method. Cadmium chloride (CdCl$_2$.H$_2$O)used as the cadmium source and sodium selenosulfate (Na$_2$SeSO$_3$) was chosen as the selenium source. Cadmium Chloride (22.8 gr) was solved in 100 ml of deionized water called solution (A). Sodium selenosulfate which was prepared by solving Na$_2$SO$_3$(12.6 gr) in 100 ml of deionized water, adding selenium powder (7.96 gr) to previous solution refluxed at 70 C$^{æ‰}$for 3 hours, red wine solution will appear called solution (B). Solution (A) (20ml) was added to solution (B)(5ml),ethylene glycol (5ml),hydrazine hydrate (5ml) were added to previous. CdSe colloidal Solutionwas adjusted10 by adding 1 mlNaOH solution. After this, the solution was filtered by high accuracy filter paper,dried in electrical oven for 2hours at 50 C$^{æ‰}$. Ceramic mortar was used tomillet CdSe powders. The millet CdSe powder was pressured as disc (diameter21mm, thickness 2mm)using hydraulic compress at7 tons / cm^2 for 10 minutes.

QUALITATIVE MEASUREMENT

XRF spectrum of CdSe sample

XRF spectrum was taken using Mo anode and applying35kV with 1mA. Figure 1 shows XRF spectrum of CdSe (4/1) sample preparation in aqueous medium. From XRF spectrum can be determined theratio in the preparation after calibration procedure with reference samples form Cd and Se. The TABLE 1 shows ratios materials involved in the sample as a result of XRF spectroscopy, where the ratio calculated spectrally was very close to the rates that took gravimetric calibration when was prepared, differences in resulting caused by usedmaterials (not purity)and analytical capacityability of the detector was small.

TABLE 1

Element	Density (gr/cm^3)	Average count for X sample	Average count for standard samples	Ratio %
Cd	8.65	326	424	85
Se	4.81	2311	9454	15

XRD spectrum of CdSe sample

X-ray diffraction (XRD) pattern of CdSedisc sample was recorded by Philips system usingCu Kα(λ=0.154056nm) radiation with 2θ in the range 20-80º as Figure 2. From the (XRD) spectrum, the CdSe sample is polycrystalline innature having all peaks corresponding to the specific planes,The extra peaks observed at 2θ (degree) $2\theta° = 27.3°,34.3°,49.6°$ with maximum intensity peak from (101),(102),(112) planes respectively.

The lattice spacing, d, is calculated from the Bragg's formula[4]:For first peak n=1,2θ =27.3$^{æ‰}$:

$$d = \frac{n\lambda}{2\sin\theta} \Rightarrow d = \frac{1 \times 1.5418}{2 \times \sin(13.65)} = 3.26A^{\cdot}$$

The peak broadening in XRD patterns may arise due to several reasons such as smaller crystallite size, instrumental error and fast scanning. As in the present case,proper precautions have been taken into account during scanning such as slow scan rateTherefore, the observed broadening (Figure 2) is due to the strain and smaller crystallite size,where their contribution to peak
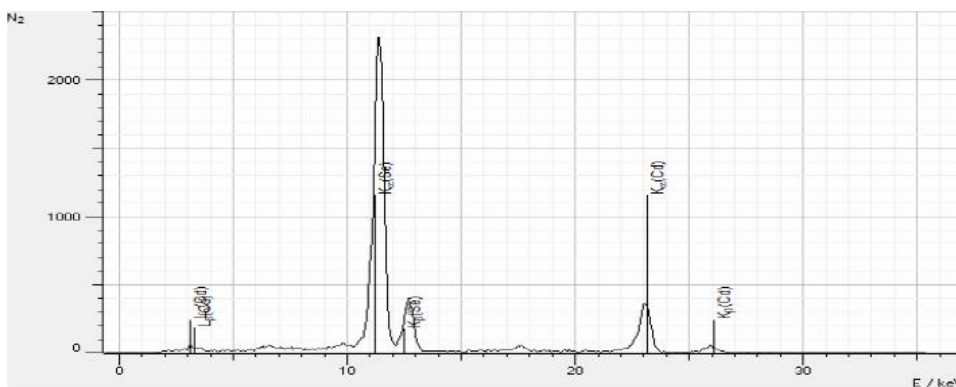
Full Paper

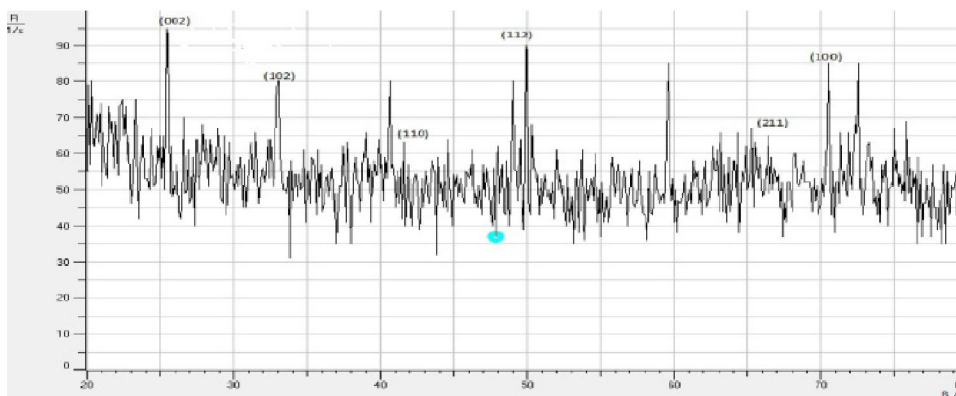**Figure 1 : Shows XRF spectrum of CdSe(4/1) sample.**

Figure 2 : Shows XRD spectra of CdSe sample with ratio CdSe (2/1)

broadening is independent of each other. Therefore, total broadening can be written as sum of these two as $\beta_{total} = \beta_{strain} + \beta_{crystallite\ size}$ and can be calculated using Williamson–Hall (W–H) equation[5]:

$$\frac{\beta_{total} \cdot \cos\theta}{\lambda} = \frac{1}{d} + \frac{\eta \cdot \sin\theta}{\lambda} \Rightarrow \beta_{total} \cdot \cos\theta = \frac{\lambda}{d} + \eta \cdot \sin\theta$$

Where η is the effective strain present in the material, d the effective crystallite size, λ the wavelength of X-ray radiation, β the full width at half maxima and θ the diffraction angle. By plotting $\beta_{total} \cdot \cos\theta$ in function of $\sin\theta$, Negative slope of pure CdSe nanoparticles as shown in Figure 3 indicate the presence of effective compressive strain in the crystal lattice.

In materials science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The dislocation density "δ" has been calculated by using the formula[6]:

$$\delta = \frac{15.\eta}{D.a}$$
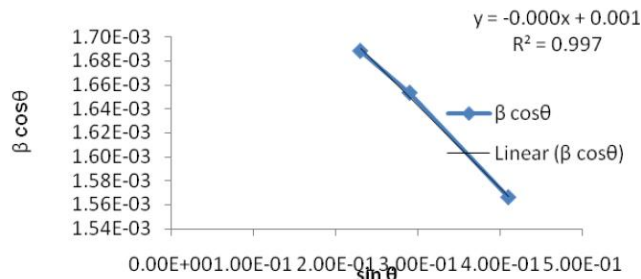
Where η effective strain values, D The crystallite size, a

Figure 3 : W–H plot for pure CdSe nanoparticles

hexagonal lattice constant equal 4.29Aæ%. The lattice parameter C is determined for hexagonal structure by the following expression[4]:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + \ell^2)}{c^2}.$$

Where h, k and ℓ represent lattice planes (102) which corresponding with diffraction angle $2\theta = 34.4$æ% Lattice constant C is close to standard value 7.01Aæ%.

FTIR Spectrum of CdSe

Sample was mixed with KBr (CdSe/KBr1/200mgr), compressed as disc using a hydraulic press (5 ton / cm²). FTIR Spectrum of CdSe was carried out

TABLE 2 : Summery of XRD spectrum.

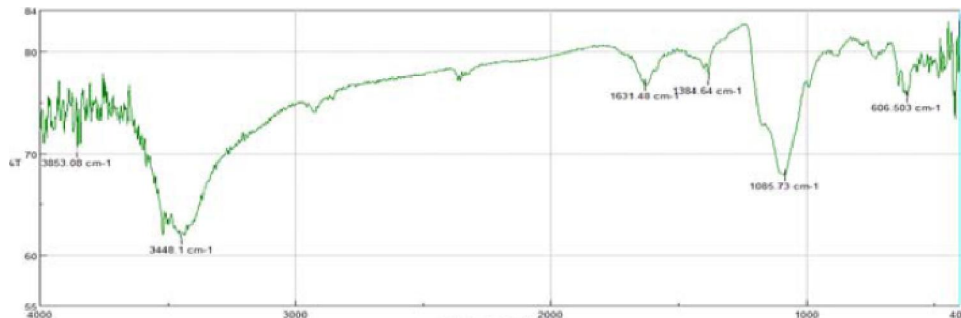| $\delta_{(lin.m^{-4})}$ dislocationdensity	η $(lin^{-2}m)$effective strain	d (A⁻) lattice space	D (nm) Averagecrystallize	C (A⁻) hexagonal
$2.85*10^{-4}$	$2.*10^{-4}$	3.26	85.6	7.28

Figure 4 : Shows FTIR spectrum of CdSe in water solution.

using JASCO.4000 IR spectrophotometer in wavenumber range (400-4000)cm⁻¹,). Figure 4 : showsFTIR Spectrum of CdSe it shows many absorption peak these peaks related toO-H (3448.08 cm⁻¹),C-H (3853 cm⁻¹) inethylene glycol and bond length 1085cm⁻¹ is due to bondingthat existing chloride cadmium.

ELECTRICAL MEASUREMENT

Impedance spectrum

AC measurement carried out using GAIN PHASE ANALYZER (Schlumberger-SI1253). A complex impedance spectrum in frequency range (1-20000HZ) andat constant voltage (v=5V), and different temperature (302,322,327and 340 K) where taken for CdSe:

$$Z = R + jX$$

Figure 5 shows the relationship between the imaginarypart $X(\omega)$ and the real part $R(\omega)$ of the complex impedance. We note that impedance spectrum has a semi-cycle whichmeans that it's due to Debye model which involves thegrain to be homogenous.

$$\frac{1}{Z} = \frac{1}{R} + j\varpi.C = \frac{1 + j\varpi.CR}{R} \Rightarrow Z = \frac{R}{1 + j\varpi.CR}$$

To defineThe charge concentration andThe change densityof trapped state, complex impedance spectrum taken for CdSesample at temperatures (302,322,327and 340)K Figure 5. From above Figure, we note that when temperature of thesamples rises, semi-cycle will be deformed and the shape ofgrain de-

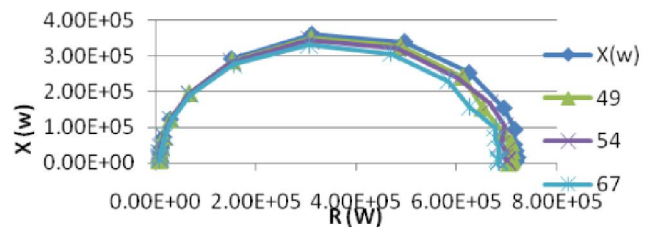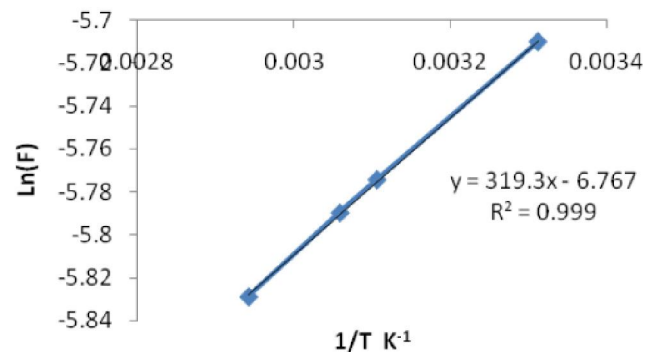**Figure 5 : Shows impedance spectroscopy for CdSe in different temperatures.**

Figure 6 : Shows Ln (f)=(1/T) for CdSe sample.

formed too. Debby model transfers to Cole-Colemodel. To calculate the activation energy of prepared CdSe sample,frequencies values had been taken at $X(\omega)=R(\omega)$ fromimpedance spectrum at different temperature, where thefollowing expression can be applied:

$$f = f_0 e^{\frac{E_a}{KT}} \Rightarrow E_a = 4.404 \times 10^{-21} joul \Rightarrow E_a = 0.0275ev \cdot$$

By taking Ln(f) in function of 1/T; activation energy can bedetermined. Thecharge concentration (elections or holes)were determined from the relation:

$$N_d = N_0 e^{-\frac{E_a}{KT}} \Rightarrow N_d = 1.57 \times 10^{21} / cm^3$$

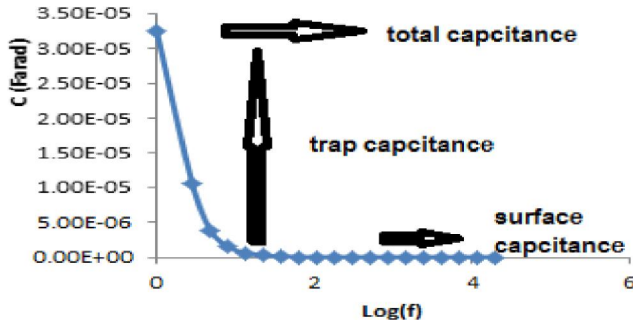The change density of trapped state calculated from

Full Paper

Figure 7 : Shows variable of C(F)=log(f).

thefollowing expression[9]:

$$N_s = \left(\frac{2\varepsilon.N_d.\psi}{e}\right)^{\frac{1}{2}} = 4.80\times10^{20} / cm^3$$

Where N_d density of donor carriers, Ψ high barrier of the sample, dielectric constantε =10.2 sample of CdSe.

Deep trapped chargethe contribution

Contribution estimation of deeptrapped charge densityin CdSenanoparticles, can be done from measuring the capacitance C in function offrequency logarithm. Figure 7 : Shows the relationship between capacitance C and Log(f) in range frequency (1Hz-20KHz) measured by using Gain Phase analyzer. Figure 7 reveals that at frequencies from 1 to 10Hz, the capacitance decreases from value($3\times10^{-5} F$ - to $0.1\times10^{-5} F$)that means carrier charge contributiondecreases rapidly that's mean there are two kind of charge (surface and deep trapped charge) contribute in charge capacitance, and in the range of frequency (10Hz up to 20KHz) capacitance remains constant that's mean surface charge only contribute to the capacitance charge[9].At low frequencies there are contributions of deep carrier due to the high relaxationtime (low frequency), carrier charge have enough time to relax and appear on electrodes capacitance. the total capacitance at low frequency can be written as:

$$C_{tot} = C_{trap} + C_s$$

$$C_{Trap} = C_{TOT} - C_s$$

Where C_{Trap} the capacitance comes from the contribution deep trapped charges, C_S the capacitance contributions of surface carrier charge (measured at high frequency). $C_{TOT} = 3.24 \times 10^{-5} F$ (measured at low

frequency), $C_s = 7.5 \times 10^{-10} F$.

Determine type of semiconductor for sample CdSe (3/1)

By calculating the capacitance between grains boundary,then by applying the following Mott – Schottky expression[10]:

$$\left(\frac{1}{C} - \frac{1}{2C_0}\right)^2 = \frac{2}{e \, \varepsilon_0.\varepsilon_r(N_d - N_a)}(\psi + v)$$

Where C_p, C_0: are the parallel capacitance between thegrain at v‴0 and v=0 respectively. Figure 6 shows, the relation between:

$$y = \left(\frac{1}{c} - \frac{1}{2c_0}\right)^2, x = V$$ as function of applied voltage.

When $N_d \gg N_a$ the slope will be positive and the semiconductor is n-type; when $N_a \gg N_d$ the slope will be negative and the semiconductor isp-type.
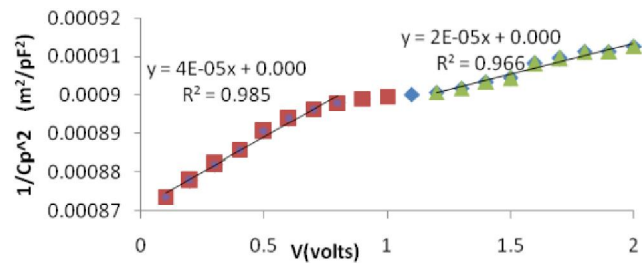

Figure 8 : Shows: $\left(\frac{1}{C} - \frac{1}{2C_0}\right)^2 = f(V)$.
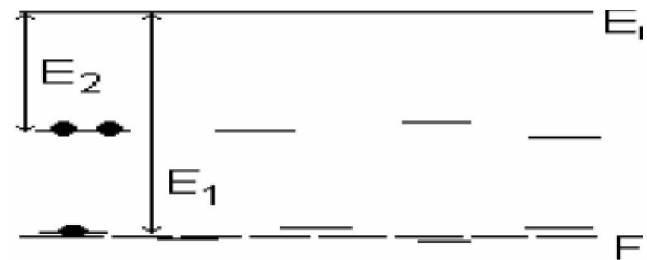

Figure 9 : Energy level corresponding to donor defects with two ionization states.
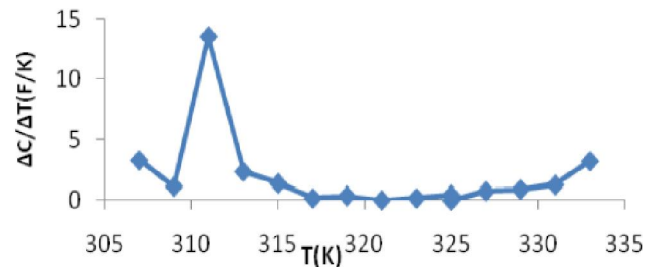

Figure 10 : Show variable capacitance with temperarure.

Full Paper

Figure 8 have two regions (slopes) due to exist two donors levels founded between conduction and valence bands[11].

That confirm by studying capacitance variable with temperature. Figure 10 shows $\frac{\Delta C}{\Delta T}$ in function of T,it revealtwo peaks appear at temperature 312 K and 334K, that means there are two donors levels[12].

By using Mott – Schottkyexpression, donor carrier density can calculate form the slope one and two in the Figure 8. TABLE 3 shows two donors density and two energies levels of donors.

TABLE 3

$N_{1d}(cm^{-3})$at low voltage	$N_{2d}(cm^{-3})$ at high voltage	E_{1d} (ev) at low temperature	E_{2d}(ev)at high temperature
$3.06*10^{22}$	$6.12*10^{22}$	0.026	0.028

CONCLUSION

Cdse nanoparticles were prepared in medium solution, the prepared samples have structure identical tohexagonal structure withspace lattice d= 3.26 A^æ%,crystallization size was 85.7nm. The value of effective strain and dislocation of theformed crystal was close to standard values,found to be (0.026, 0.028)eV respectively. Electrical properties show CdSe nanoparticles were n-type semiconductoror. the CdSe prepared found to have twodonors level sit at energy close to activation energy which it equal to (0.0275 ev) energy diagram of CdSe nanoparticle was drown as it indicated in Figure 9, there are deep trapped carrier density in CdSe nanoparticles.

REFERENCES

[1] A.Acharya; R.Mishra, G.S.Roy; "Characterization of CdSe/polythiophene nanocomposite by TGA/DTA, XRD, UV-VIS spectroscopy, sem-edxa and ftir".armenian journal of physics, **3(3)**, 195-202 **(2010)**.

[2] P.Gupta, M.Ramrakhiani; "Influence of the Particle Size on the Optical Properties of CdSe Nanoparticles "The Open Nanoscience Journal, **3**, 15-19 **(2009)**.

[3] Y.Wang, N.Herron; "Optical properties of cadmium sulfide andlead II sulfide clusters encapsulated in zeolites". J.Phys.Chem., **91**, 257 **(1987)**.

[4] Şaban Mustafa Huş; "Physical Properties Of Cdse Thin Films Produced By Thermal Evaporation And E-Beam Techniques" thises,middle east technical university,September, **(2006)**.

[5] N.J.Suthan Kissinger, M.Jayachandran, K.Perumal, C.Sanjeevi Raja; "Structural and optical properties of electron beam evaporated CdSethin films" Bull.Mater. Sci., **30(6)**, 547–551 **(December 2007)**.

[6] Jaspal Singh, N.K.Verma; "Structural, optical and magnetic properties of cobalt-doped CdSe nanoparticles "Bull.Mater. Sci., **37(3)**, 541–547 **(May 2014)**.

[7] Aurobinda Acharya, Rajkishore Mishra, G.S.Roy; "Comparative Study of Performance of CdS, CdSe thin filmCdS-PTh, CdSe-PTh nanocomposite thin films Using SEM-EDXA(Scanning Electron Microscope) and FTIR (Fourier Transform Infrared Spectroscopy)". Lat.Am.J.Phys.Educ., **4(3)**, **(Sept. 2010)**.

[8] P.R.Bueno, M.R.Cassia-Santos, E.R.Leite, E.Longo, J.Bisquert, G.Garcia-Belmonte, F.Fabregat Santiago; Nature of the Schottky-type barrier of highly dense SnO2 systems displaying nonohmic behavior, Journalof Applied Physics, **88**, 6545-6548 **(2000)**.

[9] P.Kharangarh, D.Misra, G.E.Georgiou, K.K.Chin; Journal of Applied Physics, **113(14)**, 144504(1-6) **(2013)**.

[10] F.D.Hevia, J.Frutos, D.E.Mott–Schottky; Behavior of strongly pinned double Schottky barriers and characterization of ceramic varistors, Journal of AppliedPhysics, **92**, 2890-2898 **(2002)**.

[11] L.Ion, S.Antohea, M.Popescu, F.Scarlat, F.Sava, F.Ionescu; "structure and electrical properties of electron irradiatedCdSe thin films".Journal of Optoelectronics and Advanced Materials, **6(1)**, 113–119 **(March 2004)**.