2) ANNEALING EFFECT ON STRUCTURAL, OPTICAL & PHOTOVOLTAIC PROPERTIES OF TERNARY $Cd_{1-x}Zn_xSe$/PVA NANOCOMPOSITES SOLAR CELL

Swati Dubey, SaritaKumari ,MeeraRamRakhiani
Department of Physics & Electronics
Rani Durgawati University Jabalpur- 482001, India

ABSTRACT- The effect of annealing duration on structural, optical and photovoltaic properties of $Cd_{1-x}Zn_xSe$/PVA nanocomposites thin films for high Zn content have been investigated. $Cd_{1-x}Zn_xSe$ ternary alloy dispersed in poly vinyl alcohol (PVA) matrix for x=0.75 have been synthesized by simple chemical route. The nanocomposites films were annealed in an electric furnace at 150ºC for1, 1½ and 2 hour. The structural, morphological and optical properties of $Cd_{1-x}Zn_xSe$/PVA nanocomposites were done by X-ray diffraction (XRD), Scanning electron microscopy (SEM),ultraviolet-visible spectrometry (UV-Vis) techniques. Peak indexing of diffraction spectra confirms that due to high Zn content in $Cd_{0.25}Zn_{0.75}Se$ composition exhibits zinc blend cubic phase under 1, 1½ and 2 hour annealing duration.XRD pattern indicates as annealing duration changes particle size also changes. Smaller particle size 3.66nm obtained for 1½ annealing hour at 150ºC.A significant change of morphology of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites thin films were observed at different annealing duration. Nanoleaf, narowire and nanorod were grown on the surface for 1,1½ and 2 houranneling duration respectively.Opticalstudy revealed on altering annealing duration nanostructure band gap varies and wider band gap 3.42eV is obtained for 1½ hour annealing duration.The $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites film was used as photo-electrode in photoelectrochemical cell having polysulfide electrolyte solution and graphite as counter electrode. The $Cd_{0.25}Zn_{0.75}Se$/PVA photo-electrode was illuminated by 50 watt tungsten lamp. Using a potentiometer, the photo-voltage & photo-current were measured at different load resistances and solar cell parameters open circuit voltageV_{oc} and short circuit currentI_{sc}were determined.

KEY WORDS-Photovoltaic effect, $Cd_{1-x}Zn_xSe$/PVA nanocomposites, Photoelectrochemical solar cells, Absorption spectra, XRD, SEM

I.INTRODUCTION-

Semiconductor nanoparticles have proven their ability in huge area of research and development, but still attempts to fabricate nanocrystals with tunable and enhanced optical properties continue. The ability to tune and enhance the physical properties of nanomaterials is imperative to moving beyond our current capabilities to more advanced technologies.The present work is aimed at preparing cadmium zinc-selenide [(CdZn)Se], one of the important ternary materials for use in electroluminescent, photo-luminescent, photo-conductive and photovoltaic device applications because of its interesting size-dependent properties as well as a high stability and wide optical band gap which covers the maximum electromagnetic spectrum [1-3]. Basically, the properties of the nanocomposites materials solely depend on the preparation process; for examples the ratio of concentration between the polymers and inorganic material, the temperature used, and types of deposition techniques. An increasing research effort is now being directed toward polymer-based photovoltaics, leading to encouraging strides in both the basic understanding of device operation and improving device efficiency. The polymer film acts as a stabilizer resulting in a high uniformity in the size of nanocrystals[4-6]. Among different polymers, poly (vinyl alcohol) (PVA) attracted the attention of researchers due to its optical characteristics, physical properties, film forming and biocompatibility.

Annealing, in materials science, is a heat treatment that alters the physical and sometimes chemical properties of a material to alter its structural, optical and electrical properties, making it more workable. It involves heating a material to above its recrystallization temperature, maintaining a suitable temperature, and then cooling gradually. In annealing, atoms migrate in the crystal lattice and the number of dislocations decreases, leading to increase crystallization strength in nanostructure.Present study explores the annealing effect of $Cd_{1-x}Zn_xSe$/PVA nanocomposites film for high Zn content prepared by simple chemical routewith x=0.75 in ternary alloy.$Cd_{1-x}Zn_xSe$ thin films have been studied by many researchers [7-10] but the effect of annealing duration on the structural, optical and photovoltaic properties of $Cd_{1-x}Zn_xSe$/PVA thin films is rarely presented in the literature. Therefore, it is worthwhile to study the effect of annealing on structural, optical and photovoltaic properties $Cd_{1-x}Zn_xSe$/PVA nanocomposites thin films .The aim of this study is to investigate the effect of annealing duration on the structural, optical and photovoltaic properties of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites thin films such as lattice parameter, particle size, absorption edge, optical band gap Eg and photo conversion efficiency η.

2. EXPERIMENTAL-

2.1 Synthesis-

In the synthesis of PVA/$Cd_{1-x}Zn_xSe$ nanocomposites film PVA is employed as surfactant-cum-stabilizer-cum-matrix for CdZnSe nanoparticles. Cadmium chloride $CdCl_2.2H_2O$ and $ZnCl_2.2H_2O$ were chose as metal ion source, sodium selenosulfate (Na_2SeSo_3) was chosen as the selenium source, and polyvinyl alcohol (PVA) was chosen as the stabilizer. No additional stabilizer was needed because the high viscosity of the polymer solution prevented the particles from aggregating. First of all a 100 ml aqueous solution of sodium sulfite (1M) was prepared. Then 0.1 mol of selenium powder was added with constant stirring, the mixture was heated to 60 ◦ C till the selenium is dissolved in the solution. Upon filtration, sodium selenosulfate solution, was obtained and marked as solution 'A'. PVA solution was prepared by adding 3 gm PVA in 50 ml distilled water and stirring at 90 ◦ C until a viscous transparent solution was obtained. (1-x) content of $CdCl_2$ and (x) content $ZnCl_2$ was dissolved in distilled water to obtained 0.10 M solution, and marked as solution 'B'. Ammonia solution was used as complexing agent.$Cd_{1-x}Zn_xSe$/PVA nanocomposites were prepared for x=0.75 as follows – 20 ml PVA solution was placed and 1.05 ml. Solution 'B' was added with constant stirring. Ammonia solution was used to adjust pH value to about 10 and then 1ml of solution 'A' was introduced. The mixture was stirred for 3 hours to obtain a resultant solution. The solution was cast on a glass substrate/ titanium substrate upon solvent evaporation, a PVA – $Cd_{0.25}Zn_{0.75}Se$ composite film was obtained. The films were washed with distilled water to remove other soluble salts. Prepared $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites films annealed at 150ºC for1hour , 1 ½ hour& 2hour.

2.2 Characterization-

The sample was characterized by X-ray diffraction (XRD) and SEM. Sample was characterized at SAIF Cochin STIC. XRD is one of the most powerful and established technique for material structural analysis capable of providing information about the structure of a material at atomic level. X-ray source is Cu, wavelength 1.5406 A°, configuration is vertical, Theta /2 Theta geometry. X-ray model using here is Bruker AXS D8 Advance. Maximum usable angular range is 3º to 135º. In order to investigate the surface morphology the sample was analyzed by scanning electron microscope. The study has been done by The SEM – EDS installed in SAIF, STIC have the following specification used for analysis; image modes- SEI,BEI; EDS Make :JEOL Model JED-2300. For optical studies, absorption spectra as recorded with systronics double beam UV-Vis spectrometer.

2.3 Photovoltaic Studies–

Photovoltaic effect of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocrystalline film was deposited on titanium substrate used as photoelectrode in two-electrode configuration with polysulfide electrolyte and graphite is used as counter electrode. Electrolyte solution was prepared from 1M solutions of NaOH, Na_2S and sulfur. The photelectrode was illuminated by a 50 watt halogen-tungsten lamp and current-voltage characteristics was obtained using potentiometer and multimeters for 315 lux intensity measured by standard lux meter.

III. RESULT ANDDISCUSSION–

3.1 Effect of Annealing Duration on Structural Characteristic of $Cd_{0.25}Zn_{0.75}Se$/PVA Nanocomposites Film -

Figure.1 shows the X-ray diffraction spectra of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites films annealed for 1hour, 1 ½ hour & 2hour at 150ºC. Diffraction pattern reveals that for 1 hour annealing duration peaks are observed at 2θ =19.855º, 23.268º, 29.879º, correspond to (100), (110), (200) plane, with 5.40 nm crystallite size confirms its nanocrystalline nature. When annealing time is 1½ hours peaks are observed at 2θ=19.845º, 23.361º, 30.865º, 40.693º, 53.694º correspond to (100), (110), (200), (211), (311) with 3.66 nm crystallite size and for 2 hour annealing duration few peaks are observed at 2θ = 27.857º, 36.562º, 54.641º correspond to (111), (210), (311) with highest crystallite size 37.5nm. The particle size was calculated using Debye-Scherrer's formula, $D = 0.9\lambda / \beta \cos\theta$ where "λ" is wave length of X-ray (0.1541 nm), "β" is FWHM (full width at half maximum), "θ" is the diffraction angle and "D" is particle diameter size. It is seen in diffraction spectra that peak become narrow with lowest intensity at longest annealing duration i.e no peak broadening is found for 2hour annealing duration in our experiment. It is clear from diffraction spectra that peak broadening is found when annealing duration is small. Peak indexing of diffraction spectra confirms that due to high Zn content in $Cd_{0.25}Zn_{0.75}Se$ composition exhibits zinc blend cubic phase under 1, 1½ and 2 hour annealing duration. It is confirmed that lattice constant varied with annealing duration. These estimated experimental values of lattice constant are nearly same for cubic phase of $Cd_{0.25}Zn_{0.75}Se$ (a=5.75) for 1½ hour annealing duration[11].

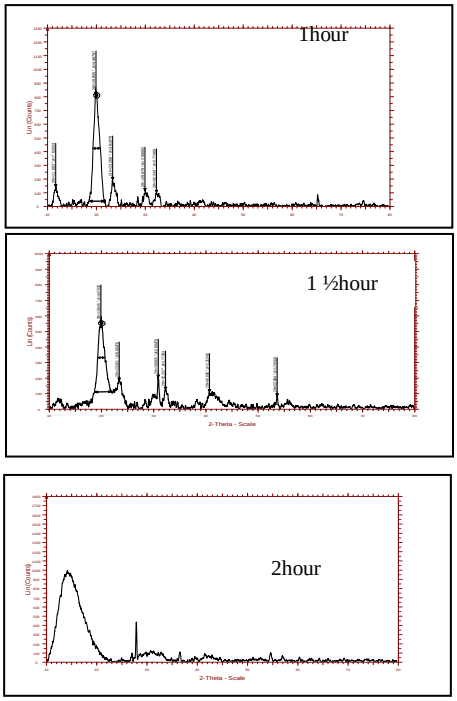

Figure 1 XRD pattern of $cd_{0.25}Zn_{0.75}Se$ for different annealing duration

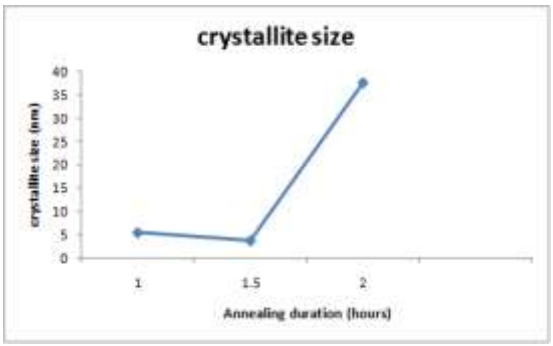

Figure 2 Crystallite size variation for annealing duration

Table I - XRD parameters from diffraction spectra

Annealing duration (hour)	Lattice constant a°	Crystallite size (nm)	Lattice strain $\varepsilon x10^{-3}$	Dislocation density $\delta x\ 10^{16}$
1 hour	5.3	5.40	37.17	3.99
1:30 hour	5.7	3.66	35.75	8.68
2 hour	5.6	37.5	3.81	.0642

3.2 Effectof Annealing Duration on Surface Morphology of $Cd_{0.25}Zn_{0.75}Se$/PVANanocomposites-

Figure 3 shows the surface morphology of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomosites at different annealing duration 1,1 ½ ,2 hours respectively.Micrograph confirms that nano leaf / nano wire/ nano rod grown on the surface for 1/1:30/2 annealing hour. It shows that annealing duration tailored the surface structure of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites and larger particle size is obtained for longer annealing hour. Table II shows average grain size from SEM images.It can be clearly seen from the result of SEM studies that beyond 1½ annealing hour particle size increses.

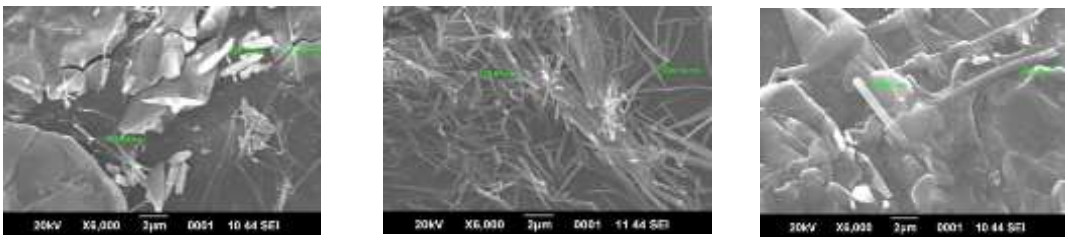

Figure 3 SEM images for different annealing duration

Table II- Average grain size from SEM

Annealing duration (hour)	Average grain size of smaller particles in (nm)
1 hour	194.37
1 ½ hour	179.51
2 hour	659.97

3.3 Optical Propertiesof $Cd_{0.25}Zn_{0.75}Se$/PVA Nanocomositesat Different AnnealingDuration–

Figure 4 shows the absorption spectra of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites film at different annealing duration. The $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites exhibit steep absorption edge in the range of 362nm-443nm.This implies that $Cd_{0.25}Zn_{0.75}Se$ nanoparticles are in the regime of spatial excitonic confinement compared to bulk of $Cd_{0.25}Zn_{0.75}Se$ nanoparticles.

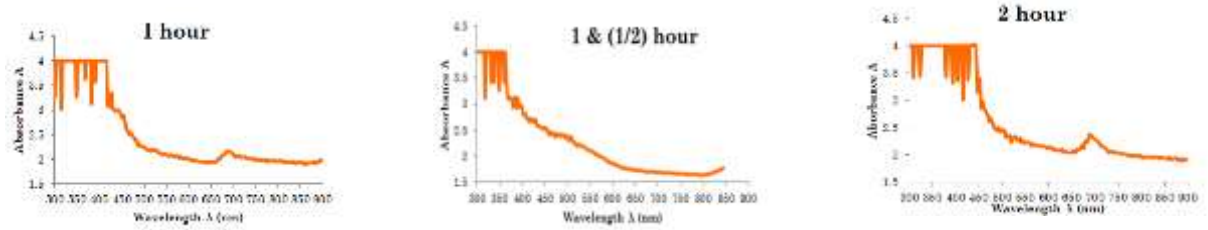

Figure 4- Absorption Spectra of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites for different annealing duration

It is observed from the spectra that the absorbance of the samples decreases slightly with increase in annealing duration and the absorption edge slightly shift lower energy.An optical band gap 2.98 eV is estimated for 1hour annealing duration of $Cd_{0.25}Zn_{0.75}Se$ nanoparticles which are much wider than that of bulk $Cd_{0.25}Zn_{0.75}Se$. The values of absorption edge wavelength, band gap and particle size estimated from absorption spectra of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites annealed for 1, 1½ and 2 hour annealing duration are given in table III.

Table –III Optical Parameter calculated by UV-Vis absorption spectra

Annealing Duration in Hour	Absorption Edge wavelength (nm)	Bulk bandgap of $Cd_{0.25}Zn0_{0.75}Se$ Composition (eV)	Band gap calculated for spectra (eV)	Shift in band gapΔE (eV)	Particle size in (nm)
1hr	415	2.401	2.98	0.579	5.11
1:30 hr	362		3.42	1.019	3.85
2hr	443		2.79	0.389	6.24

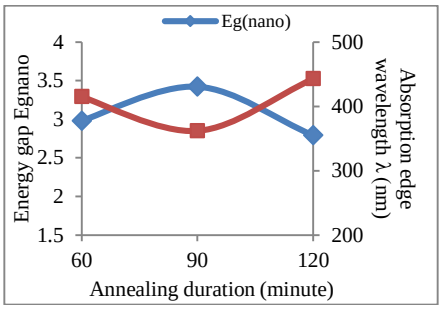

Figure 5 E_g& absorption edge variation at different annealing time

Absorption edge 362nm is blue shifted for 90 minute (1½ hour) annealing. Above study revealed that on altering annealing duration nanostructure band gap varies and wider band gap 3.42eV is obtained for 1½ hour annealing duration.Energy band gap of nanocomposite is calculated by -$E_g = \frac{hc}{\lambda}$ where h is plank constant, c is speed of light and λ is absorption edge wavelength in (nm).

In the bulk ternary system of $Cd_{1-x}Zn_xSe$, the dependence of band gap $(E_{gnan})_{ternary}$ on composition (x) can be expressed by following equation [12] –

$(E_{gnano})_{ternary} = (1-x)\ E_g^{CdSe} + (x)\ E_g^{ZnSe} - 0.35\ x\ (1-x)$.

Fromabsorption spectra particle size of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites calculated by following equation [13]

$r = \sqrt{\frac{2\pi^2\hbar^2 E_{gbulk}}{\left(\frac{1}{m^*e}+\frac{1}{m^*h}\right)(E^2 gnano - E^2 gbulk)m_0}}$ Where $E_{g\,bulk}$ – energy gap of bulk $Cd_{0.25}Zn_{0.75}Se$

E_{gnano} – Energy gap of nanocomposite, m_e^* / m_h^* effective mass of electron & hole respectively.

3.4 Photovoltaic Propertiesof $Cd_{0.25}Zn_{0.75}Se$/PVA Nanocomposites Filmat Different Annealing Duration-

With the help of two electrode configuration in polyelectrolyte solution phtoelectrochemical cell configuration was prepared and current-voltage characteristics were obtained using potentiometer and multimeters. During photovoltaic measurement open circuit voltage V_{oc}& Short circuit current I_{sc} were measured. Figure 6 shows the V-I characteristics of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites films for different annealing time.Photocurrent voltage performance of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites films annealed under different duration indicates that open circuit voltage (V_{oc}) and

short circuit current (I_{sc}) are influenced by annealing duration. Form V-I curve photovoltaic cell parameter open circuit voltage (V_{oc}), Short circuit current (I_{sc}), Fill Factor (FF), Efficiency (η) are determined.Table IVshows all the photovoltaic parameter observed by V-I curve. Figure7 shows the Efficiency and Fill Factor variation for different annealing duration. It indicates that maximum efficiency is achieved for 1½ hour annealing.

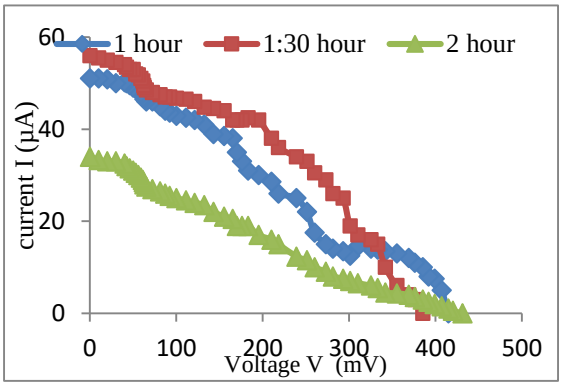

Figure 6 V-I curve of $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites films for different annealing time (1 hour/1 ½ hour/2hour)

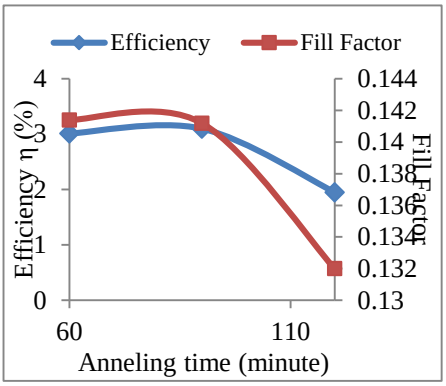

Figure 7 Efficiency & FF variation for different annealing duration

The cell parameters are affected by annealing duration. Annealing can alter surface structure, band gap, particle size and hence cell efficiency. Improvement of crystal quality of the $Cd_{0.25}Zn_{0.75}Se$ nanoparticles by annealing treatment will decrease the internal defects, which can reduce the recombination of photo excited carriers and result in a higher power conversion efficiency for 1½ hour.

Table – IV Photovoltaic parameter from V-I Curve

Annealing Duration (hour)	Open circuit voltage V_{oc} (mV)	Short circuit current I_{sc}(μA)	Efficiency (η)	Fill Factor FF
1	415	51	3.01	0.141
1½	385	56	3.10	0.142
2	431	34	1.95	0.132

Formula used for Efficiency(η) & $FF\eta = \frac{Pout}{Pin} \rightarrow \eta_{max} = \frac{Pmax}{Pin} FF = = \frac{Im \times Vm}{Isc \times Voc}$

4. Conclusion–

It is concluded that structural, morphological, optical and photovoltaic properties of ternary alloy $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites are influenced by annealing time. $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites give best performance for 1½ hour annealing in terms of smaller particle size (3.66nm), wider band gap (3.42eV), surface structure (nanowire) and highest photovoltaic efficiency (3.1%) at 150°C annealing temperature. SEM study reveals that the $Cd_{0.25}Zn_{0.75}Se$ nanoparticles are well dispersed in polymer matrix. Good contact between the $Cd_{0.25}Zn_{0.75}Se$/PVA ternary alloys is formed when annealing duration is 1½ hour. In this case nanowires are formed in ternary alloy $Cd_{0.25}Zn_{0.75}Se$, and produce a superior interface between the photo-electrode and electrolyte, which is responsible for its higher efficiency. Peak indexing of diffraction spectra confirms that due to high Zn content in $Cd_{0.25}Zn_{0.75}Se$ composition exhibits zinc blend cubic phase under 1, 1½ and 2 hour annealing duration. It is confirmed that lattice constant varied with annealing duration. These estimated experimental values of lattice constant are nearly same for cubic phase of $Cd_{0.25}Zn_{0.75}Se$ (a=5.75) for 1½ hour annealing duration. In $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites PVA act as a host matrix and for longest annealing duration (2 hour) PVA decomposes rapidly, it can undergo pyrolysis for longer annealing duration. Larger particle size (37.5nm) obtained for 2 hour annealing because there could be some difference in the bond lengths in $Cd_{0.25}Zn_{0.75}Se$/PVA nanocomposites caused by uneven stress, coming from the difference in the thermal expansion coefficient of the films and substrate. For improving photovoltaic performance annealing is must for photo electrode.

5. REFERENCES-

[1] Hankare P.P., Chate P.A., Asabe M.R., Delekar S.D., Mulla I.S., garadkar K.M., J. Mater.2006 Sci.-Mater. El., 17 1055.

[2]Vartanian A.L., Asatryan A., Kirakosyan L.,Physica B.2007.389 258.

[3] Tamargo M. C. 2002 II–VI Semiconductor Materials and their Applications (New York:Taylor and Francis)ch 2.

[4]O. M. Folarin, E. R. Sadiku, and A. Maity.2011 "Polymer-noble metal nanocomposites: review," International Journal of Physical Sciences, Vol. 6, No. 21 pp. 4869–4882.
[5]R.Shenhar, T.B.Norsten, and V.M. Rotello. 2005 "Polymer-mediated nanoparticle assembly: structural control and applications," Advanced Materials, Vol. 17, No. 6 pp. 657–669.
[6]X. Liu, Y. Adachi, Y. Tomita, J. Oshima, T. Nakashima, and T. Kawai.2012 "High-order nonlinear optical response of a polymer nanocomposite film incorporating semiconducotorCdSe quantum dots," Optics Exp3ress, Vol. 20, No. 12 pp. 13457–13469.
[7]Ijaz Ali, AmjidIqbal, ArshadMmahmood, A. Shah, M. Zakria, Asad Ali.2016 Materials Science-Poland, 34(4) pp. 828-833.
[8] Mustafa Kh Mustafa, Manal M Abdullah, Zaidoon T Mohammad Noori&Mustefa A Jumaa.2015, " Effect of annealing temperature on the optical properties of spin coated CdS/PVA thin films" Indian Journal of Pure & Applied Physics ,Vol. 53, pp. 617-624.
[9] M. Verma, A. Kaswan, D. Patidar, K. B. Sharma, N. S. Saxena. 2016"Phase transformation and thermal stability of ZnSe QDs due to annealing: emergence ofZnO" J Mater Sci, 825.
[10] K.Y. Pechers'ka, L.P.Germash, N.O.Korsunska.2010"Effect of annealing on the luminescent characteristics of CdSe quantum dots in a polymer,"Ukrainian Journal of Physics,Vol.55, No. 4pp. 403–409
[11] Mohammed AmeriMeriemFodil, Fatma Zahra Aoumeur-Benkabou, ZoubirMahdjoub, Fatima Boufadi, Ali Bentouaf.2012 "Physical Properties of the $Zn_xCd_{1-x}Se$ Alloys: Ab-Initio Method"Materials Sciences and Applications3, 768-778.
[12] Jong –UK Kim, Jong-Jin Lee , Ho Seong Jang , Duk Young Jeon, and Hessun Yang.2011Journal of Nano Science and Nanotechnoloty, (11) 725-729.
[13] Ekpekpo Arthur and Akpojivi Lucky.2013 "Synthesis and Characterization of Cds and Cdse Quantum Dots by UV-VIS Spectroscopy" Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS), 4(2) 273-280.