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Abstract:

Present work describes chemisynthesis of CdSe thin films on stainless steel and fluorine doped tin oxide coated glass substrates. These films are characterized by means of X-ray diffraction (XRD), UV–Visible spectrophotometry, contact angle measurement and field emission scanning electron microscopy (FE-SEM) techniques, to study the effect of pH on the structural, optical, wettability and morphological properties.With change in pH of deposition bath, crystallinity of bath found to be influenced along with phase transformation. Optical studies show band gap energy and absorption edge found to be modulated by pH of bath. Surface morphology of CdSe thin films found to be drastically altered by pH of bath.

Keywords: CdSe, Thin film, pH, XRD, FE-SEM, optical properties.

Introduction

II-VI group compound semiconductors have drawn a great extent of attention from past few decades because of their extensive applications [1, 2]. Cadmium selenide (CdSe) is one of well-known II-VI group semiconductors, which has captivated global researchers due to its appropriate properties. Quantum size effect shown by the CdSenanocrystals is maybe the mainly attractive property [3].s Band gap energy of CdSe (Eg = 1.7eV) is positioned in close proximity of solar spectrum, making it more favorable for various optoelectronic applications, optical sensing agents,laser diodes, photoelectrochemical solar cells, light emitting diodes, photodetectors, photoelectric applications etc [4,5,6,7,8,9]. Researchers used variety of synthesis techniques such as vacuum evaporation [10], successive ionic layer adsorption and reaction [11], spray pyrolysis [12], electrode position [13], pulse plating [14] chemical bath deposition [15] to grow CdSe thin films. Among various methods, chemical bath deposition (CBD) has paramount benefits with other methods as simple, low temperature, no need of conducting substrate, suitable for large area deposition, with no requirement of sophisticated instrumentation. In CBD thin film deposition takes place after supersaturation explicitly when ionic product just go above solubility product [16]. Various preparative parameters like concentrations of precursor solution, temperature, pH etc strongly influence the solubility product of bath consequently controls growth rate of the deposit [17]. pH of deposition bath plays key role in deciding the structural, optical and morphological properties of deposit. Thus in the current investigation, the effect of bath pH on structural, optical, wettability and morphological properties is studied.

Experimental details

Chemical synthesis of CdSe thin films

The CdSe thin films were chemically deposited on the pre-cleaned stainless steel and F:SnO_2 (FTO) coated glass substrates. Since substrate cleaning plays prime role in the deposition process thus all the substrates were cleaned by procedure reported elsewhere [13]. All the chemicals used for deposition process were analytical reagent grade and used with no further purification. Cadmium sulfate ($CdSO_4$) and sodium selenosulphate (Na_2SeSO_3) were used as sources of cation and anion respectively. Cd^{+2}cations were complexed using liquor ammonia. Sodium selenosulphate solution was prepared by dissolving 0.1M selenium (Se) powder in an aqueous solution of 0.5M sodium sulphate (Na_2SO_3), which further refluxed at 85-90°C for 8-9hs. Then this solution was allowed to cool to room temperature and very tiny amount of suspended selenium powder filtered out to get clear solution. Different preparative parameters such as precursor concentrations, deposition temperature and deposition time were optimized with numerous trials and using well known photoelectrochemical method [18].

For chemical bath depositon of CdSe thin films, 0.05 M CdSO4 solution (10ml) was poured into a beaker of 30ml capacity. 30 vol% Liquid ammonia was added drop wise with constant stirring. Initially addition of ammonia to cadmium precursor solution shows formation of milky cadmium hydroxide $Cd(OH)_2$ precipitate , which entirely dissolves after extra adding up of ammonia solution. Finally, 0.05 M Na_2SeSO_3 solution (10ml) was poured to the same. A substrate was kept 15-20° slanted to the wall of beaker. The temperature of bath was maintained at 85°C. pH of bath was varied 11, 11.5, 12 and 12.5(±0.2) with addition of appropriate amount of ammonia. After 8hs, substrates were removed, repeatedly rinsed in doubly distilled water, dried and stored in sealed box for further study.

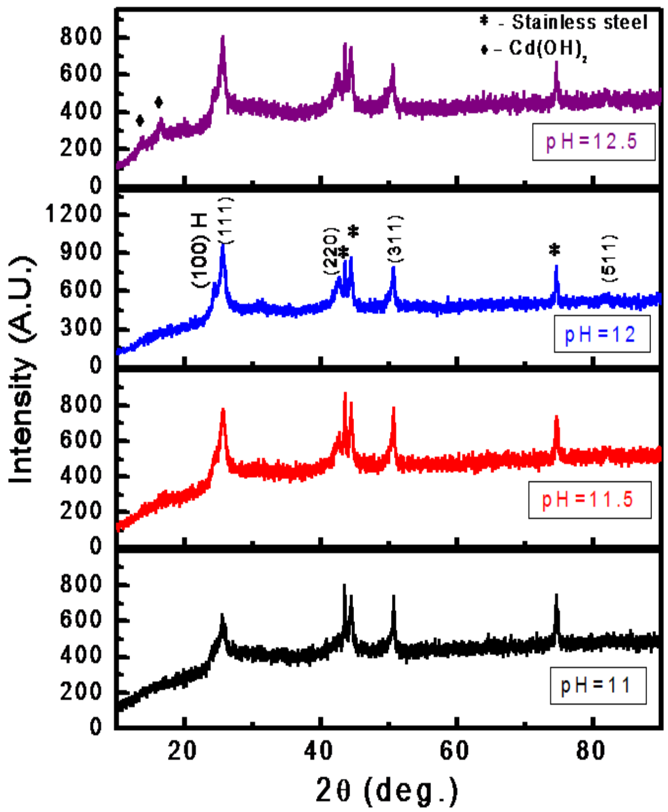
Characterizations

The study of structural properties of CdSe thin films was carried out using Philips X-ray diffractometer PW-3710 with Cu Kα source (λ=1.54Å) in the 2θ range from 10◦ to100◦. The optical absorption study was carried out inthe wavelength range 300–900 nm using a UV spectrophotometer UV-1800 SHIMADZU. The contact angle measurements were done using by Rame-Hart USA equipment equipped with a CCD camera to study the solid –liquid interface. The JEOLJSM 6360 unit was used for surface morphological study.

Results and discussion

Structural analysis

XRD patterns of chemically deposited CdSe thin films at different pH values are shown in Fig. 1 The observed XRD patterns matches well with Standard JCPDS data card no. 00-019-0191 confirming the formation of CdSe with a



metastable cubic (Sphalerite) crystal structure. The peaks designated by symbol * corresponds to contribution of stainless steel substrate which may be due to interference from XRD signals of the substrate.

Figure 1:X-ray diffraction spectra of chemically deposited CdSe thin films at different pH values.

Table 1:Comparision of XRD data for chemically synthesized CdSe thin films at different pH values.

Standard "d" values (Å)	Observed "d" values (Å)				Planes (h k l)
	pH=11	pH =11.5	pH=12	pH=12.5	
3.74	-	-	3.66	-	(1 0 0) Hexagonal
3.51	3.49	3.49	3.49	3.49	(1 1 1) Cubic
2.15	-	2.13	2.12	2.12	(2 2 0) Cubic
1.83	1.8	1.8	1.81	1.81	(3 1 1) Cubic
1.17	-	-	1.17	-	(5 1 1) Cubic

At lower pH value (pH=11), the diffraction pattern shows only two diffraction peaks at 2θ = 25.5◦ and 50.6◦, corresponding to (111) and (311) planes of cubic phase respectively. The diffraction pattern for thin films deposited at pH=11.5 observed to contain (220) plane, the along with (111) and (311) planes at 2θ values 42.4◦, 25.6◦, 50.6◦, respectively. The XRD pattern corresponding to pH=12 reveals that the diffraction peaks become more sharp with drop off in full width at half maximum showing enhancement in crystallinity and particle size in company with phase transformation. The diffraction pattern for pH=12 contains five diffraction peaks at 2θ values 24.3◦, 25.5◦, 42.7◦, 50.5◦ and 81.8◦. The diffraction peaks observed at 25.5◦, 42.7◦, 50.5◦ and 81.8◦ are indexed as (111), (220), (311) and (511) planes confirming formation of cubic phase which are in good agreement with earlier reports [19, 20]. While the diffraction peak observed at 24.3◦ is indexed as (100) plane of wurtzite hexagonal phase [JCPDS data card no.00-002-0330] confirming phase change. Enhancement in crystallinity is observed with increase in pH values from 11 to 12, afterwards it declines. At higher pH value (pH=12.5) the diffraction peaks observed at 25.5◦, 42.6◦ and 50.6◦ are indexed as (111), (220) and (311) planes, respectively. The (100) plane corresponding to hexagonal phase and (511) plane corresponding to cubic phase (which are observed at pH=12) are found to be absent in this pattern. While two peaks noticed at 2θ values 13.6◦ and 16.5◦ (designated as ♦ in Fig.1) shows presence of cadmium hydroxide ($cd(OH)_2$) in the film deposited only at higher pH (pH=12.5).

Table 2: Variation in intensity of (111) plane with respect to pH.

pH	Intensity of (111) plane
11	648
11.5	791
12	981
12.5	818

The observed values of interplaner spacing 'd' are found to be matches well with standard values of interplaner spacing 'd' as illustrated in Table 1, signifying the formation of CdSe in thin film form. In all XRD patterns obtained at different pH, a peak corresponding to the plane (111) is found to be prominent as compared to the other planes. Intensity of this plane increases with increase in pH from 11 to 12, which further decreases with increase in pH as shown in Table 2. It shows that the pH value of deposition bath has an effect on the crystal structure and crystallinity of the deposited thin film.

Optical absorption and band gap studies

Optical properties play major role in enhancing device performance in various applications such as solar cells, optoelectronic devices etc. The optical absorption study of CdSe thin films deposited at different pH values was carried out in the wavelength range 300–900 nm by means of UV–visible spectrophotometer. Band gap energy estimation was made using plots of "$(\alpha h\nu)^2$" in opposition to "hν" by extrapolating a tangent to plot on photon energy axis at zero absorption coefficient [21]

Figure 2 (a) shows Plots of $(\alpha h\nu)^2$against hν for cdSe thin films deposited at different pH values from 11 to 12.5. The $(\alpha h\nu)^2$against hν plots are found to be linear in nature confirming the presence of direct transition. The energy band gap value found to decrease from 2.16 to 1.94eV with increase in pH value from 11 to 12, respectively. For further increase in pH of bath from12 to 12.5, the band gap value found to increase from 1.94 to 1.99 eV respectively. This behavior explained as, at lower bath pH smaller CdSe crystallite forms. Increase in pH of bath enhances agglomeration process resulting in formation of larger crystallite. Thus this red shift in band gap energy can be explained on basis of quantum confinement effect [22]. Increase in band gap energy at higher pH (pH=12.5) may be attributed to compositional changes occurred in CdSe thin films. This variation band gap found to be in well harmony with X-ray diffraction studies.

Fig. 2(b) shows absorbance spectra of CdSe thin films deposited at different pH values. Enhanced absorbance with red shift in absorption wavelength observed corresponding to thin film deposited at pH=12, which may be due to enhanced crystallinity of the same. Fig. 2(c) shows a plot of band gap energy as a function of bath pH.

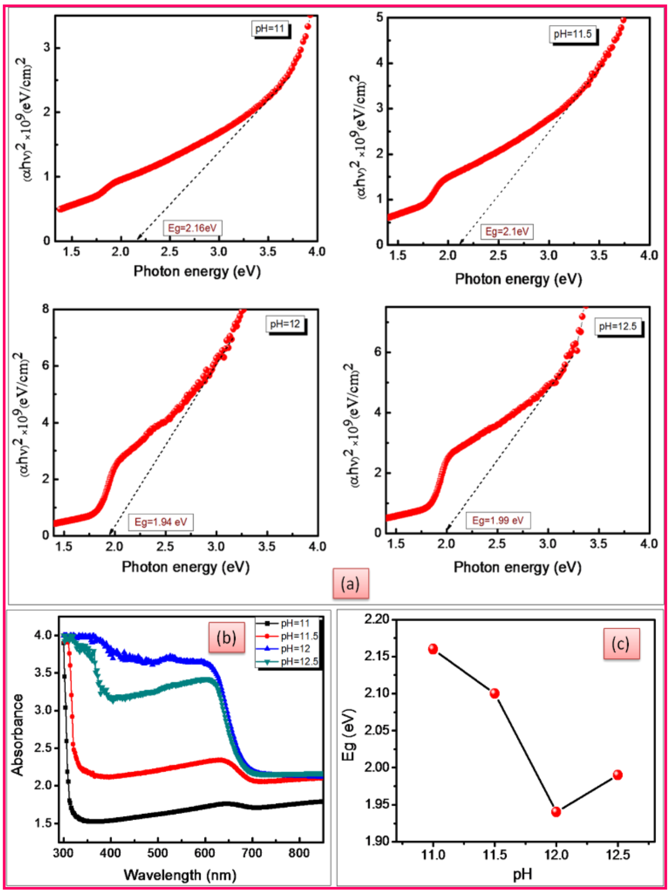


Figure 2: (a)Band gap plots of CdSe thin films deposited at different pH values and (b) Absorbance spectra of the same.(c)Band gap variation as a function of pH.

Wettability studies

Wettability study contains study of the interface between solid and liquid in contact, which is described by means of contact angle. Interpretation of surface energy can be done with use of contact angle and young's equation [23]. Contact angle is inversely related to hydrophilic property of thin film surface. Figure.3 shows the photo images of contact angle measurement of CdSe thin films deposited at pH values 11, 11.5, 12 and 12.5. Water contact angle values are found to be decreased with increase in the bath pH up to 12, further increase in pH, increases the value of contact angle. The lowest value of contact angle is found corresponding to pH=12 and is 48.2◦. Lower value of the contact angle signifies more hydrophilic nature of thin film, assuring better contact between thin film surface and electrolyte solution. This hydrophilic nature of thin film is extremely useful for various applications such as photoelectrochemical solar cells.

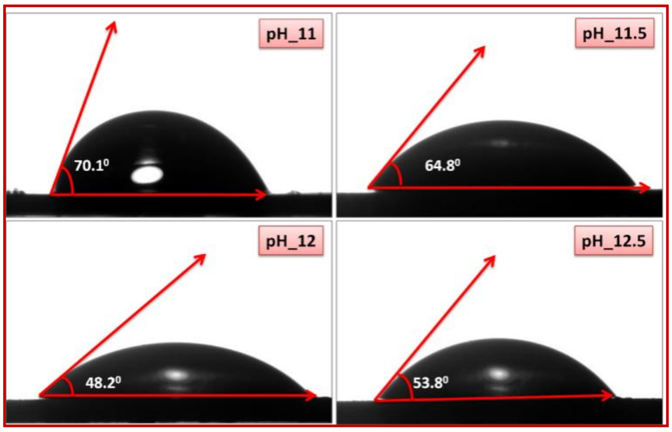


Figure 3: Contact angle measurement images ofCdSethin films deposited at different pH values.

Morphological studies

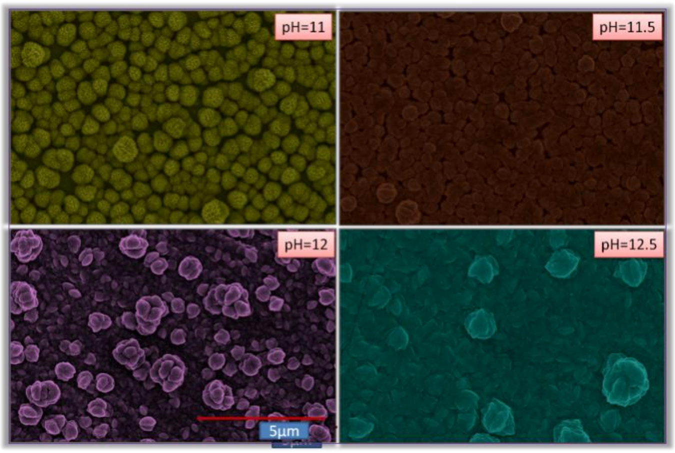


Figure 4: FESEM photographs of chemically deposited CdSe thin films at different pH values of magnification 10Kx.

The surface morphology of CdSe thin films deposited at different pH values was inspected using field emission scanning electron microscopy (FESEM). Figure 4 shows FESEM images of 10KX magnification at pH values 11, 11.5, 12 and 12.5. CdSe thin films deposited at lower pH (pH =11) shows marigold flower like morphology with small voids between them. Films deposited at lower pH (pH= 11) films are powdery and detachable.FESEM image of thin films deposited at pH=11.5 shows little more compact surface. It shows fused pebbles like morphology. Compact structure with agglomerated grain like structure found to be deposited corresponding to pH value 12. Well adherent and good quality films are found to be obtained corresponding to pH value equal to12. With increase in pH values compactness of thin film found to be increased. For higher bath pH (pH=12.5) this granular structure found to be distorted. At higher pH values smaller grains observed. Surface morphology found to be significantly altered with the pH values.

Conclusions

CdSe thin films are successfully synthesized by the chemical bath deposition method at different values of pH. Structural studies reveal enhancement in crystallinity and particle size in company with phase transformation with increase in pH from 11 to 12. Optical studies show maximum red shift in absorbance and decrease in band gap energy corresponding to pH=12.Wettability study shows,film deposited at pH=12 have more hydrophilic nature with contact angle of 48.2◦. Surface morphology of CdSe thin films found to be significantly modulated via the parameter, pH of bath.

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