Synthesis and Characterization of Na and K Dual Doped CdS Thin Films by Chemical Bath Deposition

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Abstract— **CdS, Sodium doped CdS (CdS:Na), Potassium doped CdS (CdS:K), Sodium and Potassium dual doped CdS (CdS:Na,K) thin films were deposited on glass substrate by chemical bath deposition (CBD) technique. Structural and morphological and optical properties of the as-grown films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), ultraviolet visible (UV–VIS) spectroscopy and photoluminescence spectroscopy. The XRD analysis revealed cubic phase for 'as-deposited' CdS, CdS:Na, CdS:K and CdS:Na,K dual doped thin films. The absorption edge in the optical absorption spectra shifts towards the shorter wavelength for CdS:Na, CdS:K and CdS:Na,K thin films compared to CdS film.**

Keywords- Thin films; CdS; Chemical Bath Deposition; XRD; Optical studies; Photoluminescence studies

I. INTRODUCTION

Cadmium sulfide (CdS) polycrystalline thin films are a representative of II-VI semiconductor materials with many applications such as large area electronic devices and solar cells. It is a wide direct band gap (2.42 eV) material and has been used as a window material together with several semiconductors such as CdTe, Cu_2S and $CuInSe_2$. The interest in CdS thin films can be attributed to its piezoelectric properties and potential laser applications [1-3]. Of the various techniques that have been used for the preparation of CdS thin films, the chemical deposition process is ideally suited on account of its simplicity, ease, and various other attractive features [4, 5].

Alkali metal doped CdS thin film exhibits interesting changes in the optical properties [6]. The effects of incorporating simultaneously two types of dopants into CdS thin film with the aim of optimizing the properties of the film were interesting [7, 8]. In this work, a detailed investigation has been carried out on structural, morphological and optical properties of CdS, sodium doped CdS (CdS:Na), potassium doped CdS (CdS:K) and sodium and potassium dual doped CdS (CdS:Na,K) thin films prepared by chemical bath deposition (CBD) technique.

II. EXPERIMENTAL DETAILS

A. Preparation of CdS Thin Fiilms

In this work, CdS, CdS:Na, CdS:K and CdS:Na,K doped thin films were prepared by a simple chemical bath deposition (CBD) technique using the precursors of cadmium chloride ($CdCl_2$), thiourea ($SC(NH_2)_2$), ammonia (NH_3), sodium chloride (NaCl) and potassium hydroxide (KOH). The aqueous bath solution for the preparation of CdS film was prepared using the following steps: 20 ml of 0.08 M $CdCl_2$ solution was taken in a beaker and aqueous ammonia solution was added to it drop by drop with continuous stirring in order to dissolve the white precipitate of cadmium hydroxide. The addition of 1 M SC $(NH_2)_2$ to $CdCl_2$ solution was done at the rate of 1 ml/min. The pH was maintained at 11, by adding ammonia solution. In order to avoid the evaporation of ammonia the beaker was sealed completely. After reaching the temperature of about 80 °C, the colour of the bath solution changed from pale yellow to orange. Before deposition, the glass substrates were ultrasonically cleaned sequentially washed with acetone, ethanol and de-ionized water, respectively and finally dried in air [9]. Then the ultrasonically cleaned glass substrate was dipped into the solution, without touching the bottom of the beaker. Under these conditions, a uniform CdS deposition on glass substrate was achieved after 45 min of chemical reaction. After depositions, the films were cleaned by flushing with triple distilled water and then kept at room temperature for drying purpose to remove the loosely adherent precipitate during deposition, and allowed to dry in ambient air. CdS:Na, CdS:K and CdS:Na,K thin films were prepared using the same procedure with the addition of 0.01 M NaCl, 0.01 M KOH and 0.01 M NaCl + 0.01 M KOH, respectively.

B. Measuring instruments

X-ray diffraction studies have been carried out by Panalytical XPert Pro MPD X-ray diffractometer using Cu Ka radiation source. The surface morphology was examined Carl Zeiss MA15/ EVO 18 Scanning Electron Microscope. The energy dispersive X-ray analysis attachment (Oxford Instruments NanoAnalysis INCA Energy 250 Microanalysis System) was used to carry out semi quantitative elemental analysis of the samples. The optical absorption spectra of the films were obtained by using Cary 5E UV–VIS–NIR spectrophotometer. The photoluminescence spectra of the films were taken in the range 180 to 850 nm by using a Jobin Yvon Flurolog-3-11 Spectrometer..

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction (XRD) Pattern:

The XRD pattern of as grown chemically deposited CdS, CdS:Na, CdS:K and CdS:Na,K thin films shown in fig.1., which shows the presence of low intensity and multiple peaks in XRD pattern indicates that the thin films are polycrystalline in nature and consist of coarsely fine grains. It is observed that there are well defined peaks corresponding to (111), (220), (311) planes of the cubic zinc blende (JCPDS-file No. 65-2887). The XRD patterns of CdS:Na, CdS:K and CdS:Na,K, shows same cubic zinc blende structure. The average crystallite size (D) of CdS and doped CdS thin film was estimated using Scherrer formula

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

Where k is the wavelength of Cu Ka radiation (k = 1.5406 Å), b is the full-width at half maximum intensity (FWHM), h is the diffraction angle (in radian) [10]. The average crystallite size of CdS, CdS:Na, CdS:K and CdS:Na,K thin films were found to be 32 nm, 41 nm, 23 nm and 36 nm, respectively.

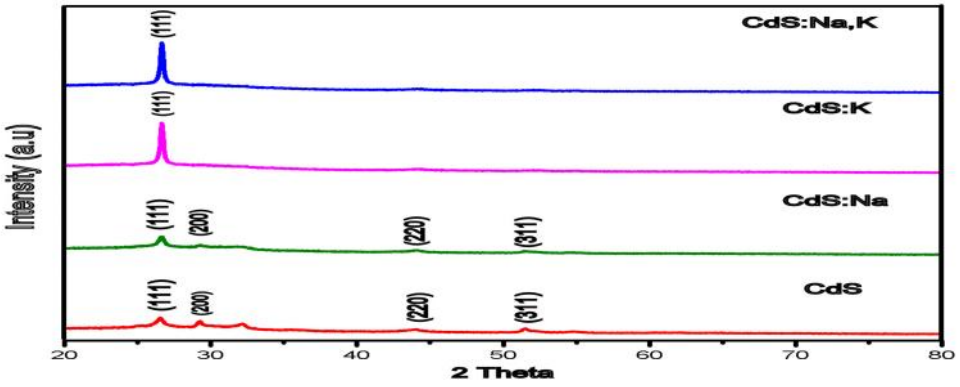
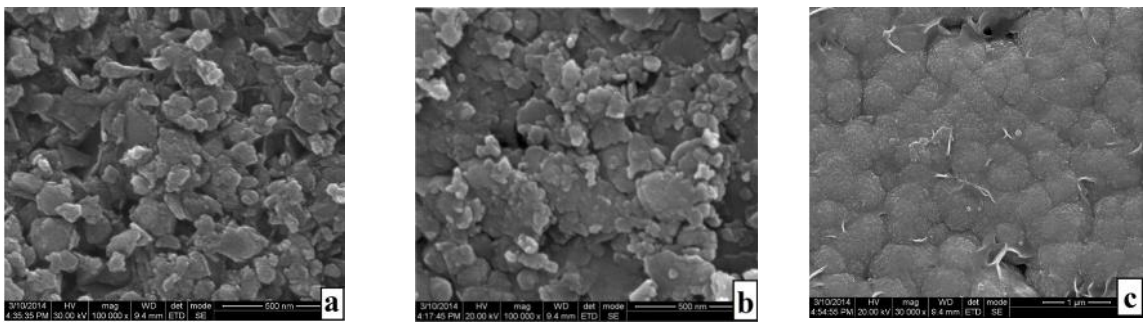


Fig.1. X-ray diffraction spectra of CdS, CdS:Na, CdS:K and CdS:Na,K.

B. Morphological and Elemental Analysis

Fig. 2(a), 2(b), 2(c), and 2(d) represent the SEM images of as grown CdS, CdS:Na, CdS:K, CdS:Na,K thin films respectively. From Fig. 2(a) indicates CdS film shows that the surface consisting of small uniform grains with few voids. From Fig. 2(b) indicates CdS:Na films shows that rough and spongy surface morphology is evident which makes it difficult to estimate the crystallite size due to agglomeration of the particles. From Fig. 2(c) indicates CdS:K film which revealed that the film is continuous, dense, homogeneous and free from pinholes. The SEM image shown in Fig. 2(d) indicates that CdS:Na,K film has relatively larger crystallites. Fig. 2(e). shows the EDAX result of 'as-deposited' CdS thin films. EDAX analysis confirms the presence of cadmium and sulphur in CdS film.



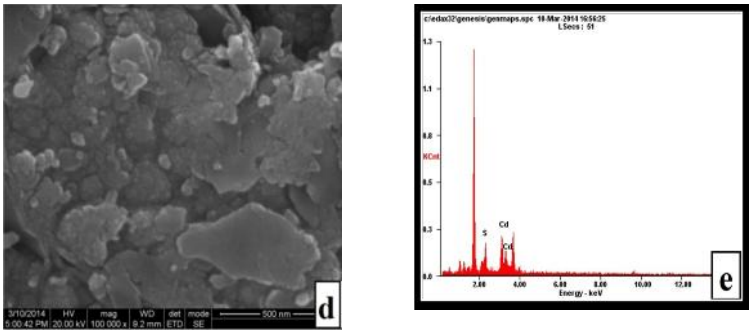


Fig. 2. SEM images of (a) CdS, (b) CdS:Na, (c) CdS:K and (d) CdS:Na,K thin films, (e) EDAX spectrum of 'as-deposited' CdS thin film.

C. Optical Properties

The optical absorption spectra of CdS, CdS:Na, Cds:K, CdS:Na,K thin films are displayed in Fig. 3. These spectra are recorded in the wavelength range 400–800 nm at room temperature in air. Fig. 3. Shows that the absorption edge shifts towards the shorter wavelength for CdS:Na, CdS:K and CdS:Na,K dual doped thin film compared to 'as-deposited' CdS thin film.

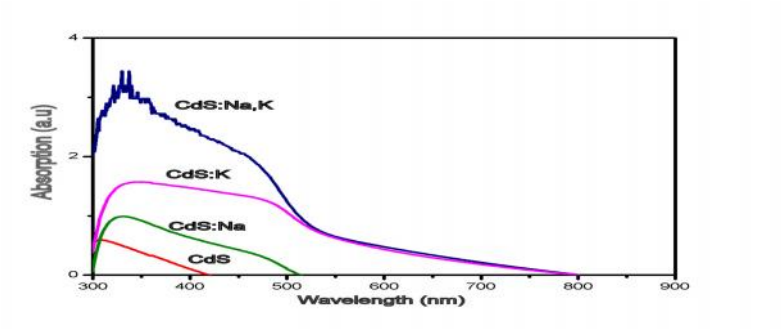


Fig. 3. Optical absorption spectra of CdS, CdS:Na, CdS:K and CdS:Na,K thin films.

D. Photoluminescence studies

Fig. 4. Shows the PL emission spectra of CdS, CdS:Na, CdS:K and CdS:Na,K thin films. The spectra have been recorded at room temperature with an excitation wavelength of 361 nm. For pure CdS films exhibit broad emission peak, called green peak located around 536 nm. As the photoluminescence peak energies are less than the energy gap, these bands can be definitely identified with transitions involving donors, acceptors, free electrons and holes [11]. Thus, the well-known green band can be attributed to the recombination between donor and acceptor levels originated from surface states i.e., grain boundaries, pinholes, micro deformation, adsorbed oxygen, etc. [12]. In CdS defects consist of cadmium vacancies, sulfur atoms adsorbed on the surface. In the photoluminescence spectra the peak can be attributed to high concentration of defects. The broadening of the peaks can be ascribed to the fact that large crystals tend to harbors more defects than small crystals. These defects may act as non-radioactive recombination centres, which band edge recombination [14]. On the other hand, the increase in the intensity of the luminescence band of doped films, as against pure CdS films, may be associated with the increase in the concentration of charge carriers in the conduction band on doping films with alkali metals Na and K.

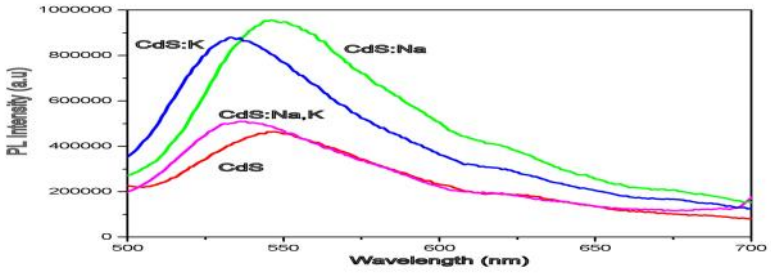


Fig. 4. The photoluminescence spectra of CdS, CdS:Na, CdS:k and CdS:Na:K thin films.

IV. CONCLUSION

In the present work CdS, CdS:Na, CdS:K and CdS:Na,K thin films were successfully deposited on the glass substrate by CBD technique. Structural, morphological and optical properties of these films were characterized using XRD, SEM, EDAX, UV– VIS spectroscopy and photoluminescence spectroscopy techniques. The XRD patterns revealed cubic phase for the 'as-deposited' CdS, CdS:Na, CdS:K and CdS:Na,K dual doped thin films. The crystallite size for CdS, CdS:Na, CdS:K and CdS:Na,K thin films were found to be 32 nm, 41 nm, 23 nm and 36 nm, respectively. The optical absorption spectra shows that the absorption edge shifts towards the shorter wavelength for CdS:Na, CdS:K and CdS:Na,K thin films compared to CdS film. The morphological analysis revealed uniform film surface with crack free and densely packed morphology for CdS:Na,K film. The PL studies show that the PL peaks shift toward shorter wavelength region for CdS:Na, CdS:K and CdS:Na,K thin films compared to CdS film.

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