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Fabrication and Characterization of Mg- and Hg-doped CdS Nanostructured Thin Films Deposited by Chemical Bath Deposition

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In this paper we report the preparation of Hg- and Mg-doped nanostructured CdS thin films deposited on commercial glass slide substrate by chemical bath deposition technique at room temperature. The asdeposited doped CdS nanostructured thin films were characterized using X-ray diffractometer, SEM and UV-VIS spectrophotometer. The SEM micrographs confirmed the formation of doped CdS thin film with nano-structured morphologies. The EDX studies confirm chemical composition of Hg- and Mg-doped nanostructured CdS thin films. The XRD studies confirmed the crystalline nature of thin films and nanostructured behavior. The optical studies reveal the optical energy bandgap of 3.82 eV(12 hrs) & 3.74 eV(24 hrs) and 3.59 (12hrs) & 3.22 eV(24 hrs) for Mg-doped CdS and Hg-doped CdS nanostructured thin films respectively. Blue shift was observed in both the doped CdS nanostructured thin films.

Keywords: Chemical Bath Déposition; Nanostructured Thin Films; Mg-CdS; Hg-CdS; Characterization

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1. INTRODUCTION

II-VI compound semiconductors are very important class of materials for their potential applications in various electronic devices such as solar cell, light emitting diodes, photo detectors, lasers etc. due to their wide energy band gap (1-4). Among them, cadmium sulphide (CdS) is the most studied chalcogenide semiconductor due to its wide band-gap (2.4eV) and better optical transmitting properties [5]. It is commonly used materials as window layer for CdTe, CdSe and Cu(In,Ga)Se2 thin films and nanostructured solar cells [6-8]. The study of nanostructured materials is of great interest among scientific community owing to their remarkable properties as compared to their bulk counterparts. Nanostructures and nanostructured thin films plays very important role in designing future nanoscale electronic devices with remarkable properties. In recent years, CdS nanostructures have greatly received much attention as a candidate for various optoelectronic devices due to their promising physical and chemical properties [9-10]. Singh et al. [11] fabricated nanostructured CdTe, CdS, TiO2 thin films and demonstrated solar cell based on them. Deng et al. [10] presented CdS nanostructures based photo detectors. The research on CdS is still under investigation to see the effect of doping to it and is therefore a current topic of research. Ixtlilco et al. [12], Shah et al. [13] and Oliva et al. [14] fabricated Ag-, Zn- & Cudoped CdS thin films/nanostructures via thermal evaporation and chemical bath deposition methods and presented their various physical properties. In this paper, Mg-and Hg-doped CdS nanostructured thin films have been fabricated via a simple & low cost chemical bath deposition method and their structural, morphological and optical properties are presented.

2. EXPERIMENTAL DETAILS

Mg-and Hg-doped CdS nanostructured thin films have been grown on cleaned commercially available glass slides at room temperature via chemical bath deposition. Commercial glass slides were first cleaned with soap solution in de-ionized water then boiled in concentrated chromic acid for 30 minutes. The slides were then rinsed with acetone and ultrasonically cleaned in de-ionized water for 15 minutes and then dried in air for further use. The clean surface of glass slides provides good nucleation growth of the film with uniform deposition and best yield. All the chemicals were of analytical grade and used without purification.

2.1 Preparation of Mg-doped CdS Nanostructured Thin Film

Mg-doped CdS nanostructured thin films were grown on glass slides via chemical bath deposition at room temperature. The bath composition for Mg-doped CdS nanostructured thin films was consist of 0.1M magnesium sulphate (MgSO₄), 0.2 M cadmium sulphate (CdSO₄), 0.5 M thiourea (CH₄N₂S), 2 ml triethanolamine (TEA) and 5ml ammonia (NH₃).

2.2 Preparation of Hg-doped CdS Nanostructured Thin Film

Hg-doped CdS nanostructured thin films were also grown on glass slides via chemical bath deposition at room temperature. The bath composition for Hg-doped CdS nanostructured thin films was consist of 0.1M mercury sulphate (HgSO₄), 0.2 M cadmium sulphate (CdSO₄), 0.5 M thiourea (CH₄N₂S), 2 ml triethanolamine (TEA) and 5ml ammonia (NH₃). A common procedure was followed in growing both Mg-and Hg-doped CdS nanostructured thin films. 20ml of 0.1M MgSO₄ is mixed with 20 ml 0.2 M CdSO₄ in a beaker A under constant stirring and a clear solution

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was obtained. Then 10 ml of $0.5~M~CH_4N_2S$ was added to it with constant stirring and the color of the solution was turned milky white and upon addition of 2ml of TEA to this solution, the color of the solution changed to light yellow. The final volume solution was made 50ml. The pH of the solution was kept 9 by the addition of NH3. Similar procedure was followed in the preparation solution for deposition of Hg-doped CdS nanostructured thin films. The final color of this solution was dark brown with pH 10. The clean glass substrates were immersed vertically in beaker for 12 and 24 hrs at room temperature to deposit Mg- and Hg-doped CdS nanostructured thin films. The as-grown samples were then characterized with different characterization techniques and studied.

3. RESULTS AND DISCUSSION

The color of the Mg-doped CdS thin film was brownish yellow and that of Hg-doped CdS thin film was dark brown. The as-obtained thin films were characterized via scanning electron microscopy, Energy dispersive X-ray spectroscopy, X-ray diffractometer and Uv-vis spectrophotometer to study their structural, morphological and optical properties.

3.1 Morphological Studies

The morphological studies of chemical bath deposited Mg- and Hg-doped nanostructured CdS thin films have been studied by scanning electron microscope. The as-obtained samples were first coated by thin layer of gold in Polaron SC7640 Sputter Coater and then viewed under scanning electron microscope (Zeiss EVO 40) an accelerating voltage of 20kV at high vacuum. The Fig. 1 and 2 shows the SEM micrographs of as-prepared Mg- and Hg-doped CdS nanostructured thin films. The SEM micrographs of Mg-doped CdS thin films are composed of leaves type nanostructures.

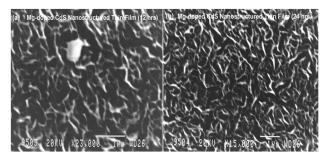


Fig. 1 – SEM Micrographs of Mg-doped CdS Nanostructured Thin films (a) 12 hrs (b) 24 hrs

The Mg-doped CdS nanostructured thin film grown for 24 hours has fewer defects as compared to the thin film grown for 12 hours. The white spot as defect is clearly visible in Mg-doped CdS nanostructured thin film grown for 12 hours.

The SEM micrographs of as-prepared Hg-doped CdS thin films are composed of seeds type nanostructures. The Hg-doped CdS nanostructured thin film grown for 24 hours has fewer defects as compared to the thin film grown for 12 hours. The

white spots as defects are clearly visible in Hg-doped CdS nanostructured thin film grown for 12 hours. SEM analysis reveal the nanostructured morphologies of Mg- and Hg-doped CdS nanostructured thin films and confirm the deposition via chemical bath deposition.

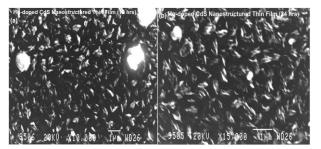


Fig. 2 – SEM micrographs of Hg-doped CdS thin nanostructured films (a) 12 hrs (b) 24 hrs)

3.2 Chemical Studies

The chemical studies were carried out to study the stoichiometric behaviour of Hg- and Mg-doped CdS nanostructured thin films by a BRUKER EDX system in conjunction with a Zeiss EVO 40 scanning electron microscope. The Fig. 3 shows the EDX spectrum of Mg- doped nanostructured CdS thin film that reveal the grown thin film is constituted of elements Cd, S and Mg with stoichiometric ratio (in At.%) of 79.02:10.13:6.54. Other elements such as O, Sn and Si are also present in the system but their percentage is very less and their presence can be attributed to impurities present in the sample that arises from chemicals and substrate material.

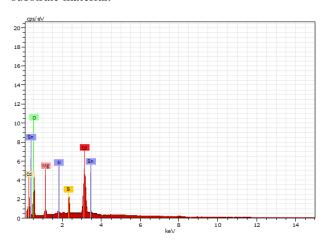


Fig. 3 - EDX spectrum of Mg-doped CdS nanostructured thin films

The Fig. 4 shows the EDX spectrum of Hg-doped nanostructured CdS thin films. The EDX spectrum reveals the chemical composition mainly consists of elements Cd, S and Hg with stoichiometric ratio (in at.%) of 80.73:9.68:4.09. Other EDX peaks arise from impurities present in chemical used and substrate material. The sulphur contents in both the films are found moderate as compared to cadmium compound.

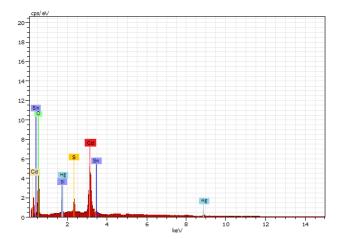


Fig. 4 – EDX spectrum of Hg-doped CdS nanostructured thin films

3.3 Structural Studies

The structural studies of as-prepared Mg- and Hgdoped nanostructured CdS thin films was performed by X-ray Diffraction system (PANalytical X'PERT-PRO X-ray powder diffractometer) using wavelength (Cu-Kα) 1.54060Å at 40 mA, 45 keV. The X-ray diffraction pattern was recorded using a step size of 0.0170 from $0-80^{\circ}$ of 2θ angle. Fig. 5 shows the diffraction pattern of Mg-doped nanostructured CdS thin films for 12 and 24 hrs. In both the spectrum, the highest peak was observed at 2θ angle of 29.2130° and is indexed as (111) and the other minor peak was observed at 20 angle of 51.7936° and is indexed as (311). The preferential direction of growth of Mgdoped nanostructured CdS thin films was found at 29.2130° and the spectrum matches with diffraction data file JCPDS (10-454) that confirms the formation of Mg-doped nanostructured CdS thin films.

Fig. 6 shows the diffraction pattern of Hg-doped nanostructured CdS thin films for 12 and 24 hrs. In both the spectrum, the highest peak was observed at 2θ angle of 29.0352° and is indexed as (111) and the other minor peak was also observed at 20 angle of 51.4094° and is indexed as (311). The preferential direction of growth of Hg-doped nanostructured CdS thin films was also found at 29.2130° and the spectrum matches with diffraction data file JCPDS (10-454) that confirms the formation of Mg-doped nanostructured CdS thin films. The broad diffraction peaks in the XRD pattern shows the nanostructured behavior of the thin films. The films deposited for 24hrs is found more crystalline in nature as compared to thin films of 12hrs formation. The XRD studies confirm the crystallinity in both the films grown by chemical bath deposition method. The major (111) and the other complimentary (311) diffraction peaks reveal the cubic structure of the doped CdS films. The average crystal size as calculated by Scherrer formula from XRD measurements was estimated in the range of 16-22nm.

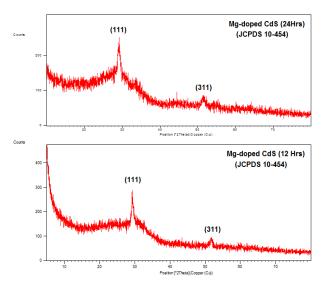


Fig. 5 – XRD patterns of Mg-doped nanostructured CdS thin films (a) 12 hrs (b) 24 hrs)

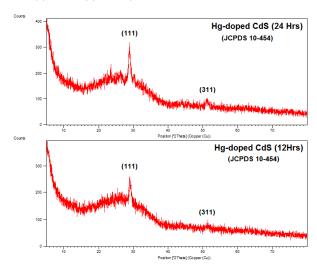


Fig. 6 - XRD patterns of Hg-doped nanostructured CdS thin films (a) 12 hrs (b) 24 hrs)

3.4 Optical Studies

The optical properties of Mg- and Hg-doped CdS nanostructured thin films were studied using Shimadzu 2550 UV-Vis spectrometer. Fig.7 shows the absorption spectra of both of the Mg- and Hg-doped nanostructured CdS thin films. Blue shifts was observed in all the doped CdS thin films as the absorption edge moves to lower wavelength region (324-385nm) in doped CdS thin films in comparison with un-doped CdS thin film (512nm) thus blue shifted.

Fig.8 shows the Tauc's plot for both of the Mg- and Hg-doped nanostructured CdS thin films to determine their optical energy band gaps. The optical energy band gap of Mg- and Hg-doped nanostructured CdS thin films is calculated from absorption coefficient data as a function of wavelength using Tauc relationship [15] given by

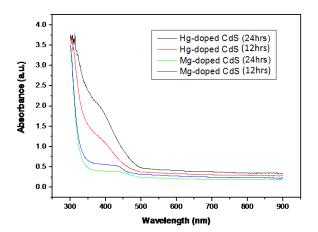


Fig. 7 - Plot of absorbance vs wavelength

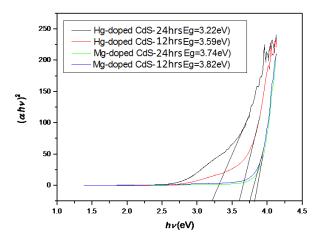


Fig. 8 - Tauc's Plot for Energy Band Gap Calculation

$$(\alpha h v)^n = B(h v - E_{\sigma}) \tag{1}$$

where α the absorption coefficient, hv photon energy, E_g the optical energy band gap, B (a constant term) the

band tailing parameter and 'n' an index and can have different values i.e. 2, 3, 1/2 and 1/3 depending on band to band transitions. It is observed that equation (1) gives the best linear fit (n=2) for the Tauc plot shown in Fig. 7 and that corresponds to the direct band to band transition. The energy band gaps are found to be 3.82 (12hrs) & 3.74eV (24hrs) and 3.22 (12hrs) & 3.59eV (24hrs) for Mg- and Hg-doped nanostructured CdS thin films respectively. The "blue shift" occurred as the energy band gaps increases for doped nanostructured CdS thin films from 2.4eV (pure CdS thin film) thus can be due to doping and the quantum size effect as well. It is also observed that mmagnesium has great effect on optical band gap compared to mercury.

4. CONCLUSIONS

The Mg- and Hg-doped nanostructured CdS thin films have been fabricated successfully from a low cost chemical bath deposition method at room temperature. The SEM studies reveal the leaf and seed type morphologies of the Mg- and Hg-doped nanostructured CdS thin films. The XRD study confirms the crystalline nature with cubic structure. The optical studies observed increased band gap of doped nanostructured CdS thin films in comparison with pure CdS thin film. The above studies reveal that Mg- and Hg-doped nanostructured CdS thin films with higher energy band gaps can be useful in future nanostructured solar cell and other optoelectronic devices.

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