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Brush electrodeposited CdS films on low temperature substrates

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Abstract

Cadmium sulphide films were deposited by the brush plating technique on titanium and conducting glass substrates using a current density of 80 mA cm^{-2}. X-ray diffraction studies indicated the polycrystalline nature of the films with hexagonal structure. As the deposition temperature decreased, the peaks were broad indicating the formation of nanocrystallites. Optical absorption measurements yielded band gap values in the range of 2.39–3.10 eV as the deposition temperature decreases. XPS studies confirmed the formation of CdS. Atomic force microscope studies indicated the roughness of the films decreases with the decrease of deposition temperature. The as deposited films were photoactive.

Keywords: CdS; II–VI; Thin films; Brush plating

1. Introduction

CdS is one of the most interesting II–VI semiconductors owing to its interesting optical, electrical and optoelectronic properties. Possessing a wide fundamental band gap, they have been used in a large variety of applications such as electronic and optoelectronic devices [1]. Polycrystalline CdS thin films are generally used in CdTe solar cells, as a window material for transmitting the light absorbed by CdTe and also as the n-type material for p–n junction of the solar cells [2]. Requirements of the CdS films are that they should be conductive (10_{16} carrier/cm_3), thin to allow high transmission (50–100 nm), and uniform to avoid short circuit effects. Techniques like molecular beam epitaxy (MBE) [3], metal organic vapor phase epitaxy (MOVPE) and metal organic chemical vapor deposition (MOCVD) [4], close spaced sublimation (CSS) [5], chemical bath deposition (CBD) [6], electrodeposition and succesive ionic layer adsorption and reaction (SILAR) [7], screen printing [8], and physical vapor deposition (PVD) [9] have been employed for the deposition of CdS films. In this work, the brush plating technique has been employed for the deposition of CdS films on low temperature substrates. The structural, optical and morphological properties of the films are reported and discussed.

2. Experimental methods

CdS films were prepared on conducting glass and titanium substrates using the selective plating technique. The precursors

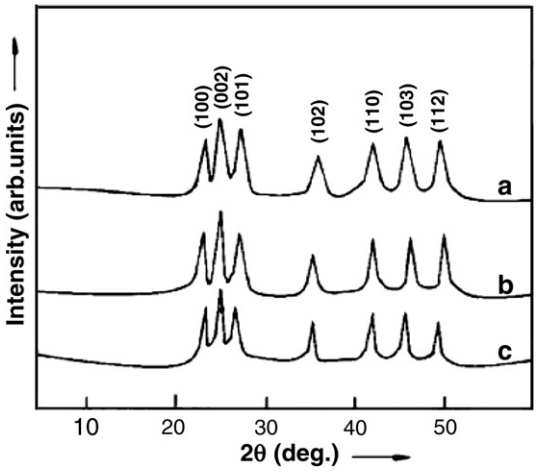

Fig. 1. XRD pattern of CdS films deposited at different temperatures: (a) 5 °C, (b) 15 °C and (c) 30 °C.

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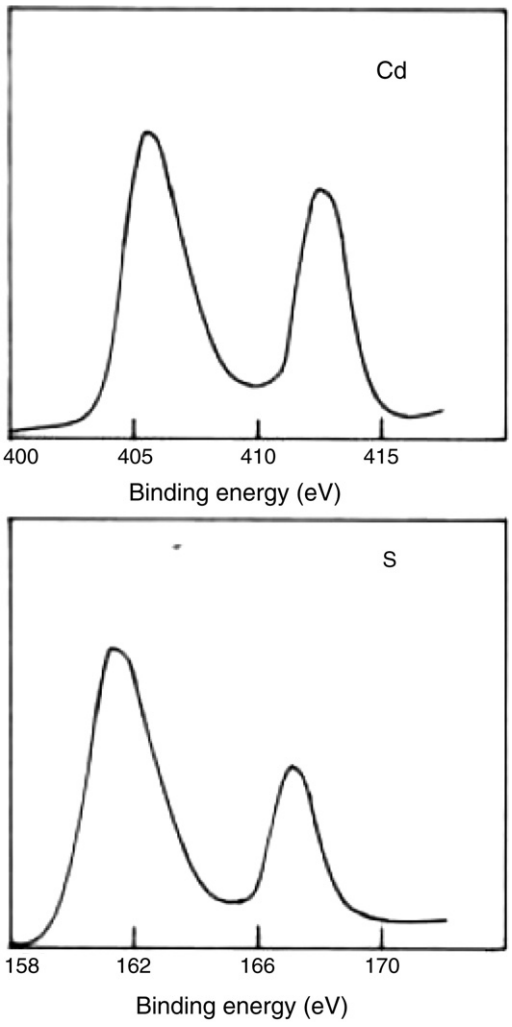

Fig. 2. XPS of CdS films deposited at 5 °C.

used for the deposition of CdS were AR grade E. Merck (Germany), 0.5 M $CdSO_4$, 0.1 M sodium thiosulphate and triply distilled water to make up the solution to 10 ml. The cotton

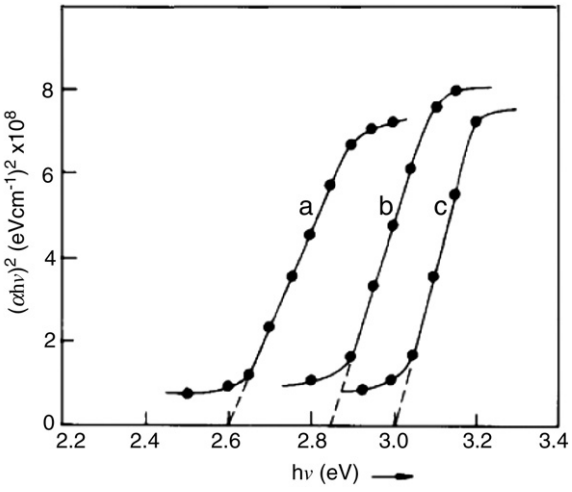

Fig. 3. $(\alpha h\nu)^2$ vs. $h\nu$ plot of CdS films deposited at different temperatures: (a) 30 °C, (b) 15 °C and (c) 5 °C.

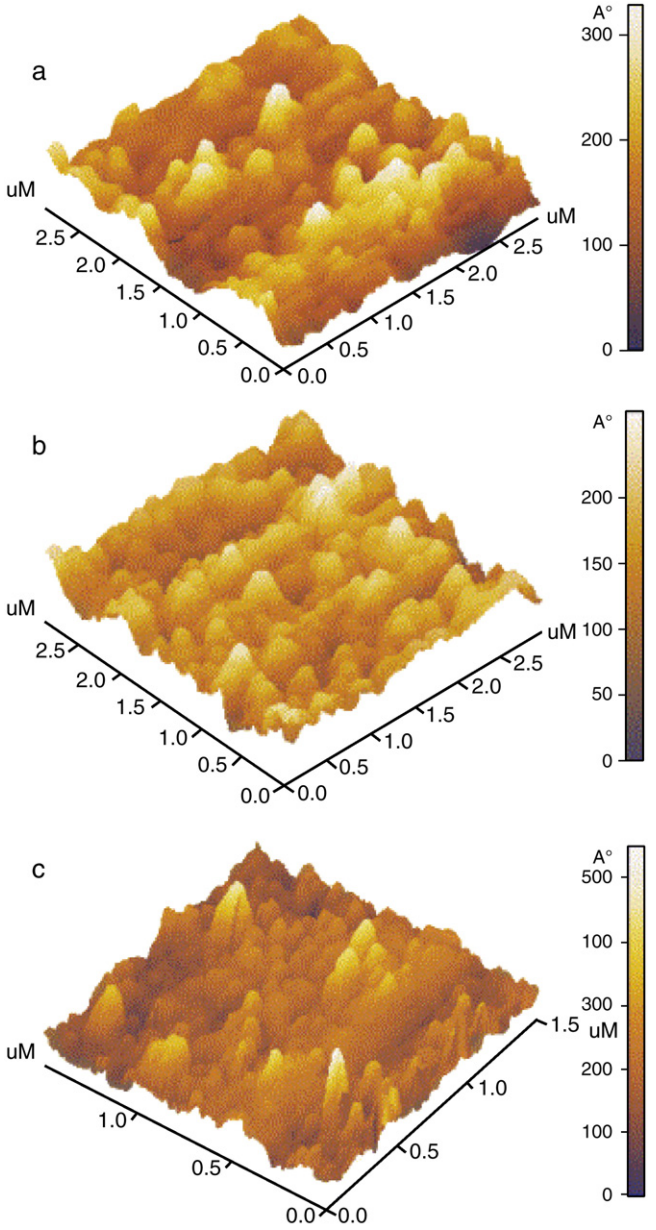

Fig. 4. Atomic force micrograph of CdS films deposited at different temperatures: (a) 30 °C, (b) 15 °C and (c) 5 °C.

wrapped graphite anode was dipped in the precursor mixture and brushed on the stainless steel substrates. The films were deposited at a current density of 80 mA cm^{-2} at different temperatures in the range 5–50 °C. The deposition current density was fixed based on our earlier experience with brush plated films [10]. It took 20 min to deposit a film with the thickness of 3.0–5.0 μm (thickness estimated from gravimetry). The films were characterized by X-ray diffraction using Phillips X-ray diffraction unit. Optical absorption measurements were made on the films deposited on conducting glass substrates using a U3400 Hitachi UV–VIS–NIR spectrophotometer. Surface morphology of the films was studied by Molecular Imaging systems Atomic Force Microscope. Laser Raman studies were made using 18 mW He–Ne laser of a Renishaw

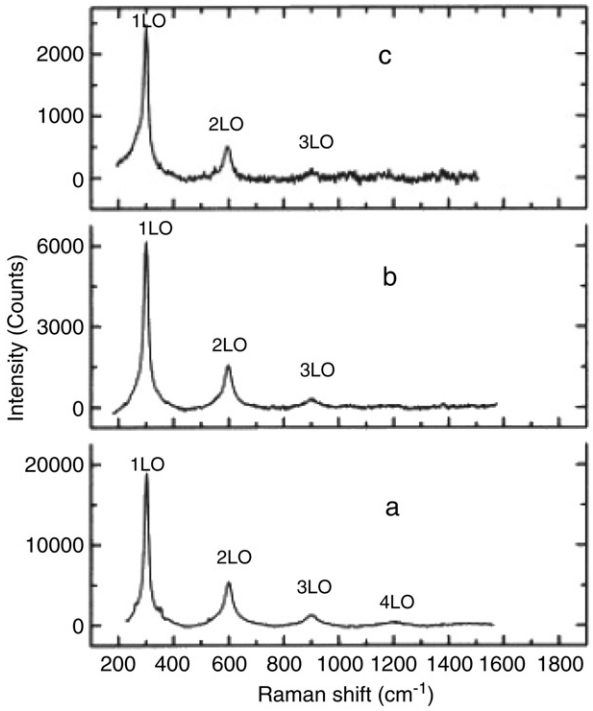

Fig. 5. Raman spectra of CdS films deposited on different substrate temperatures: (a) 5 °C, (b) 15 °C and (c) 30 °C.

Invia Raman system. Photoelectrochemical measurements were made using an ORIEL 250W Tungsten Halogen lamp.

3. Results and discussion

The XRD pattern of the CdS films is deposited on low temperature substrates. The prominent peaks corresponding to (100), (002), (101), (110), (103), (112) and (003) of the hexagonal phase are observed in all cases. It is observed that as the substrate temperature increases, the width of the peak decreases due to improved crystallinity. The lattice constants 'a' and 'c' calculated using the XRD data are 4.14 Å and 6.75 Å, which are in close agreement with the ASTM data. The crystallite size calculated using the Debye Scherrer equation is found to increase with increase of substrate temperature (Fig. 1). EDAX studies indicated the composition of the films to be Cd(64.1%) and S(35.9). XPS studies show the binding energies of the Cd($3d_{5/2}$ and $3d_{3/2}$) and S($3d_{5/2}$ and $3d_{3/2}$) levels of the CdS films annealed at different temperatures. As shown in the Fig. 2, the peak energy levels associated with the Cd($3d_{5/2}$ and $3d_{3/2}$) appeared at 405 and 411.7 eV respectively, and these values are in close agreement with the literature values. The figure also shows the binding energies of S ($3d_{5/2}$ and $3d_{3/2}$) levels at 168.0 eV and 173.0 eV respectively. Atomic concentration measurements made on the annealed samples yielded an apparent Cd/S ratio of 1.62, this calculation is based on the consideration of the area sensitivity factors for Cd and S and agrees very well with the composition estimated by EDAX measurements. Optical absorption measurements were made on the CdS films deposited on conducting glass substrates. Substrate absorption, if any was corrected by placing an uncoated conducting glass substrate in the reference beam. A plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the films deposited at different substrate temperatures is shown in Fig. 3. The plot is linear indicating the direct band gap nature of the films. Extrapolation of the line to the $h\nu$ axis indicated a direct band gap in the range 2.40–2.80 eV as the substrate temperature is decreased. This is due to the decrease in particle size with the decrease of temperature. The variation of the band gap at various substrate temperatures is due to the variation of crystallite size with substrate temperature. Strong and weak confinements were noticed in the films .For strong confinement, the exciton energy is given by

$$E_s = E_g + h_2\pi_2/2\mu_2 - 1.786e_2/4\pi\varepsilon_0\varepsilon R - 0.248E_{Ry}$$

Where E_g is the band gap of bulk CdS, the first term is related to the quantum localization energy, the second term represents the Coulomb energy and the third term represents the correlation energy in which E_{Ry} is the effective Rydberg energy and can be written as $\{\mu e_4/2(4\pi\varepsilon_0\varepsilon)_2\ h_2\}$, where, μ is the reduced effective mass, ε is the dielectric constant for CdS and ε_0 is the permittivity of free space. The estimated band gap of 2.80 eV due to strong confinement matches with the band gap value obtained from absorption measurements for the films deposited at 5 °C. Surface morphology of the films deposited at different temperatures is shown in Fig. 4. AFM images are characterized by slight surface roughness with a uniform crack-free, densely-packed microstructure. The surface roughness (RMS) of the films is calculated by using the equipment's software routine. The surface roughness of the films deposited at different temperatures is 4.86, 3.65,and 2.3 nm, respectively. Thus, surface roughness, decreases as the temperature of deposition decreases. This is due to the fact that with a decrease in temperature, the grain size decreases and surface morphology becomes smoother. Laser Raman studies indicated LO phonons corresponding to CdS. Up to fourth order phonons are observed in all the cases. Fig. 5 shows the Raman spectra of the films deposited at different temperatures. The intensity of the Raman peaks increased with substrate temperature.

4. Conclusion

The results of this investigation indicate that the brush plating technique can be used to deposit nanocrystalline CdS films useful for optoelectronic devices.

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