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PVA assisted growth of hydrophobic honeycomb network of CdS thin films

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ABSTRACT

A simple, facile and inexpensive method of polyvinyl alcohol (PVA) assisted chemical bath deposition (CBD) is adopted for the growth of hydrophobic honeycomb network of cadmium sulfide (CdS) thin films. Further their physical properties were characterized by X-ray diffraction (XRD), Raman spectroscopy, filed emission scanning electron microscopy (FESEM), contact angle measurement and optical studies. The XRD pattern shows that CdS films are oriented along (3 3 0) plane. The presence of characteristic bonds of CdS is observed from Raman shift experiment. The FESEM images reveal porous and interconnected honeycomb-like morphology. Air trapping in the pores of honeycomb network prevents water from adhering to the film results into hydrophobicity having contact angle of 141°. The CdS film showed a direct band gap with energy 2.5 eV.

1. Introduction

Today nanostructured materials and quantum dots have immense importance in the field of optoelectronics. The experimental and theoretical progress has opened new era of fundamental physics and chemistry as researchers can make and study artificial analogues of atoms, molecules and crystals. Nanocrystalline thin films of II–VI semiconductor have attracted ever increasing attention due to their potential, experimental and of course interesting applications in many industries. Among them, cadmium sulfide (CdS) nanoparticles have potential applications as optoelectronic devices [1], lasers, [2], photocatalysts [3], electrochemical cells [4], fluorescent labeling of cell organelles [5], etc. These exciting applications have focused attention on the synthesis, size control and organization of nanoclusters [6]. One such aspect is the formation of thin films of semiconductor nanoparticles. To realize this, procedures such as the Langmuir–Blodgett technique [7] and liquid–liquid interface reaction technique [8] have been developed. Aslo CdS in a nanocrystalline thin films form can be prepared by a variety of methods (both physical and chemical) like sol–gel [9,10], electrostatic deposition [11], gas evaporation [12], CBD [13], etc. However, limited and poorly controlled, film fabrication routes represent a key factor impeding the development of such devices. Such studies have recently been extended to the application of an alternative film fabrication technique notably that of chemical bath deposition (CBD), to growth of the CdS thin film.

One interesting feature of CBD is that, under specific conditions of supersaturation, highly reticulated layers may be obtained, such an observation suggesting that control of morphology is possible. From the structural point of view, growing of nanostructured materials with high aspect ratio by low temperature chemical methods such as CBD can find extensive scope. The CBD method is well known as prevalent low temperature aqueous method for directly depositing large-area thin films of semiconductors. Moreover, it requires no sophisticated instruments such as vacuum systems and the starting chemicals are commonly available and cheap. Also, the preparative parameters are easily controlled. The principles of direct deposition of film via CBD method are based on a gradual release of metal ions from supersaturation solution. A chelating agent is usually used to limit the hydrolysis of the metal ion and impart some stability to the bath, which would otherwise undergo rapid hydrolysis and precipitation. It is well known that there are distinct mechanisms or models leading to the formation of CBD films, notably: (a) adsorption and coagulation of colloids performed solution by homogeneous reaction (as usually called cluster-by cluster process), and (b) ion-by-ion condensation at the surface of the substrate by heterogeneous reaction. In practice, both processes may occur and/or interact in the growing films. The predominance of one mechanism over another is controlled by the extent of heterogeneous and homogeneous nucleations. Key parameters include the degree of supersaturation of the solution and the catalytic activity of the surface of the substrate. Many metal chalcogenide [14]

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thin films have been deposited by CBD method, however, only a few reports are available via PVA assisted [15].

In the present communication, we wish to report the evolution of hydrophobic honeycomb network-like morphology of CdS thin films synthesized within the self-organized pores of polyvinyl alcohol (PVA) via the soft chemical bath deposition (CBD) process at room temperature (300 K). Further, these honeycomb networks of CdS thin films were characterized for their structural, morphological, surface wettability and band gap studies through the range of techniques including X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), contact angle measurement and optical properties and the results are discussed.

2. Experimental details

Nanocrystalline CdS thin films were deposited onto glass substrates by CBD technique. The deposition was carried out in a mixture of matrix solution and thiourea. The matrix solution was prepared by adding 0.1 M cadmium sulfate to an aqueous solution (2%) of PVA with constant stirring at a constant temperature (343 K) maintained for 90 min. The solution was then left for 24 h to get a transparent liquid indicating complete dissolution of PVA. The pH of the solution was maintained at around 11 by slowly adding NH_4OH solution. Then the equimolar solution of 0.1 M thiourea was added to the mixture of matrix solution and glass substrates were introduced vertically into the solution with the help of a substrate holder. Within a few minutes color of the solution changed to yellow. The substrates were kept in the solution for 18–24 h at room temperature for deposition of CdS thin films. After deposition, the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air. Further, these films were annealed in air at 423 K for 2 h which generally facilitates decrease in dislocations, stresses, inhomogeneities, etc. Film thickness is important parameter in the study of film properties. For thickness measurement, gravimetric weight difference method with the relation $t = m/(\rho \times A)$ [16] where, m is the mass of the film deposited on the substrate in g, A is the area of the deposited film in cm^2 and ρ is the density of the deposited material (CdS = 4.82 g/cm^3) in bulk form. The maximum thickness obtained for CdS thin film was 0.75 μm and used for the further characterization.

The crystal structural characterization of film was studied by using Philips PW-1710 X-ray diffractometer with Cu-K_α radiation (λ = 1.5406 Å). Raman spectrum was measured using a MultiRam spectrophotometer at room temperature. The spectrum was excited by the 1050 nm line of an Nd:YAG laser. The spectral resolution of the instrument was about 0.1 cm^{-1}. The surface morphology was investigated using filed emission scanning electron microscope, FESEM (XL30 ESEM FEG). The static contact angle against water was measured using a contact angle meter (Rame-Hart, USA) at room temperature. Droplets were placed at five positions for one sample and the averaged value was adopted as the contact angle. For the optical studies, UV–vis absorption spectrum was recorded on a Systronic spectrophotometer-119.

3. Result and discussion

3.1. Structural studies

Fig. 1 shows XRD pattern of PVA assisted CdS honeycomb network on glass substrate. The crystal structure of CdS is orthorhombic [17] (a = 14.3150 Å, b = 14.0740 Å and c = 14.5680 Å). From spectrum, it is clear that CdS film is oriented along (3 3 0) plane. The broad hump is due to an amorphous glass substrate and/or some amorphous phase present in it. The grain size was calculated using the Scherer's relation:

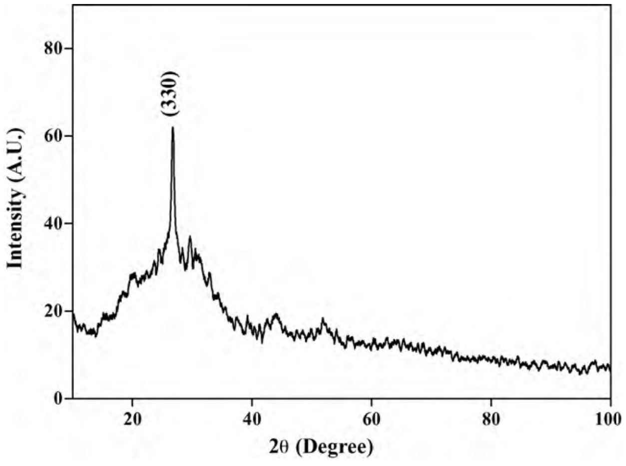

Fig. 1. The X-ray diffraction pattern of CdS thin film.

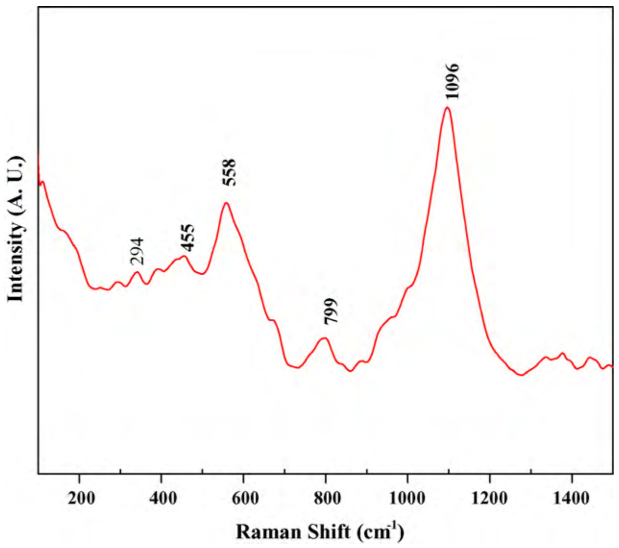

Fig. 2. Raman spectrum of CdS thin film. The excitation wavelength is 1050 nm.

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

where D is the crystallite size, λ the X-ray wavelength used, β the angular line width of half maximum intensity and θ is the Bragg's diffraction angle. The calculated crystallite size is found to be 16 nm for (3 3 0) plane.

3.2. Raman study

The phase identification of the sample has been carried out using Raman spectroscopy. It is a non-destructive characterization method of choice for many recent studies of CdS [18]. As shown in Fig. 2, the Raman spectrum of the prepared CdS film exhibits different specific bands at 294, 455, 588, 799, 1096, 1931 and 2116 cm^{-1}. The predominant Raman modes in LO modes are in the frequency region range from 500–1100 cm^{-1}. They are identified as 1LO (294 cm^{-1}), 2LO (558 cm^{-1}) and 3LO (1096 cm^{-1}) optical phonons. The results are consistent with the previous Raman spectroscopy studies of the CdS of single crystal and CVD grown nanorod [19,20]. Raman peaks centered around 455 and 799 cm^{-1} is due to 1TO and 2TO optical phonons, respectively. The different number of observable overtones is due to the resonant effect of the scattered Raman signal with exaction energy. The small number of overtones observed in the present study is due to our sample being a polycrystalline film. In this presented work, the down-frequency shift of the 1LO Raman peak and the degraded TO phonon line in CdS thin film are mainly ascribed to the grain size and stress effects [21], which change the vibrational characteristics of CdS thin films, leading to the shift of Raman frequency.

3.3. Surface morphological studies

The surface morphological study of PVA assisted CdS thin film has been carried out using FESEM images at two different magnifications (×25 K and ×50 K) is shown in Fig. 3(a and b). The FESEM micrograph reveals the film surface looks highly porous and interconnected network of honeycomb. Also there is no any overgrowth

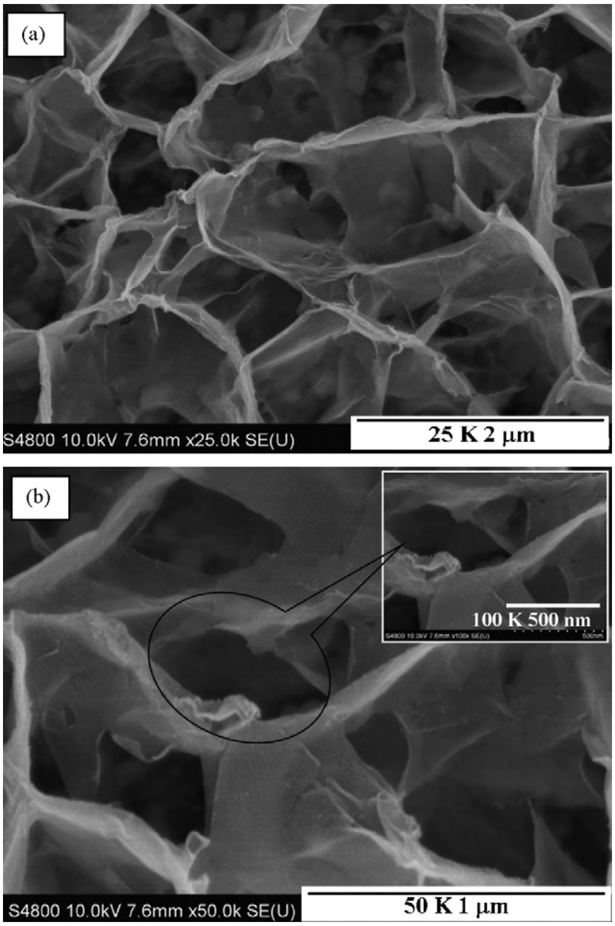

Fig. 3. FESEM micrographs of CdS thin films at two different magnifications (×25 K and ×50 K) (Inset of (b) shows porous structure at the ×100 K magnification).

which means PVA assisted CdS thin films grown uniformly on the substrate surface without any void, pinholes or cracks and they covers the substrate well. An enlarged view (×100 K) shown in inset of Fig. 3(b) clearly revealed that the pore diameter typically ranges from 1 to 2 μm. Devi et al. [15] reported non uniform surface of film with nanosized grains engaged in fibrous like structure for the films prepared by CBD method.

3.4. Wettability test

The contact angle is the angle at which a liquid/vapor interface meets the solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. If the liquid is very strongly attracted to the solid surface the droplet will completely spread out on the solid surface and the contact angle will be close to 0°. On the other hand, if the solid surface is hydrophobic, the contact angle will be larger than 90°. On highly hydrophobic surfaces, water contact angles as high as 150° or even nearly 180°. On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent. In present work, the water lies with contact angle of 141° on the PVA assisted CdS surface shows extremely high water repellency forming a spherical droplet as seen in Fig. 4 indicating hydrophobic material which is lower than reported earlier [22]. This might be due to air trapping in the pores of honeycomb prevents water from adhering to the film results into hydrophobicity of PVA assisted CdS surface. The growth of hydrophobic CdS structures may be attributed due to the long chain of PVA molecules. During the growth of CdS colloid in PVA matrix, a uniform and ordered structure of PVA chain is easily adsorbed at the surface of the colloid [23,24]. When the surface of the colloid adsorbs this type of polymer, the activity of colloid reduces greatly [23]. From the viewpoint of growth kinetics, if the colloid adsorbs the polymer on its surface, the growth rate of the colloids will be confined in certain directions. At room temperature, growth is probably confined in one dimension in the PVA matrix, resulting in hydrophobic honeycomb network of CdS nanostructures. The hydrophobic films may provide novel platforms for photovoltaic, sensor and other device applications [22].

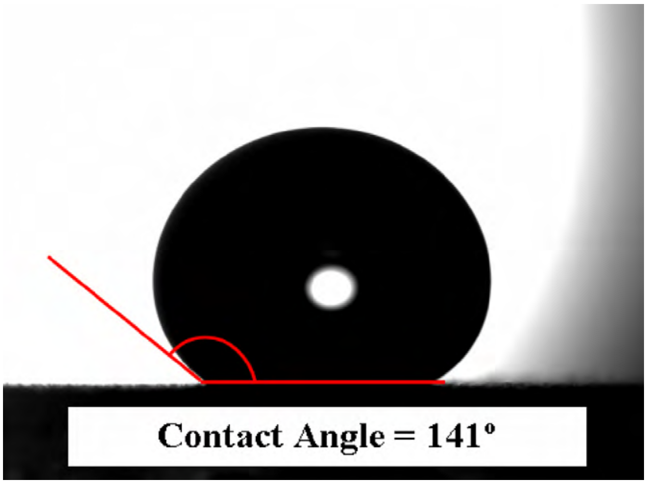

Fig. 4. Water contact angle measurement with the CdS thin film surface.

3.5. Optical studies

The optical absorption of PVA assisted CdS thin film with thickness 0.75 μm has been investigated in the wavelength range 350–750 nm. Fig. 5 shows variation of absorbance (αt) of PVA assisted CdS film with wavelength (λ). This spectrum reveals that CdS honeycomb network have high absorbance of light in the visible region, indicating applicability as an absorbing material. The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon

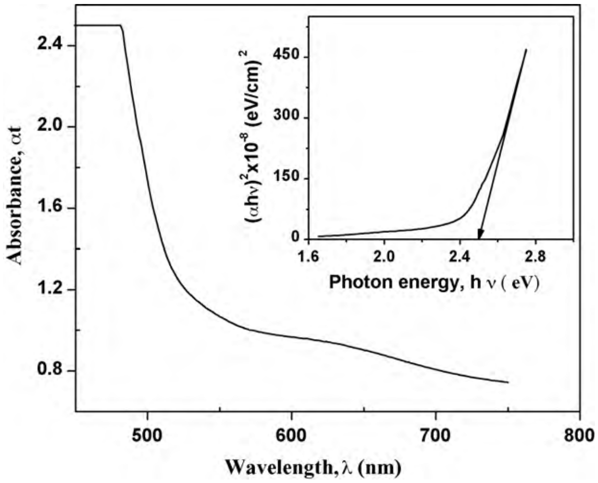

Fig. 5. Optical absorption spectrum of CdS film. Inset shows the corresponding plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$.

energy ($h\upsilon$) can be written as,

$$\alpha h\upsilon = \alpha_0(h\upsilon - E_g)^n \qquad (2)$$

where α is the absorption coefficient, α_0 is a constant, E_g is the band gap, and n is equal to 1/2 for a direct and 2 for indirect transition. The band gap can be estimated from a plot of $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$). The intercept of the tangent to the plot will give a good approximation of the band gap energy for this direct band gap material (shown in inset of Fig. 5). The band gap energy for PVA assisted CdS thin film is found to be 2.5 eV. Devi et al. [15] found the optical band gap of 2.5 eV for chemical bath deposition of CdS thin films in PVA matrix.

4. Conclusions

An aqueous solution system for growing hydrophobic honeycomb network of CdS thin film was investigated via PVA assisted route. The CBD method is simple, economic and easily reproducible for CdS honeycomb network with orientation along (3 3 0) plane. From the Raman spectroscopy, presence of different characteristic bonds of CdS thin film was confirmed. Contact angle measurement showed CdS thin film surface was hydrophobic with contact angle 141°. The optical studies showed direct band gap energy of 2.5 eV.

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