

Studies on Cadmium Sulfide/Porous Silicon (CdS/PS) Nanocomposite Structure

I. Rathinamala¹, N. Jeyakumaran² and N. Prithivikumar²

¹Department of Physics, V.V.Vanniaperumal College for Women, Virudhunagar – 626001, Tamilnadu, India.

²Nanoscience Research Lab, Department of Physics, VHNSN College, Virudhunagar – 626001, Tamilnadu, India.

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ABSTRACT

In this work Cadmium Sulphide/Porous Silicon (CdS/PS) nanocomposite structure was successfully synthesized by depositing CdS film over PS substrate at room temperature. CdS was incorporated into the pores of PS and thereby making a protecting layer. The XRD, SEM, FTIR and PL analysis were carried out to characterize the CdS/PS structure. XRD result suggests the formation of CdS hexagonal structure on PS surface. The diffraction peaks pertaining to PS along with those corresponding to CdS were observed. The surface morphology of the prepared CdS/PS layer was studied by SEM analysis. The information about the vibration and rotation of molecular groups and the bonding of inorganic molecules on silicon surfaces are confirmed by transmission FTIR spectra. The PL measurements on CdS/PS structure show emission peaks at around 620 & 660 nm with 2.0 & 1.9 eV band gap respectively. These results show the incorporation of CdS into the pores of PS and capable of utilizing for device applications.

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Introduction

Researches of nanostructured materials obtained by forming semiconductor clusters and nanoparticles or inserting them into porous matrices [1–3] comprise one of the challenging directions in modern microelectronics. Porous silicon has attracted great attention due to its room temperature photoluminescence in the visible light range [4]. As we know that, the bulk crystalline silicon has an indirect gap at 1.1 eV at room temperature, which results in a very inefficient radiative recombination and produced light in the infrared region. Therefore, the strong visible light emission in porous silicon is quite surprising and such structure can exhibit a large variety of morphologies and particles sizes. Porous silicon shows different features in comparison to the bulk silicon such as shifting of fundamental absorption edge into the short wavelength and photoluminescence in the visible region of the spectrum. Porous silicon allows nanocomposite with diverse electronic, optical, photo-electric, and adsorption properties to be fabricated using rather simple and inexpensive technologies. Composite structures with nanocrystallites of semiconducting metal sulfides incorporated into a porous silicon matrix are promising for their application in photo-electric and microelectronic devices.

The II–VI semiconductor nanocrystals exhibit interesting properties and their emission spectra is very narrow (spectrally pure) and the emission color is simply tuned by changing their size. CdS with hexagonal structure is highly favorable for solar cell application as a window layer because of its suitable band gap and stability. CdS is one of the important materials for application in electro-optic devices, such as laser materials, transducers, photoconducting cells, photosensors, optical wave-guides and non-linear integrated optical devices [5]. They can be deposited by different deposition techniques, such as sputtering [6], molecular beam epitaxy [7], chemical bath deposition [8], spray pyrolysis [9], thermal evaporation

[10], flash evaporation [11], pulsed laser deposition [12] and spin coating technique [13]. Comparing with some sophisticated techniques, sol – gel spin coating technique is very simple and inexpensive one, which can be used for large area thin film deposition.

In this work CdS/PS nanocomposite structure has been synthesized by sol – gel spin coating method. Its structural, surface morphological and optical properties were studied and reported.

Experimental Details

Preparation of Nanoporous Silicon

Crystalline silicon wafers (Boron doped; 0 -100 Ωcm resistivity) in (1 0 0) orientation used to prepare PS by using the electrochemical etching process. The silicon wafer was cleaned to remove any contamination on the surface. It was rinsed with ethanol to remove dirt, followed by etching in dilute Hydrofluoric acid (HF) for 10 minute to remove the native oxide layer. The wafer was rinsed with ethanol and left in environment for a few minutes to dry.

The PS sample was prepared by electrochemical anodic dissolution of p-type silicon substrate in hydrofluoric acid and ethanol with platinum electrode as cathode. The electrolyte was prepared by mixing HF and ethanol (C₂H₅OH) in 1:1 ratio. The porous layer was prepared at a current density of 50mA/cm² with an etching time of 10 minute.

Preparation of CdS/PS nanocomposite structure

Nanostructured CdS thin film was coated onto nanoporous silicon by sol – gel spin coating technique. The required precursor solution for CdS film was prepared by dissolving 3.08 gm of Cd (NO₃)₂·4H₂O and 0.76 gm of (NH₂)₂CS in 100 ml ethanol. The mixed solution was stirred for 4 hour and this solution was kept hydrolysis for 48 hour at room temperature before coating. It was then spin-coated on PS substrate at 1000 rpm for 30 sec at room temperature. To

evaporate the solvent; the sample was then annealed in a furnace at 400°C for 1 hour.

Results and Discussions

X-ray diffraction Study

The crystallographic structure of film was analyzed with X-ray diffractometer (PANalytical XPERT- PRO) using $\text{Cu-K}\alpha$ ($\lambda=1.54\text{\AA}$) radiation. Diffraction patterns have been recorded over the 2θ range of 20° to 80° at the scan rate of $10^\circ \text{ min}^{-1}$. The crystal structure and purity of the prepared samples were identified by using X-ray diffraction analysis. Figure 1 shows the XRD pattern of CdS coated PS sample.

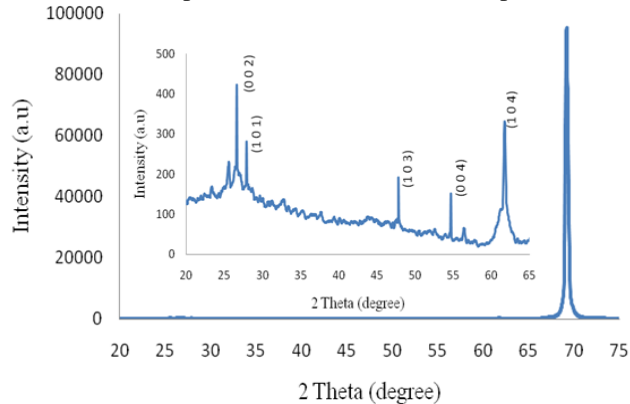


Figure 1. XRD pattern for CdS/PS nanocomposite structure

The diffraction along (0 0 2) (1 0 1) (1 0 3) (0 0 4) and (1 0 4) planes have been observed for CdS. (0 0 2) plane is the major plane which corresponds to CdS with hexagonal structure. The results are in good agreement with the standard JCPDS File No: 06 – 0314 data. Thambidurai et al reported that (0 0 2) is the major plane for CdS prepared via sol – gel spinning method [13]. XRD pattern shows that the PS structure (Figure 1) exhibited a dominant diffraction peak at $2\theta = 69.2^\circ$ corresponding to the PS (4 0 0) plane (JCPDS File No: 89 – 2955). No other peaks were present which indicates the purity of the samples. The particle size has been calculated along the major plane by using Debye-Scherrer formula.

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

where θ - the diffraction angle, β - Full Width at Half Maximum, λ -Wavelength of the X-ray.

The calculated crystallite size was 51.66 nm for the CdS coated PS sample. From the XRD data the lattice parameters 'a' & 'c', was evaluated using the relation [14],

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

where 'd' is the interplanar spacing.

The volume of a hexagonal unit cell is given by,

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (3)$$

The CdS/PS bond length L was calculated by,

$$L = \sqrt{\left(\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2\right)} \quad (4)$$

where the parameter 'u' for wurtzite structure related to 'a' and 'c', is given by

$$u = \frac{a^2}{2c^2} + 0.25 \quad (5)$$

These values are found to coincide well with previous report [10].

Table 1. The structural parameters of CdS/PS nanocomposite structure

d – spacing Experimental (Å)	3.3560
d – spacing Standard (Å)	3.3670
2θ (Degree)	26.54
h k l plane	(002)
FWHM (Degree)	0.42
Grain size (D) (nm)	51.66
Phase	Hexagonal CdS
Lattice Constants(Å)	a = 4.1295 c = 6.7120
Volume(Å) ³	99.1237
Bond Length(Å)	2.4187

Surface Morphological Study

The Surface morphology and EDAX spectrum of the CdS/PS sample was recorded using Scanning electron microscope (SEM) (Model TESCAN VEGA-3 LMU & Bruker EDAX) and it was shown in Figure 2(a) and 2(b) respectively. Figure 2(a) exhibits a nanorod like morphology due to the agglomeration of nanoparticles. Figure 2(b) shows the EDAX spectra and it reveals incorporation of CdS into the PS surface. It was observed that the CdS thin film covers well the PS substrate, thus acting as a transparent capping which could improve the structural stability of the PS substrate. Figure 3 shows the possible formation mechanism of CdS/PS nanorods.

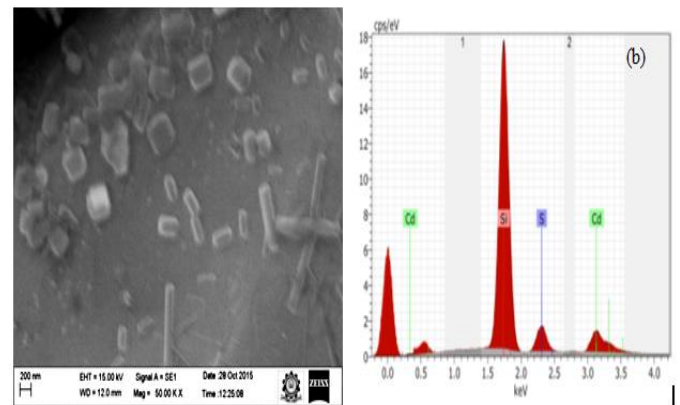


Fig 2 (a). SEM micrograph & 2(b). EDAX spectrum of CdS/PS nanocomposite structure

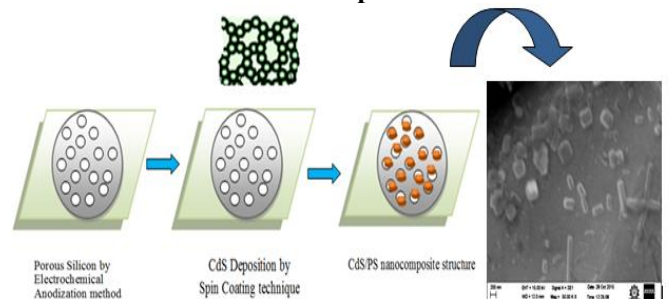


Fig 3. Formation mechanism of CdS/PS nanorod FTIR Spectral Study

FTIR spectra were recorded by a spectrophotometer (Perkin Elmer FTIR Spectrum-GX); at laser power 0- 450 mW, the wave number ranging from 400-3000 cm^{-1} . FTIR spectra give information about the vibration and rotation of molecular groups in a material which is mainly used to determine the concentration of the impurities and their bonding with the host material [15]. FTIR analysis has also been used to detect chemical composition of the samples. The FTIR spectra of CdS/PS nanocomposite structure was shown

in Figure 4. The vibrational bands at 545.85 and 694.37 cm^{-1} are attributed Cd-S (belonging to CdS groups) stretching vibrations.

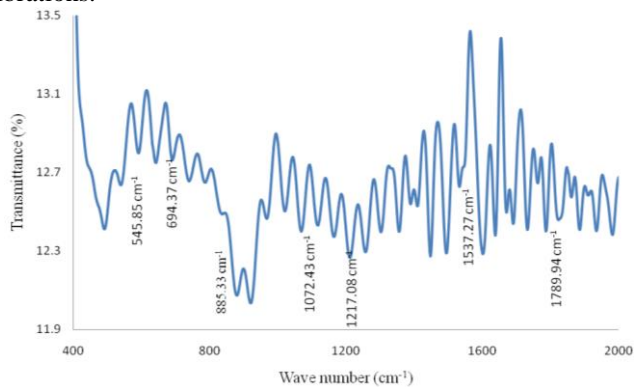


Fig 4. FTIR spectra for CdS/PS nanocomposite

The FTIR spectra of CdS/PS nanocomposite structure shows strong and weak bands are observed at 885.33, 1072.83, 1217.08 and 1537.27 cm^{-1} are associated with Si-H (or) Si-H₂ wagging, O₃-SiH, Si-O-Si, Si-H_x and Si-OH vibrations, which arises due to PS.

Photoluminescence Study:

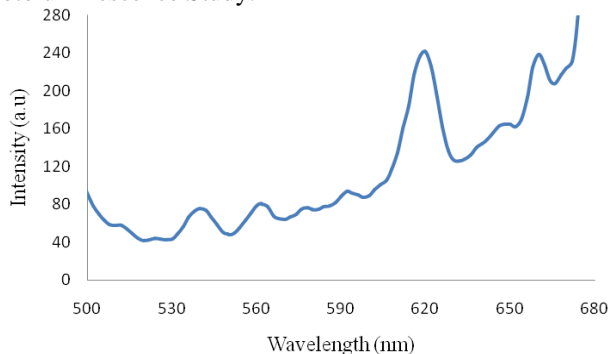


Fig 5. PL Spectra of CdS/PS nanocomposite structure

The photoluminescence (PL) spectra of the samples have been recorded using Perkin Elmer LS 55 Luminescence Spectrometer in the emission wavelength range of 400 – 800nm, fixing the excitation wavelength at 450nm. All the measurements were carried out at room temperature. PL spectra observed for CdS/PS sample was indicated in Figure 5. Room temperature luminescence observed in porous silicon has been attributed either to direct radiative recombination in nano-meter-size silicon in the porous silicon network, or to chemical complexes of silicon, hydrogen and/or oxygen [16].

Synthesis of nano CdS/PS at room temperature also creates more defect/trap states arising due to the high surface to volume ratio. The appearance of two emission peaks (620 & 660 nm) was due to the types of structure in the sample, and the energy gap for each structure is different. The PL maximum is obtained at a wavelength of 620 nm which can be interpreted as due to transition of electron trapped at surface states to the valence band. In addition, the emergence of emission peaks in the range of 600 – 700 nm can be attributed to porous silicon, which increases its optical band gap to the visible region of the optical spectrum [17]. The occurrence of strong PL spectra may be attributed to the transition among the quantum confined states in nanoscale Si, which are influenced by the surface bonds.

Conclusion

Nanostructure CdS/PS structure was fabricated by sol – gel spin coating technique. X-ray diffraction pattern exhibit peaks with a hexagonal phase and the value of average grain size is about 51.66 nm. The Scanning electron micrograph

image reveals that the nano rod like morphology is formed due to the agglomeration of nanoparticles. FT-IR spectroscopy shows that the vibrational bands at 545.85 and 694.37 cm^{-1} are attributed CdS (belonging to CdS groups) stretching vibrations. The PL spectra show that the maximum peak is obtained at a wavelength of 620 nm which can be interpreted as due to transition of electron trapped at surface states to the valence band. Thus the incorporation of CdS into the pores of PS enhances the film surface and improves the surface roughness of the composite structure. Consequently, it removes the recombination centers at the surface and changes the surface morphology. These factors together are apparently responsible for improving the stability of the CdS/PS structure for device applications.

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