

Effect of Particle Size on Dielectric Properties of CdS Nanoparticles

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Abstract

The dielectric constant of the thin films of CdS nanoparticles grown in polymer matrix (PVA) deposited on Si substrates has been studied at room temperature as a function of frequency under vacuum (10^{-3} Torr). The samples of CdS nanoparticles have been prepared with different particle sizes and dispersibilities (η) by varying the chemical bath deposition temperature. The room temperature dielectric constants of the CdS-PVA composites lie in the range 120 to 255 at high frequency range (>1 kHz) which are much higher than that of only PVA having dielectric constant ~ 28 and CdS having dielectric constant 8.9. The dielectric constant of the films increases with the decrease of particle size.

Keywords: *nanoparticles; PVA /CdS; dielectric properties*

1. Introduction

Nanocrystalline semiconductors have attracted much attention due to their novel properties and varieties of promising potentials in extensive applications [1-2]. Numerous technical advancements in the field of nanostructured materials have stimulated the wide range of research interest in recent years because of various new properties exhibited by them. Recently, nanostructured semiconductors are widely used to design rich varieties of device for microelectronics. One-dimensional nanostructured materials have gained special interest in the assembly of nanodevices. Nanometer-scale electronics have been predicted to play an important role in device technology [3]. Quantum wires of semiconductors [4] and metallic alloys [5] have found to exhibit interesting magnetic and electrical properties. The nanostructured transparent conducting oxides have also gained tremendous importance due to their size dependent optical and electrical properties and possible applications in near future.

Polymer / nanoparticles composites have been increasingly studied because of their enhanced optical and electronics properties. II-VI semiconductors like CdS and ZnS are widely used as window layers of solar cells. CdSe polymer composites can be used to make blue light emitters [6]. Nanostructured ZnS thin film may also be utilized in photovoltaic devices due to the larger bandgap than that of the bulk material. Depending on the sizes of the materials, the nanoscale semiconductors show interesting properties, and great efforts have been imposed upon controlling their sizes. Starting from the zero-dimensional nanoparticles, various structures, such as nanowires, nanorods, nanotubes and nanobelts have been produced from different materials [7-8], among them CdS is one of the widely studied materials. Recently, various research groups around the world are working on the synthesis of nanocrystalline CdS thin films in different routes such as pulsed laser deposition (PLD), vacuum deposition, spray pyrolysis, chemical bath deposition (CBD) etc. Lee et al. [9] prepared $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ thin films by co-evaporation of CdS and ZnS powder and Zn incorporation in CdS nanoparticles were also reported by

Persans *et al.* [10]. Enriquez *et al.* [11] and Oumous *et al.* [12] prepared CdS thin films by CBD, and CdS nanowire was also fabricated through this route by Zhang *et al.* [13]. The studies of dielectric properties of different materials were done by different worker [14-16] in different routes. Recently, a method of making nanostructure by electro-chemical deposition of materials into an array of self-organized pores has been developed [17].

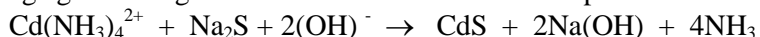
In this paper we have reported the Effect of particle size on dielectric properties of nanocrystalline CdS particles grown in a polymer matrix by chemical bath deposition (CBD) technique.

2. Experimental Details

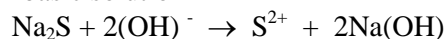
2.1. Synthesis

The films were deposited on glass and Si substrates using CBD process at different temperature to obtain the different particle size. We prepared PVA solution by adding 200 ml of doubled distilled water with 5.3×10^{-5} moles of solid PVA $(-C_2H_4O)_n$ (where $n = 1700$) and this mixture was stirred by a magnetic stirrer and was also heated at temperature ~ 85 °C for one and half an hour. After ageing the solution nearly one hour, when temperature dropped to 40 °C, a solution prepared by taking 0.0011 moles of $CdCl_2$ (99.99 %) and 0.013 moles of NH_4Cl (99.98 %) dissolved in 1.3 moles of NH_3 (taken in the form of $NH_4(OH)$ of density 0.91 gm/cc and containing 25% NH_3) was added with it and again heating and stirring were continued. After 10 min., 0.0132 moles of thiourea ($NH_2.CS.NH_2$, 99.99 %) dissolving in 30 ml distilled water, was also added with the first solution. When temperature of the solution reached at 70 °C, 75°C, 80 °C, 85 °C and 90 °C, different cleaned glass and Si slides were dipped into it at above maintained temperature for deposition of films by CBD method. The glass substrates were cleaned first by mild soap solution and then washed thoroughly in de-ionized water and also in boiling water. Finally, they were ultrasonically cleaned in acetone for 15 minutes and Si substrates were immersed in 20 % HF solution for 5 minutes for removing surface oxide layers. Then they were cleaned in de-ionized water and finally with alcohol in an ultrasonic cleaner. The process was done for 20 min. at above maintained temperature.

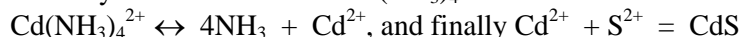
This is achieved by controlling the precipitation of cadmium sulfide in the reaction bath. As the solubility product of cadmium sulfide is very small, the precipitation is controlled by controlling the concentration of free cd^{+2} ions in the chemical bath. This is done by using a suitable complexing agent, which releases a small concentration of ions, according to the complex-ion dissociation equilibrium. In this case, ammonia was used as the complexing agent. The global chemical reaction for the deposition of CdS by CBD is:



In our CdS thin films the source of sulphur and cadmium are due to release of S^{2+} ions by Na_2S in basic solution



and Cd^{2+} ions by the dissociation of $Cd(NH_3)_4^{2+}$ as follows:



When the ionic product of Cd^{2+} and S^{2+} exceed the solubility product of CdS, the precipitation of CdS can occur either in solution or in surface of the substrates.

2.2. Characterization

After the deposition of the films, they were characterized by different techniques. Structural characterizations of the films have been done by studying transmission electron microscopy (TEM, Hitachi-H600), X-ray diffraction (XRD, BRUKER D-8 ADVANCE) and scanning electron microscopy (SEM, JEOL-5200). XRD patterns of PVA / CdS thin films deposited on Si substrates have been studied in 2θ range 20 - 70 ° using $Cu K\alpha$

radiation of wavelength $\lambda = 0.15406$ nm. The dielectric properties have been studied by using a L-C-R meter (HP - 4284A) at room temperature.

3. Results and Discussion

3.1. Structural characterization

Figure 1 shows the X-ray diffraction patterns of the thin films deposited on Si substrates at CBD temperature (a) 70 °C and (b) 90 °C. Only one peak of cubic CdS was obtained due to reflection from (111) plane as in JCPDS data card [18]. Also one high intense peak appeared due to reflection from (004) plane of Si substrates. The particle size calculated from the XRD peaks lie in the range 5 nm to 9 nm. This result fairly supports the TEM results. The interplanar spacing (d) corresponding to XRD peaks, TEM measurement and JCPDS data card have been compared as shown in Table-1. X-ray diffraction patterns of CdS-nano inside the polymer matrix show broadening of peaks, which indicate CdS is nanocrystalline in nature within the amorphous polymer (PVA).

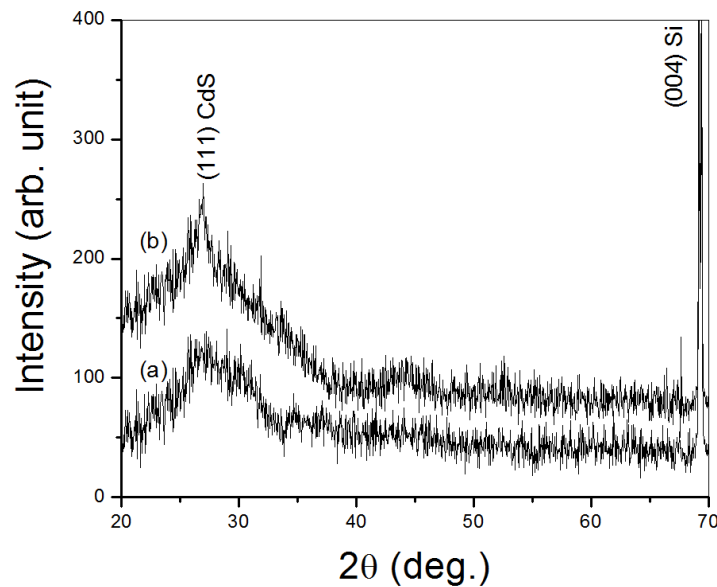
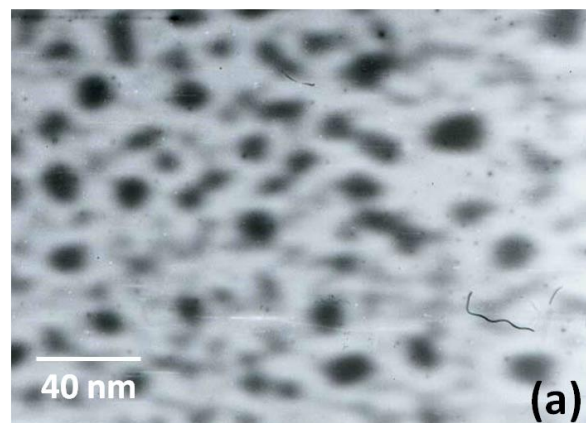


Figure 1. XRD Pattern of PVA /CdS Thin Film Deposited on Si Substrate for Different CBD Temperature (a) 70 °C and (b) 90 °C



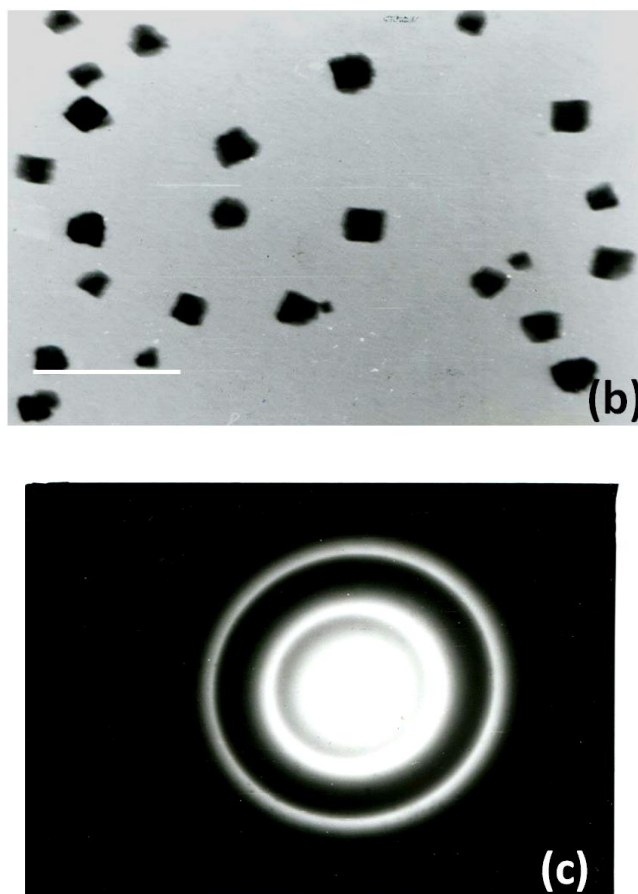


Figure2. TEM Micrographs for Deposition Temperature (a) 70 °C, (b) 90 °C and (c) one of Typical Selected Area Electron Diffraction Pattern 70 °C

Table-1. Interplaner Spacing (d) from TEM, XRD and JCPDS Data Card and Corresponding (hkl) Values

$d_{(TEM)}$ (Å)	$d_{(XRD)}$ (Å)	$d_{(JCPDS)}$ (Å)	(hkl)
3.36	3.35	3.36	(111)
2.059	---	2.05	(220)

The nanostructured of the films, prepared by dispersing the nanoparticles on carbon coated copper grid, were studied by TEM. The micrographs and one selected area electron diffraction (SAED) patterns of the films have been shown in Figure 2. (a), (b) and (c) for deposition temperature 70 °C, 90 °C and 70 °C respectively. From the electron diffraction patterns, we calculate the inter-planer spacing (d) values, which correspond to reflection from (111) and (220) planes of cubic CdS. The average particle sizes are determined from TEM micrographs; lie in the range 5 nm to 12 nm.

The dispersibility (η) of the films has been obtained from the ratio of the diameter of the particle ($2r$) to the separation between the particles (s). The average dispersibility ($\eta = 2r/s$) and particle size of the films obtained from the TEM images lies in the range 0.86–0.3 and 5- 12 nm respectively for different films with variation of deposition temperature from 70 to 90 °C. Table 2 shows the Comparison of deposition temperature, particle size

and dielectric constant at high frequency for different thin films deposited on silicon substrates.

Table 2. Comparison of Deposition Temperature, Particle Size and Dielectric Constant at High Frequency

Sample	Deposition temperature(⁰ C)	Particle size (nm)	Dielectric constant at frequency 3×10 ⁴ Hz
(a)	70	5.0	255
(b)	75	6.2	245
(c)	80	8.2	230
(d)	90	12.0	120

3.2. Dielectrics Studies

The dielectric constants of the films have been obtained using the relation:

$$\epsilon = \frac{Cd}{\epsilon_0 A}$$

where C is the capacitance of the ideal capacitor, ϵ_0 , the permittivity of the free space, d and A, the film thickness and electrode area, respectively.

Figure 3 shows the variation of dielectric constant as a function of frequency for different samples of CdS nanoparticles dispersed in PVA with different particle sizes (a) for 5 nm, (b) for 6.2 nm and (c) for 8.2 nm. The dielectric constant of PVA / CdS nanocomposite has been measured under vacuum (10⁻³ Torr) by using a L-C-R meter and the value of it lies in the range 120 to 255 at high frequency (as shown in Fig.3) which are much higher than that of only PVA having dielectric constant ~28. The large value of dielectric constant of nanocomposite (PVA / CdS) is due to the fact that the nanoparticles of CdS within PVA are disconnected from each other and under the application of voltage, this nanoparticles act as nanodipole. As the particle size is in nanometer order, the number of particles per unit volume increases, hence dipole moment per unit volume increases, so dielectric constant increases. It has also been observed that, for each size of CdS nanoparticles in the films, the dielectric constant is almost constant at high frequency range *i.e.* there is no dispersion at high frequency.

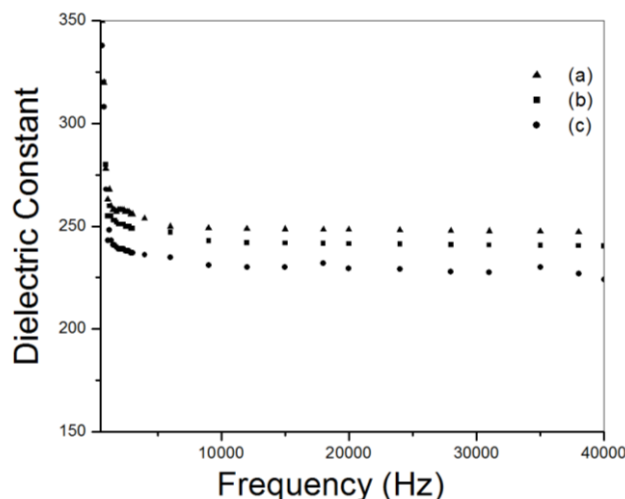


Figure 3. Dielectric Constant vs. Frequency Plot of PVA / CdS Nanocomposite Deposited on Si Substrate for Different Particle Sizes (a) 5 nm, (b) 6.2 nm and (c) 8.2 nm

4. Conclusions

The electrical properties of transparent nanocrystalline CdS thin films, grown via CBD within the pores of PVA have been studied. X-ray diffraction and transmission electron microscopy measurements confirmed the nanocrystalline nature of the CdS particles with an average particle sizes lying in the range 5 to 12 nm. The high dielectric constant lies in the range 120 to 255 at high frequency of PVA / CdS thin films compared to that of pure PVA (~ 28) and CdS (~8. 9) have been observed. The dielectric constant decreases with increase in size of the CdS nanoparticles.

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