

Optical properties of polycarbonate organic matrix/cadmium sulphide clusters composite material

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This paper presents the investigation of the optical properties of bisphenol A polycarbonate organic matrix/CdS clusters composite material in correlation with the method for the films' preparation using as precursors cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$), respectively ammonium thiocyanate (NH_4CNS), and as general solvent for all the components, is dimethylformamide. The effect of the heat treatment temperature (90 °C or 150 °C) on the position and shape of the fundamental absorption edge was investigated for given substrate, drying conditions and duration (1.5 h or 0.5 h) of the heat treatment. A large blue shift of the absorption edge was evidenced in films prepared in vertical configuration and thermally treated at 90 °C for 1.5 h, which can be associated with a small dimension of the CdS crystallites and in consequence with quantum confinement effects. Using the effective mass theory we have deduced a crystallite dimension in the range 8.8-15 nm. We also have studied the interaction of the light with this composite material evaluating an optical band gap between 2.92 and 3.69 eV (depending on the preparation and annealing conditions) and an absorption mechanism in CdS clusters closer to an indirect transition and deviated from the normal direct absorption process in bulk CdS semiconductor.

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1. Introduction

In the last years a special interest has been paid to the field of nanometer-sized semiconductor compound crystalline clusters synthesized in different matrix (inorganic or organic), due to their special physical and chemical properties intermediate between the molecular and bulk limits [1-6].

Research in the field of organic matrix/inorganic clusters films has developed from fundamental studies to the synthesis of novel materials for new devices because of their potential application in electronics and nonlinear optics [7-9].

The polymeric matrices are preferred to the vitreous ones because on one hand are not necessary preparation restrictions (they are soluble in different ordinary solvents and involve low processing temperatures and, on the other, polymers show adequate optical properties (large range of transparency and high, homogeneous refraction index).

In the selection of the semiconductor inclusion we have to take into account some restrictions imposed by the quantum confinement effects: a dimension of the inclusion closed to the Bohr exciton radius of the material and high binding energy of the exciton [10, 11]. As a consequence, GaAs and III-V semiconductor compounds are not adequate as inclusions because exhibit low effective masses for electron and hole and high dielectric constants, that imply higher quantification energies for electron and hole than the binding energy for the exciton. Special attention must be paid to the large band gap semiconductor materials, that have to be avoided because for these semiconductors the Bohr exciton radius is very small and it

is very difficult to satisfy the condition of smaller inclusions dimension, using conventional technologies. Materials satisfying these conditions are I-VII and II-VI semiconductor compounds.

Following these criteria the selected components of our composite system are bisphenol A polycarbonate (transmission range = 330-1100 nm, $n=1.587$ at 25 °C) and CdS (with a Bohr exciton radius $r \sim 3$ nm).

We have studied the effect of the temperature and duration of the heat treatment on the CdS clusters generation and development in polycarbonate matrix and the influence of these inclusions on the optical properties.

2. Experimental methods

To obtain thin film samples of composite material formed of II-VI semiconductor particles, CdS, embedded in a polymeric transparent matrix, bisphenol A polycarbonate, we have started with cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$) respectively ammonium thiocyanate (NH_4CNS) as precursors and followed a process containing many steps [12].

We have prepared the so-called "mother solution" dissolving the precursors and polymeric matrix in dimethylformamide (DMF), a general solvent for all the components of the system [13]. 0.5 g of polymer was dissolved in 5 ml of DMF (solution 1), 0.1 g of cadmium acetate dried at 80 °C was dissolved in 5 ml of DMF (solution 2) and 0.1 g of ammonium thiocyanate in 5 ml of DMF (solution 3). To prepare the "mother solution" solution 2 was added drop by drop into polymer solution 1 and the mixture was stirred. Then solution 3 was added

drop by drop and this new solution was stirred again obtaining a transparent, very pale yellow “mother” solution.

The films were deposited by dipping the standard microscope glass slides substrates cleaned in hydrofluoric acid, rinse with acetone and distilled water in the ‘mother solution’.

Coated glass samples were then dried at different temperature (40 °C; 60 °C for 3 h respectively 1.5 h) to assure the reaction and the formation of small CdS particles embedded in the polymeric film.

The drying was done in air and the product was a polycarbonate film incorporating CdS particles. The growth of CdS particles at a certain average dimension embedded in polymeric matrix was determined by the initial concentrations of the primary solutions and the removing rate of the excess solvent (DMF) in the drying stage of the process correlated with the thermal regime and experimental configuration.

The last step was the thermal treatment of the prepared samples at different temperature (90 °C; 150 °C) for different time period (1.5 h respectively 0.5 h).

The thickness of the films varied depending on the drying configuration, between 5-19 µm for vertical configuration respectively 13-33 µm for horizontal configuration and was measured with a special thickness gauge.

The effect of the experimental drying configuration (vertical or horizontal) and of the thermal treatment process parameters (temperature and duration) on the position and shape of the fundamental absorption edge and also on the quality and homogeneity of different samples (P1, P2, P3, P4, P5, P6) obtained in different experimental conditions have been investigated by transmission measurements recorded at room temperature with an Perkin-Elmer Lambda 25 Spectrophotometer computer assisted.

3. Results. Discussions

The aim of our study is to analyse the influence of different parameters as thermal treatment temperature and duration, on the particularities of the light absorption process in composite material consisting in CdS clusters thermally developed and randomly distributed into a noncrystalline polymeric matrix of polycarbonate bisphenol A. From the position and the shape of the fundamental absorption edge we have obtained information on the semiconductors inclusions’ growth process and deduced some intrinsic properties of the material, as the optical band gap energy and the particularities of the absorption mechanism compared to those characterizing the corresponding bulk (CdS) semiconductor.

The changes after heat treatment in the optical properties (as the position of the fundamental absorption edge) of the samples prepared in the same conditions (P1 and P2 in Fig. 1; P4 and P5 in Fig. 2) can be associated with the development in the polymeric matrix during this thermal process of the semiconductor phase.

For sample prepared in the same configuration and drying conditions, the effect of temperature (increasing the annealing temperature from 90 °C to 150 °C) on the absorption edge position and shape for a given duration of 1.5 h respectively 0.5 h, has been emphasised. Generally, the increase in the temperature of annealing determined a larger average CdS crystallite size because at higher temperatures it is favoured the diffusion process of cadmium and sulphur to the crystallites’ germination sites.

In vertically dried sample an annealing at 90 °C for 1.5 h (P2) has generated some modification in the film composition compared to untreated sample (P1) favouring the development of CdS clusters. The blue shift of the fundamental absorption edge in this case (60-70 nm) for sample treated at 90 °C for 1.5 h (absorption edge at 274 nm) compared to the untreated one (absorption edge at 335 nm) has suggested an adequate crystallites size for quantum confinement effects that has disappeared in sample (P3) at higher heat treatment temperature, 150 °C (Fig. 1).

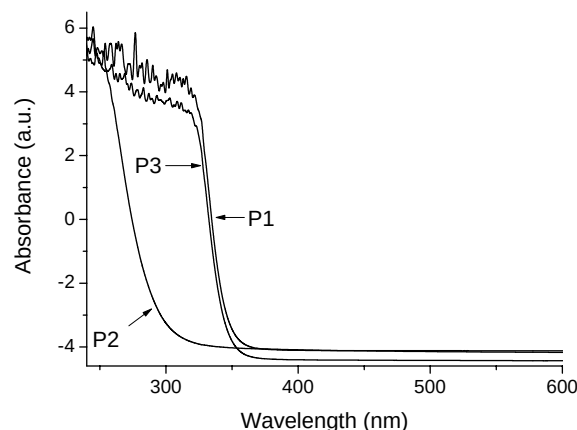


Fig. 1. Absorbance spectra of thin films of CdS doped polycarbonate bisphenol A matrix on glass substrate prepared in vertical configuration by drying at 40 °C for 3 h, untreated (P1) and thermally treated for 1.5 h at 90 °C (P2) and 150 °C (P3).

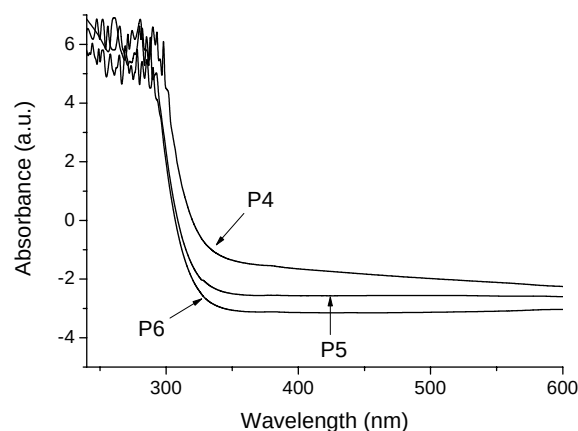


Fig. 2. Absorbance spectra of thin films of CdS doped polycarbonate bisphenol A matrix obtained on glass substrate in horizontal configuration by drying at 60 °C for 1.5 h, untreated (P4) and thermally treated for 0.5 h at 90 °C (P5) and 150 °C (P6).

For horizontally dried samples (Fig. 2) a small blue shift effect (15-20 nm) also was evidenced in the treated sample (P5) and P(6) compared to the untreated sample (P4). This experimental configuration favours for untreated sample (P4) the agglomeration process and a bigger dimension of the clusters. A subsequent thermal treatment at 90 °C or 150 °C for 0.5 h moves the absorption edge to shorter wavelength (306 nm) compared to untreated sample (319 nm), suggesting lower cluster dimension in treated samples, (P5) and (P6), compared to untreated one, (P4). The effect of the temperature increases from 90 °C (5) to 150 °C (P6) on the optical properties was not significant (Fig. 2).

The spectra present a long featureless tail, mainly in the visible region (Fig. 1 and Fig. 2). In general, the lack of exciton shoulder at the edge of the absorption tail (Fig. 3) can be a result of size distribution of the particles generating an inhomogeneous broadening, [6;14].

Plotting the UV-VIS transmission spectra in different position on the composite material coated substrate (P3 and 1P3; P6, 1P6 and 2P6) we have evaluated the quality and homogeneity of the samples.

The films prepared in vertical configuration are thinner (thickness between 5-19 µm) than those prepared horizontally (thickness between 13-33 µm) as can be remarked from the transmission level (Fig. 1 and Fig. 3; Fig. 2 and Fig. 4). Small variations in the homogeneity of the samples have been evidenced by variation in the transmission in different regions of the films prepared in horizontal and vertical configuration (Fig. 3 and Fig. 4).

Our spectrophotometric measurements have also offered information on the light absorption process in this composite material. To evaluate the band gap energy and identify the absorption mechanism for samples prepared and annealed in different conditions, we have processed the experimental transmission data using a power function:

$$\alpha(E) = A + B(E - C)^D \quad (1)$$

where α is the absorption coefficient, C [eV] is the band gap energy, D is a dimensionless coefficient correlated with the absorption mechanism and A [cm^{-1}], B [cm^{-1}], E =photon energy [eV] are constants (Table 1 and Table 2).

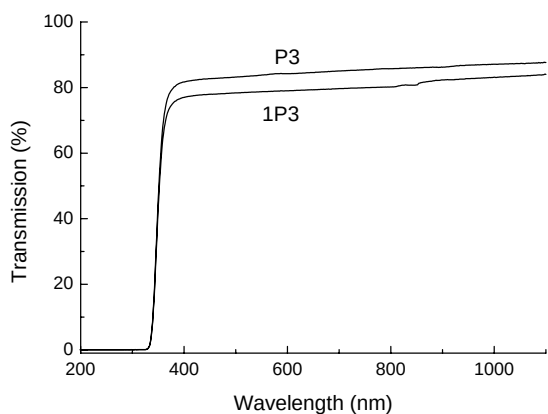


Fig. 3. Spectrophotometric investigation of the homogeneity of the films obtained in vertical configuration and thermally treated at 150 °C for 1.5 h.

Average film thickness=12 µm.

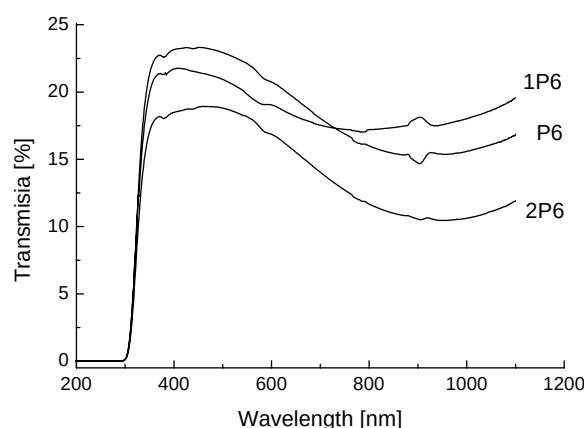


Fig. 4. Spectrophotometric investigation of the homogeneity of the films obtained in horizontal configuration and thermally treated at 150 °C for 0.5 h.

Average film thickness = 33 µm.

Table 1. Comparative presentation of the fitting parameters (using function (1)) of the experimental absorption data for vertically and horizontally prepared CdS/polycarbonate films on glass substrates.

Sample	Drying conditions	Heat treatment regime	Fitting parameters	
			C(eV)	D
P1	40 °C, 3 h (vertical)	untreated	3.40	2.76
P2		90 °C, 1.5 h	3.69	2.87
P3		150 °C, 1.5 h	3.25	4.45
P4	60 °C, 1.5 h (horizontal)	untreated	2.92	6.10
P5		90 °C, 1.5 h	3.32	4.30
P6		150 °C, 1.5 h	3.29	4.30

Comparing the absorption threshold in CdS doped polycarbonate (Table 1) and CdS bulk semiconductor ($E_g=2.55$ eV [15]) we have remarked an increase in the optical band gap energy, confirming a process of small crystallites development in polymeric matrix.

Table 2. Variation of the fitting parameters (obtained using Eq. (1)) of the absorption data in different region of vertically (P3; 1P3) and horizontally (P6; 1P6; 2P6) prepared CdS/polycarbonate films on glass substrates.

Sample	Preparation conditions	Fitting parameters	
		C(eV)	D
P3	40 °C, 3 h/150 °C, 1.5 h (vertical)	3.28	3.87
1P3		3.27	3.90
P6	60 °C, 1.5 h/150 °C, 0.5 h (horizontal)	3.25	4.45
1P6		3.26	4.56
2P6		3.32	4.05

The signification of the parameters is given in the text, Eq. (1).

The small variations in the homogeneity of the samples were also confirmed by the behaviour of the fitting parameters of the absorption data determined from experimental transmission data in different points on the films.

Examples of the fitting curves are given in Fig. 7 (vertically dried sample treated at 90 °C for 1.5 h (P2) compared to vertical dried sample untreated (P1)) and Fig. 8 (horizontally dried sample treated at 90 °C for 0.5 h (P5) compared to horizontally dried sample untreated (P4)).

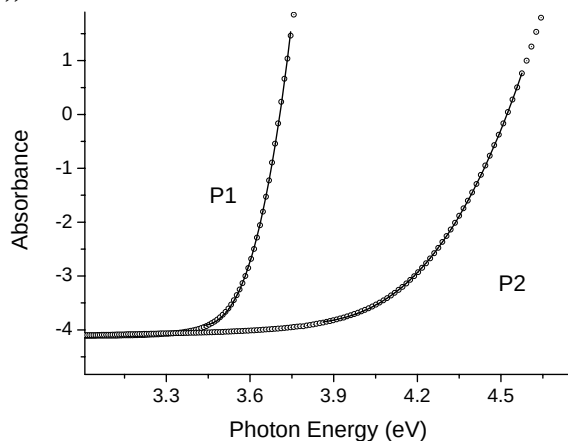


Fig. 5. Experimental data fitting for samples of CdS doped polycarbonate film dried at 40 °C for 3 h, untreated (P1) and thermally treated at 90 °C for 1.5 h (P2).

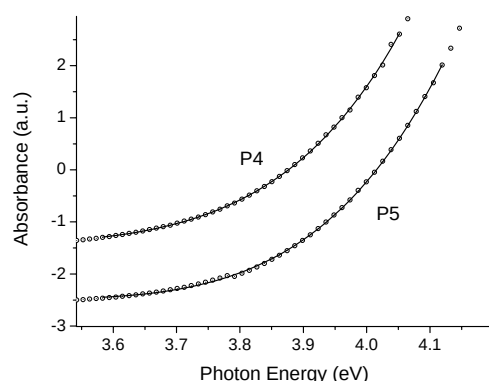


Fig. 6. Experimental data fitting for samples of CdS doped polycarbonate film dried at 60 °C for 1.5 h, untreated (P4) and thermally treated at 90 °C for 0.5 h (P5).

The light absorption mechanism is by indirect transitions in P2 sample presenting blue shift ($D=2.87$) as for the corresponding untreated sample P1 ($D=2.76$). For all the other samples (P3, P4, P5, P6) a deviation from this mechanism is observed ($D=3.8\div 6$), which for polymeric matrix can not be explained by the effect of the high pressure exercised by the matrix on the semiconductor crystallites as for vitreous matrix [16,17].

A rough evaluation of the size of CdS crystallite in polymeric noncrystalline matrix has been done using the effective mass theory [18,19] from the equation:

$$\Delta E_g = (\hbar\pi)^2 / (2m_{e-h} R^2) \quad (2)$$

where: ΔE_g is the difference between the band gap energy for the cluster and the band gap for the corresponding bulk

semiconductor compound, CdS, m_{e-h} is the effective mass and R is the radius of the cluster. For particle size associated with blue shifts the Bohr exciton diameter is comparable with the cluster dimension and the effective mass, m_{e-h} , is the reduced mass of the electron-hole system. Because for CdS $m_e=0.205 m_0$ [20] and $m_h=0.98 m_0$ [20], where $m_0=0.9109534 \times 10^{-30}$ kg is the mass of the free electron, the equation (2) becomes:

$$\Delta E_g = (\hbar\pi)^2 / (0.338 m_0 \cdot R^2) \quad (3)$$

ΔE_g has been evaluated comparing the band gap energy E_g , obtain from the absorption data for samples of CdS doped polycarbonate bisphenol A (Table 1), with the band gap energy for bulk CdS semiconductor, $E_g=2.55$ eV [15]. The deduced average radius of the CdS crystallites developed in our polycarbonate bisphenol A matrix varied between 8.8 and 15.4 nm (Table 3).

Table 3. CdS cluster radius in polycarbonate matrix in correlation with the films' preparation and annealing conditions.

Sample	Drying conditions	Heat treatment regime	E_g (eV)	R (nm)
P1	40 °C, 3 h (vertical)	untreated	3.40	10.16
P2		90 °C, 1.5 h	3.69	8.81
P3		150 °C, 1.5 h	3.25	11.20
P4	60 °C, 1.5 h (horizontal)	untreated	2.92	15.41
P5		90 °C, 1.5 h	3.32	10.68
P6		150 °C, 1.5 h	3.29	10.89

The smallest crystallite dimension is associated with the strongest blue shift of the absorption threshold ($\Delta E_g=1.14$ eV) in sample (P2), compared to the bulk CdS.

4. Conclusions

This paper presents a study of the correlation between the preparation and annealing conditions and the optical properties of the composite material containing CdS clusters embedded in polycarbonate bisphenol A matrix.

The effect of the experimental configuration (vertical or horizontal) and of the thermal treatment process parameters (temperature: 90 °C; 150 °C) and duration: 1.5h; 0.5 h) on the position and shape of the fundamental absorption edge and also on the quality and homogeneity of different samples obtained in different experimental conditions have been investigated.

Blue shifts of the absorption thresholds were evidenced in all composite samples compared to the bulk CdS suggesting small dimensions of the clusters between 8.81-15.4 nm, but the most significant shift compared to the bulk CdS ($\Delta E_g=1.14$ eV) was obtained for vertically dried samples thermally treated at 90 °C for 1.5 h for which an absorption mechanism by indirect transitions have been emphasised. This shift has been associated with calculated optical band gap $E_g=3.69$ eV and a cluster radius of 8.81 nm.

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