

INORGANIC-ORGANIC SOL-GEL PROCESSING OF SEMICONDUCTOR QUANTUM DOTS AND SOME PRELIMINARY SELF-DIFFRACTION STUDIES ON CdS-PbS

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ABSTRACT

Films and monoliths, containing clusters (sizes < 5 nm) of the binary semiconductor CdS and sandwiched CdS-PbS, were prepared via multifunctional inorganic-organic sol-gel processing. As a sulfur source, hexamethyldisilylthiane was employed. In precursor sols, the metal sulfide clusters are carrying functionalized silanes acting as stabilizing centers as well as inorganic and organic network formers. Hydrolysis and condensation produces an inorganic network yielding viscous liquids useful to prepare optically transparent films or monoliths. The final organic cross-linking at $T < 100^\circ\text{C}$ results in materials of variable spectral response, thickness and optical density. In preliminary degenerate four-wave mixing experiments, self-diffraction from laser-induced gratings was observed on unsupported 200 μm thick CdS-PbS doped monoliths. The maximum first order grating efficiency, measured at different wavelengths between 490 and 520 nm, was $0.5 \cdot 10^{-3}$ and the corresponding calculated effective third order susceptibility was of the order of 10^{-9} esu.

INTRODUCTION

Semiconductors of reduced dimensionality are known to possess size dependent electronic and optical properties which make them potentially interesting for tunable linear and non-linear optics (NLO) [1-3]. The chemical parameters during the preparation of the materials play a decisive role for the adjustment of spectroscopic properties [4,5]. Flexible preparation and processing techniques are required to control the factors determining NLO properties or efficiency (size distribution, excited state relaxation dynamics, refractive index, photostability etc.).

The sol-gel technique therefore offers appropriate means, and semiconductor quantum dot composites have been already prepared by this route. In [6] the consolidation of CdS or ZnO clusters to optically transparent materials has been demonstrated and in [7,8] an "in situ" CdS cluster growth through H_2S exposure of Cd^{2+} doped silica and alumina gels was performed.

In this paper, an inorganic-organic sol-gel route is presented employing bifunctional silanes $\text{L}-(\text{CH}_2)_3-\text{Si}(\text{OR})_3$ as quantum dot sol stabilizers ($\text{L} = -\text{NH}_2, -\text{SH}$ to form bonds to the quantum dots) and inorganic-organic matrix formers ($\text{L} = \text{-epoxy}$ for organic polymerisation and $\text{Si}(\text{OR})_3$ for inorganic hydrolysis and condensation). This route has already been successfully applied to design materials with high abrasion and mechanical resistance [9] and very low surface energy [10], patterned coatings for integrated optics [11] and inorganic-organic quantum dot composites [12-14].

The goal of this sol-gel study was to prepare highly concentrated 0.1 - 1 molar CdS and CdS-PbS sol precursors for single step coatings, to transform them subsequently to nanocomposites and characterize them by UV/VIS- and degenerate four-wave mixing spectroscopy.

EXPERIMENTAL

CdS-PbS nanocomposites were synthesized by the following route: 0.01 molar CdS sols were prepared by addition of 2.5 ml 1 molar $(\text{CH}_3)_3\text{Si-S-Si}(\text{CH}_3)_3$ /tetrahydrofuran solution as a sulfur source to a stirred 250 ml ethanolic 0.01 molar cadmium ethoxide solution containing 0.25 mole diamine functionalized trimethoxy

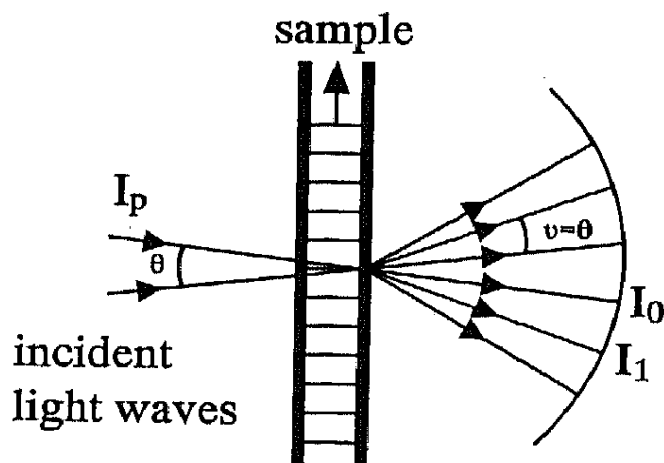
silane as a quantum dot stabilizer (the silane stabilizers formulas are depicted in Figure 2). The procedure was carried out under nitrogen atmosphere.

2.5 ml of 0.04 molar lead methoxy ethanolate/tetrahydrofuran solution was added to this freshly prepared yellowish colored CdS sol, the resulting Cd/Pb molar concentration ratio being 25. During addition of the lead compound, the sol became brown colored indicating development of PbS.

Subsequently, a prehydrolysed glycidyloxypropyl trimethoxy silane solution (the hydrolysis and condensation occurred under CO₂ atmosphere, the Si(OR)₃/H₂O ratio being 2) was added to the PbS-CdS sol. By partial solvent removal, the sols were concentrated to 0.1 - 1 M and used for coating of glass substrates via dip technique or for mold casting.

Curing was carried out at 80°C by reacting the epoxy grouping with excess amino groups of the silanes or by polymerizing them to polyether chains in presence of aluminium alkoxides as catalysts. Films with thicknesses up to 30 μm or crack-free unsupported monoliths with thicknesses between 100 and 200 μm were obtained. Optical characterization was performed in a four-wave mixing experiment.

The basic feature of the device is shown in Figure 1.

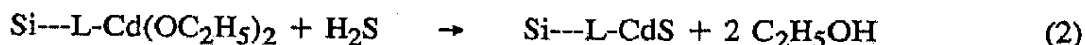
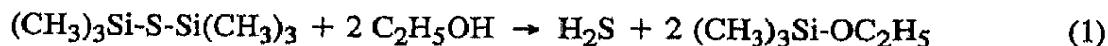


This method (described in detail in [15]) is based on the interference of two spatially and temporally overlapped beams, producing a spatial modulation of the intensity-dependent refractive index and of the optical absorption coefficient of the material. The light source was a XeCl excimer laser pumping a dye laser emitting pulses of 10 ns duration of an energy 30-100 μJ per pulse. The dye used was Coumarin 307, giving tunability in the range from 490 to 520 nm. The incident light waves were parallel polarized to each other.

Figure 1. Laser induced grating by interference of two lightwaves with the same wavelength and an angle Θ between the propagation directions. I_p = input pulse intensity, I_0 = transmitted zero order intensity, I_1 = first order diffracted intensity.

RESULTS AND DISCUSSION

The details of the reaction mechanism to the quantum dot colloids are not quite clear at present, but it can be assumed that the -SH or NH₂ ligands play an important role for the colloid stabilization, since in the absence of mercapto- or amino functionalized silanes L-(CH₂)₃-Si(OC₂H₅)₃, turbid CdS precipitates are formed. The CdS cluster growth is initiated by the formation of H₂S from hexamethyldisilylthiane according to (1) and (2):



In tetrahydrofuran as a reaction medium, the CdS cluster growth is very slow and can be controlled by the addition of ethanol or water. The PbS formation occurs by addition of lead methoxy ethanolate to CdS sol (without excess sulfide), and can be explained by the lower solubility product of PbS (3):



The PbS formation quenches completely the intense room temperature photoluminescence of CdS colloids indicating PbS growth occurring at the surface of CdS particles.

Figure 2 shows the optical absorption spectra of three differently stabilized optically transparent 0.01 M CdS sols.

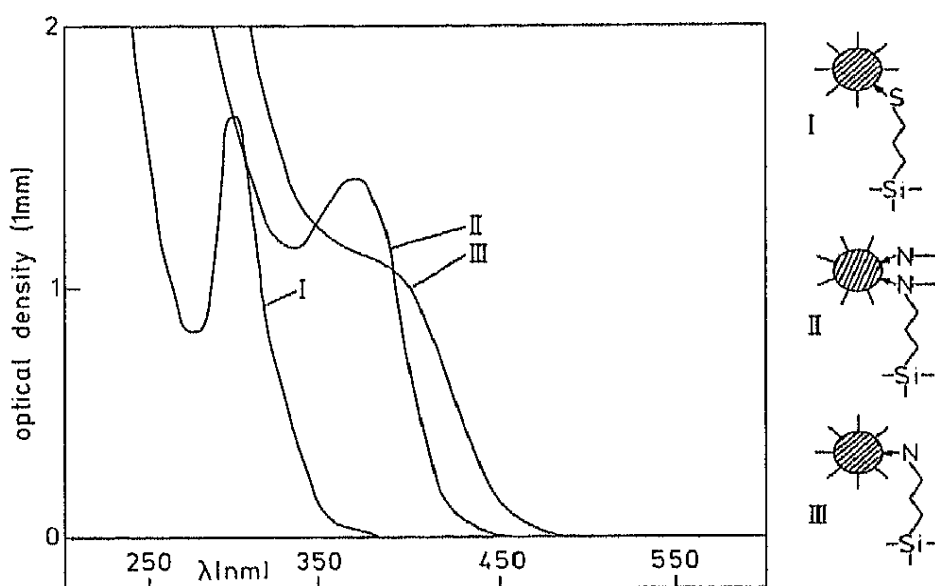


Figure 2. The effect of different silane stabilizers on the optical spectra of 0.01 M CdS sols.

The monoamine silane based sols show a shoulder at 400 nm, indicating a band gap of 3.1 eV, characteristic of average cluster sizes of about 4 nm which could be proved by TEM analysis. The pronounced excitonic band at 370 nm in the diamine sol indicates narrower size distribution than in monoamine stabilized one, the average cluster size being 3 nm. Mercaptopropyl silane stabilized sols possess remarkable strong excitonic band at 300 nm (cluster sizes smaller than 2 nm). Comparing the optical spectra one can conclude that mercapto-based cluster synthesis offers smaller and narrower distributed CdS quantum dots than the amine based preparations. Similar observations were made in studies on equally stabilized CdS sols prepared via H_2S gas exposure [12], where the effect of stabilizer on the cluster size was explained in terms of different complexing power of the ligands. Mercapto silane cadmium complexes seem to be stronger than amino silane ones yielding smaller particles. All three samples exhibit room temperature photoluminescence with a quantum yield of about 10%, the photoluminescence colour of mercapto sols being blue and that of monoamine sols being green-yellow. A band edge luminescence has not been detected in these samples.

The resulting optically transparent monoliths or films show generally very similar spectroscopic properties as the colloidal sols which can be explained by the ligand environment shielding effects from the matrix on the interface. Figure 3 shows optical absorption

spectra of a CdS and a CdS/PbS film prepared via single step dip coating procedure using diamine silane stabilized 0.8 M coating sols (gelation time of these sols was of about 2 hours).

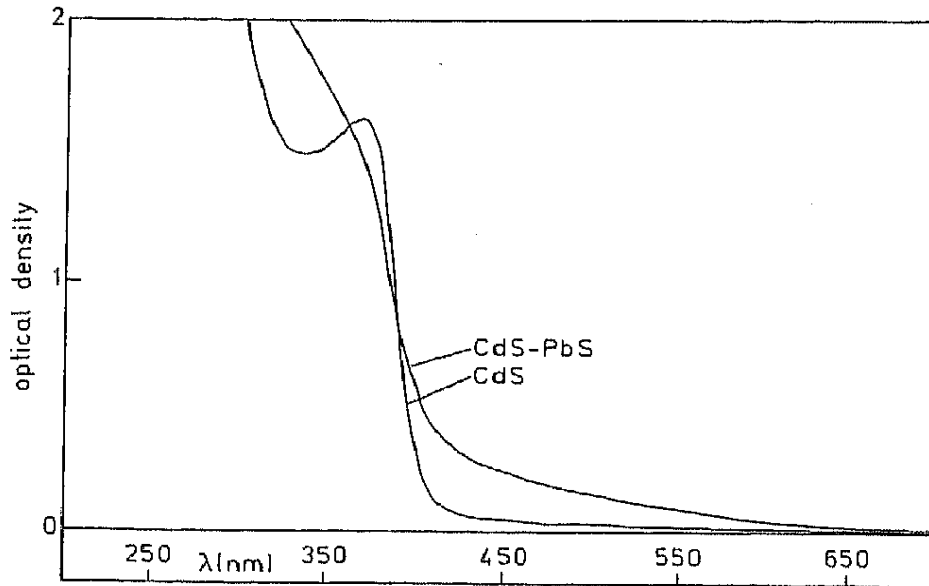


Figure 3. Optical absorption spectra of CdS and CdS/PbS films prepared via a single step dip coating procedure.

Both of the film samples are optically transparent. While the CdS films show a pronounced excitonic band at 370 nm, CdS/PbS films possess less structured spectrum with a smooth onset of absorption between 700 and 800 nm. The long wavelength tail above 400 nm reflects the presence of broadly distributed PbS clusters with an average size of 3 nm (the band edge in PbS bulk crystals is located at 2500 nm).

The unsupported CdS and CdS/PbS monoliths (with thicknesses between 100 and 200 μm and refractive indices of about 1.54) used for four-wave mixing experiments were cured in the molds employing a 0.1 M sol solutions (the gelation time of these sols was about 8 hours). The observed optical absorption spectra were identical to those shown in Figure 3.

Figure 4 depicts results from a self-diffraction experiment using ns laser-induced gratings on a 200 μm thick CdS/PbS sample.

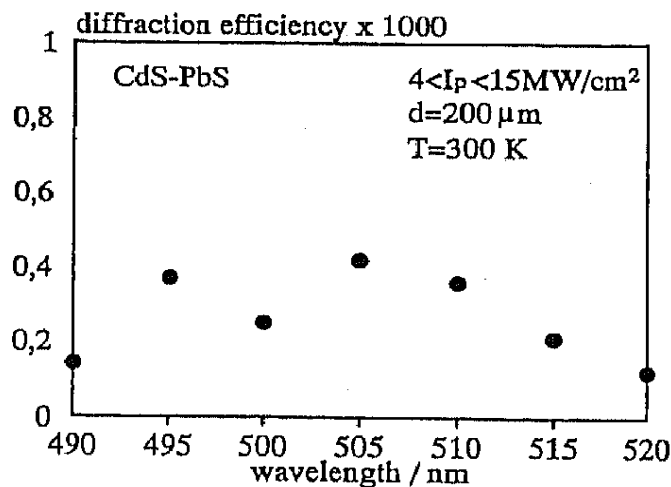


Figure 4. Spectral dependence of the grating efficiency from LIG experiments on unsupported 200 μm thick CdS/PbS monolith samples.

The spectral dependence of the grating efficiency η ($= I_1/I_0$) exhibits a flat maximum around 505 nm, not seen in the optical absorption spectra. Since the transmission T of the investigated sample differs only by 5% within this wavelength range ($T_{490} = 0.588$ and $T_{520} = 0.562$) and the pump light intensity decreases below and above 505 nm, the observed spectral dependence can be interpreted in terms of an increase in the grating efficiency with increasing intensity of the pump light. The grating constant f has been determined to be 20 μm which corresponds to the diffraction at a thin grating $d \ll f^2/\lambda$ (d is the thickness of the sample and λ the experimental wavelength). Under thin grating conditions, an expression relating the first order diffraction efficiency to the effective third-order material susceptibility $\chi_{\text{eff}}^{(3)}$ is known [15] (4),

$$\chi_{\text{eff}}^{(3)} = -4\epsilon_0 c n^2 \lambda \alpha \eta^{0.5} / 3\pi I_p (1-T) T^{0.5} \quad (4)$$

where c is the speed of light, ϵ_0 is the permittivity of free space, n is the refractive index, α is the absorption coefficient, and I_p is the input pulse intensity.

For the grating efficiency maximum and an α value of about 52/cm at 505 nm, a resonant $\chi_{\text{eff}}^{(3)}$ value of about $1.6 \cdot 10^{-9}$ esu has been calculated which is of the same order of magnitude as values determined on the commercial Schott glass OG 505 (CdSSe/ZnO doped borosilicate glasses) [16]. On CdS/diamine silane derived monoliths where resonant excitations occur outside the wavelength range of the above experiment, first order diffraction has not been seen. Results from investigations on larger CdS particles including an extension of the experimental wavelength range will be published elsewhere.

CONCLUSIONS

Inorganic-organic sol-gel processing of CdPbS nanocomposites has been presented. It has been shown that functionalized organoalkoxy silanes can be used as stabilizers, surface modifiers as well as sulfide source for synthesis of metal sulfide quantum dots. This opens up the possibility to synthesize highly concentrated sols for single-step coatings by excluding the handling of large amounts of H_2S gas and solvents. It further has been shown, that PbS containing monoliths possess third order non-linear optical properties as observed in preliminary laser-induced grating experiments. The measured grating efficiencies of about $0.1 - 0.5 \cdot 10^{-3}$ and the corresponding calculated $\chi_{\text{eff}}^{(3)}$ values ranging between 10^{-10} and 10^{-9} esu relate to PbS samples with missing excitonic bands (due to broad size distributions) and do not take reflection and scattering losses (due to imperfect flatness of the investigated monolith samples) into account. Further material synthesis optimization is the subject of our current work.

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