Preparation and Characterization of CdS Films Synthesized in Situ in Zirconia Sol−Gel Matrix

M. Zelner, H. Minti, and R. Reisfeld*

Department of Inorganic Chemistry, the Hebrew University, Jerusalem 91904, Israel

H. Cohen and R. Tenne

Departments of Chemical Services and Materials and Interfaces, Weizmann Institute, Rehovot 76100, Israel

Received April 22, 1997. Revised Manuscript Received July 24, 1997[⊗]

A new method for the synthesis of sol−gel films of zirconia-containing nanoparticles of CdS is demonstrated. The method consists of dip-coating of the substrate from a preprepared mother solution containing zirconia tetrapropoxide, cadmium acetate, and ammonium thiocyanate and subsequent annealing of the dried film at elevated temperatures. The films were characterized by optical absorption spectra, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The satellite spectrum of the Cd core levels was analyzed, and thereby the plasmonic structure of the film was resolved. The potential of the process for the fabrication of a class of sol−gel films with semiconductor nanoparticles having optical quality is discussed.

Introduction

The synthesis of nanoparticles of II−VI compounds, which exhibit a quantum size effect, has attained a great deal of attention over the past few years.[1−8] Incorporation of nanoparticles in sol−gel glasses has been demonstrated.[9−11] Transparent sol−gel glasses with optical-quality surface finish are an ideally suited matrix for hosting dyes and chromophores which can serve in nonlinear optical devices. The incorporation of CdS into silica films prepared by the sol−gel method has been reported before.[12−14] Preparation of zirconia and zirconia−ORMOSIL planar waveguides have been reported recently.[15]

In the present paper, a new in situ method for the preparation of CdS nanoparticles in zirconia sol−gel film is described. In this technique, cadmium and sulfur precursors are inserted into a sol prepared by hydrolysis of zirconia tetrapropoxide solution in *n*-propanol. Afterward the glass was dipped into the mother solution containing the ingredients of CdS, and the sample was made to react at elevated temperatures. The reaction leads to the formation of small CdS nanoparticles (ca. 40−70 nm) embedded within the zirconia sol−gel film. The film is deep yellow and translucent, which alludes to its optical quality.

Preparation of the Films

The films were prepared by dipping microscope glass slides into the mother solution (described below) and heat treated to complete the reaction between cadmium and sulfur. Preparation of samples with zirconia film doped by CdS nanoparticles consisted of three steps: preparation of mother solution, film deposition, and heat treatment.

1. Preparation of the Mother Solution. *Preparation of the Zirconia Solution (**1**).* Glacial acetic acid (3 mL) was slowly added to 10 mL of zirconia tetrapropoxide ($Zr(OC_3H_7)_4$, TPOZ) and stirred for 30 min. Then 20 mL of *n*-propanol (C_3H_7OH) was added to the solution, which was further stirred for 15 min at room temperature. The solution was hydrolyzed with 4 mL of 50% diluted solution of acetic acid in deionized water. Following this step, the solution was stirred for another

* Holding Enrique Berman Chair of Solar Energy. Member of Farkas Center for light-induced process. Author for correspondence.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

(1) Reisfeld, R. New Materials for Non-Linear Optics in Optical and Electronic Phenomena in Sol−Gel Glasses and Modern Application. *Struct. Bonding* **1996**, *85*, 99−147.

(2) Ekimov, A. I.; Al Efros, L.; Onuschenko, A. A. *Solid State Commun.* **1981**, *56*, 921.

(3) Hodes, G.; Albu-Yaron, A.; Decker, F.; Motisuke, P. *Phys. Rev. B* **1989**, *36*, 4215.

(4) (a) Zhao, X. K.; Fendler, J. H. *Langmuir* **1991**, *7*, 520. (b) Zhao, X. K.; McCormick, L. D.; Fendler, J. H. *Langmuir* **1991**, *7*, 1255.

(5) Weller, H. *Angew. Chem., Int. Ed.* **1993**, *32*, 41.

(6) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.

(7) (a) Routkevitch, D.; Bigioni, T.; Moskovitch, M.; Xu, J. M. *J. Phys. Chem.* **1996**, *100*, 14037. (b) Rotkevitch, D.; Tager, A. A.; Haruyama, J.; Almawlawi, D.; Moskovits, M.; Xu, J. M. *IEEE Trans. Ed.* **1996**, *43*, 1646.

(8) Petti, C.; Jain, T. K.; Billoudet, F.; Pileni, M. P. *Langmuir* **1994**, *10*, 4446.

(9) Minti, H.; Eyal, M.; Reisfeld, R. *Chem. Phys. Lett.* **1991**, *183*, 277.

(10) Atta, A. K.; Biswas, P. K.; Ganguli, D. CdS nanoparticles in gel film network: synthesis, stability and properties. In *Polymer and Other Advanced Materials: Emerging Technologies and Business Opportunities*; Prasad, P. N., Mark, J. E., Fai, T. J., Eds.; Plenum Press: New York, 1995; pp 645−651.

(11) Sanchez, C.; Livage, J. *Neuv. J. Chem.* **1990**, *14*, 513.

(12) Reisfeld, R. *Nanoparticles in Amorphous Solids and Their Nonlinear Properties, Advances and Applications*; Di Bartolo, B., Ed.; NATO ASI Series B Physics; Plenum: New York, 1994; Vol. 399, pp 491−529.

(13) Reisfeld, R. Nanoparticles in Amorphous Solids. In *Advanced Materials in Optics Electrooptics and Communication Technologies*; Vincenzini, P., Righini, R. G., Eds.; Proceedings of Topical Symposium VII on Advanced Materials in Optics and Communication Technologies; *Techna* **1995**, 3−13.

(14) Spanhel, L.; Arpac, E.; Schmidt, H. *J. Non-Cryst. Solids* **1992**, *147* and *148*, 657.

(15) Sorek, Y.; Zevin, M.; Reisfeld, R.; Hurvits, T.; Rushin, S. *Chem. Mater.* **1997**, *9*, 670.

S0897-4756(97)00245-7 CCC: $14.00

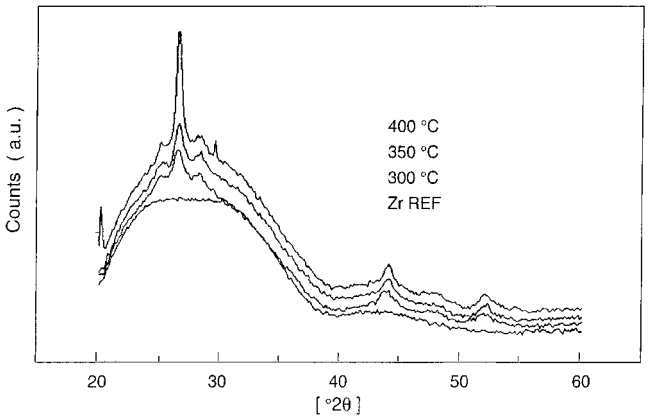

Figure 1.

30 min at room temperature, filtered, and stored in a refrigerator for up to 4 days. The solution is transparent, and its color pale yellow.

*Preparation of the Cd Acetate Precursor Solution (**2**).* Cadmium acetate was dried at 80 °C until its weight became constant. Dried Cadmium acetate ($Cd(CH_3COO)_2$, 1.6 g) was dissolved in 20 mL of boiling *n*-propanol (97.2 °C). Subsequently, the solution was stirred for 15 min. The solution was filtered and stored in a refrigerator for up to 4 days. The solution is transparent and colorless.

*Preparation of the Thiocyanate Solution (**3**).* Ammonium thiocyanate (NH_4CNS, 20 g) was dissolved in 100 mL of *n*-propanol by intensive stirring with magnetic bar on a hot plate heated to 80 °C and cooled to room temperature. The solution is transparent and colorless.

*Preparation of the Mother Solution (**4**).* Solution **2** was added drop by drop into the zirconia tetrapropoxide hydrolyzed solution **1** and the mixture was stirred for 30 min. Finally, 5 mL of the thiocyanate solution **3** was added drop by drop, and the solution was stirred for 30 min. An excess of sulfur up to 20% is needed in order to bring the reaction to completion. The mother solution served for the preparation of the sol−gel film by dip-coating. The solution is transparent and pale yellow.

2. Film Deposition. Standard glass slides were precleaned in carbon tetrachloride at 76.7 °C (boiling temperature) for 15 min. Sol−gel films were obtained by dip-coating from the mother solution. Coated samples were dried at 40 °C for 30 min.

3. Heat Treatment of Samples. Samples were treated at temperatures between 300 and 400 °C for 10 min. Before the heat treatment, films were transparent and colorless. After the treatment they became deep yellow.

Results and Discussion

Nanocrystals of CdS and their crystal modification were identified by X-ray powder diffraction (XRD). Reference sample of ZrO_2 film was used to eliminate peaks belonging to the matrix background. Figure 1 shows XRD spectra of various CdS films which were formed under somewhat different annealing conditions. At the temperature range 300−400 °C, the hexagonal form was predominant. The strongest peak at about 26.5° can be assigned equally to the hexagonal as well as to the cubic form. The average size of the crystallites was determined using the Debye−Scherrer formula and

Table 1. Some Characterizations of CdS-Doped Zirconia Film

temp (°C)	calcd size (Å)	inflection point (nm)	structure
300	43.6	486	hexagonal
350	50.6	502	hexagonal
400	72.1	504	hexagonal

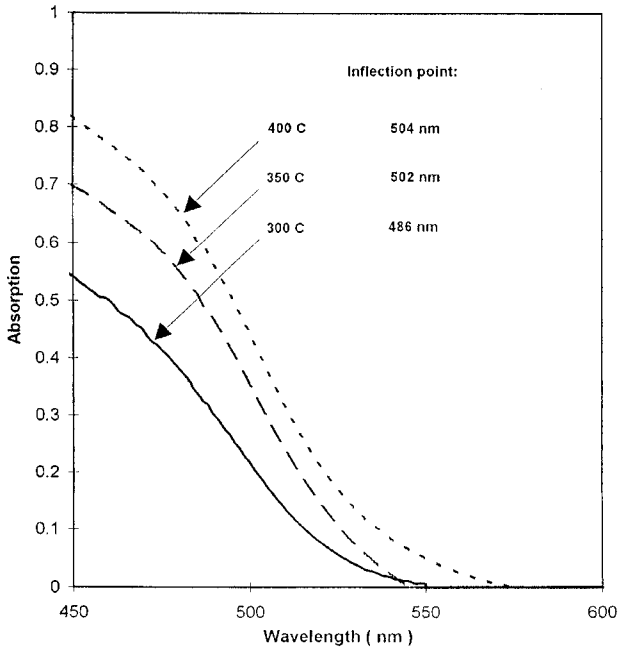

Figure 2.

is shown in Table 1. In the following paper we shall extend our studies to measurements using the TEM in order to define exactly the particles size distribution.

Figure 2 shows the optical absorption spectra of films which were annealed at 300, 350, and 400 °C. As the annealing temperature increases, the long-wavelength edge shifts to the red and the slope of the absorption curve becomes more steep. This observation alludes to the gradual crystallization of the CdS nanocrystallites. A modest blue-shift (ca. 20−30 nm) of the absorption edge relative to that of bulk CdS film[16] (520 nm) is observed.

Detailed X-ray photoelectron spectroscopy (XPS) analysis of the films was undertaken. The Cd 3d (405.1 and 411.8 eV) and 4d (11 eV) lines and the S 2p lines (161.5 and 162.7 eV) were well behaved. An excess sulfur of 15−20% in the film was estimated from the XPS semiquantitative analysis. This excess coincides with the sulfur excess in the mother solution. Deconvolution of the S 3p line revealed only one kind of sulfur atoms, indicating that the excess sulfur remained chemically bound, though not as an oxide, after the annealing. A large amount of carbon was found at the film surface. Chlorine and sodium contamination was evident as well, but not in large percentages. The good quality of the CdS film could be also inferred from the results of the photoelectron spectra of the valence band and from the plasmonic satellites of the Cd core levels of the films which are described below. The concentration of the components in the CdS-doped zirconia film before and after removing the upper surface (100 Å) by bombarding the surface with Ar^+ ions are presented in Table 2.

(16) Eychmüller, A.; Hasselbarth, A.; Katsikas, L.; Weller, H. *Ber. Bunsen-Ges. Phys. Chem.* **1991**, *95*, 79.

Table 2. Concentration of the Components in CdS-Doped Zirconia Film

peak	at. % concentrated before sputter	at. % concentrated after sputter	mass % concentrated before sputter	mass % after sputter
Zr 3d	3.47	10.75	8.11	18.79
Cd 3d	18.51	24.52	53.08	52.64
S 2p	23.76	29.31	19.54	18.03
O 1s	16.73	24.08	6.86	7.38

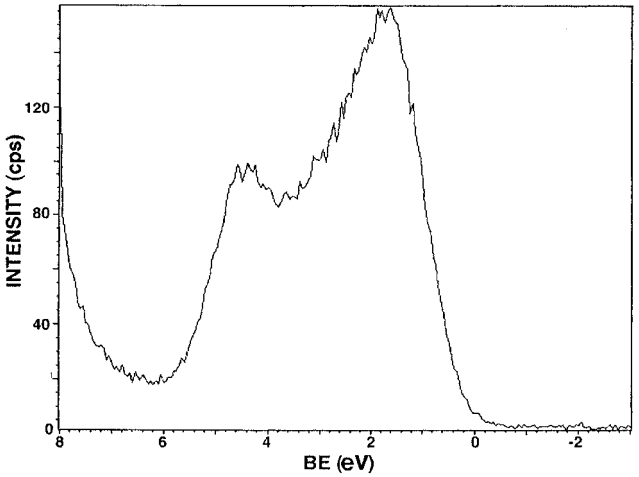

Figure 3.

Note that the oxygen concentration is appreciably higher than twice the zirconium concentration at the film surface. However, after very short Ar^+ sputtering, the composition of the zirconium oxide becomes almost stoichiometric. Table 2 also shows clear out-diffusion of some of the CdS to the top surface, during annealing.

The XPS valence-band analysis is shown in Figure 3. This spectrum is very similar to the published valence band spectrum of single-crystal CdS.[17]

An additional way to characterize the crystalline structure of the films is through plasmonic satellites of the core XPS lines.[18] This kind of analysis is equivalent to electron energy loss spectroscopy (EELS); however, X-ray is used as the excitation source of the sample in these kind of experiments, rather that electron beam. The two most typical plasmons, which can be excited in a solid, are the bulk (19 eV for CdS) and surface plasmons, the latter with a typical energy of about two-thirds of the bulk plasmon (12 eV for CdS).[19] In the case of the present CdS film, the plasmonic satellites of Cd 3d and Cd 4d lines were used for the analysis. A well-resolved plasmon satellite spectrum is indicative of a high degree of a crystalline order and crystallites exceeding 10 nm in size. For crystallites smaller than 10 nm, the dispersion in the momentum of the plasmon excitations leads to highly convoluted spectrum, and the peaks cannot be easily distinguished. Furthermore, the core level of the Cd (3d) consists of a doublet 5/2 and 3/2 lines which are separated by 6.7 eV. Therefore the plasmon loss spectrum of Cd 3d line is more complex than that of the Cd 4d core line.

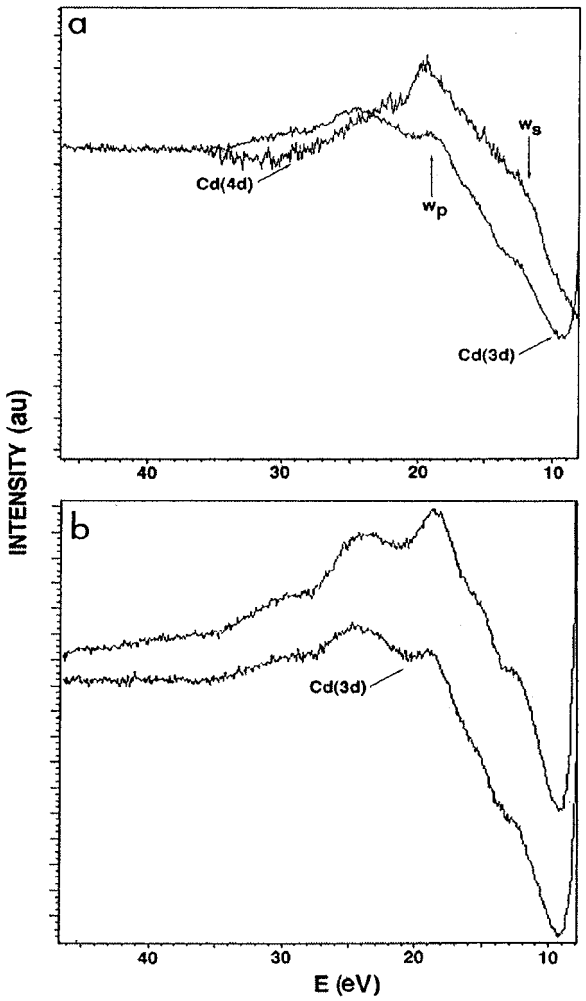

Figure 4.

Figure 4a shows the plasmon loss spectrum of Cd 3d and Cd 4d lines of the film, whereas Figure 4b shows the plasmon loss spectrum of the Cd 3d core level of a single-crystal CdS as is (lower curve) and after a short sputtering aimed at cleaning the crystal surface (upper curve). The good quality of the CdS film can be appreciated from the similarity between the Cd 3d spectra of the film (Figure 4a) and that of the single crystal (lower curve of Figure 4b). Obviously, the plasmonic peaks can be more easily resolved after a short cleaning of the semiconductor surface (compare the lower and upper curves of Figure 4b).

These results clearly show that optical-quality CdS films can be obtained by the sol−gel technique. The mechanism of the process includes slight inter- (out)-diffusion of both Cd and S atoms in the sol−gel zirconia matrix; chemical reaction and crystallization. Further research is necessary for the determination of the exact reaction mechanism. Refining the present method will lead to a synthesis of smaller particles of various II−VI compounds which will reveal strong quantum-size effects and nonlinear optical phenomena.

Acknowledgment. We are grateful for the Israeli Ministry of Science for the support of this research.

CM970245J

(17) Functional Relationships in Science and Technology. *Landolt-Bornstein*; Springer-Verlag: Berlin, 1982; Vol. 17b III, p 409.

(18) Practical Surface Analysis, 2nd ed.; Briggs, D., Seah, M. P.; John Wiley & Sons: New York, 1990; Vol. 1, p 106.

(19) Hengehold, R. L.; Pedrotti, F. L. *Phys. Rev. B* **1972**, *6*, 2262.