

The photoluminescent properties of CdS clusters of different size in porous glasses

E. RYSIAKIEWICZ-PASEK¹, J. POLAŃSKA¹, S.A. GEVELYUK²,
I.K. DOYCHO², V.T. MAK², S.A. ZHUKOV³

¹Institute of Physics, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27,
50-370 Wrocław, Poland

²Non-Crystalline Media Department, Odessa National University, 42 Paster-St., Odessa 65023, Ukraine

³Institute of Physics, Odessa National University, 42 Paster-St., Odessa 65023, Ukraine

CdS nanoclusters were formed in the porous glass matrix by sequential chemical deposition from liquid-vapor phase and their chemical content was investigated. The room temperature photoluminescence spectra of specimens excited with a 235 nm wavelength had typical narrow peaks at 400 nm. The peaks can be explained by quantum effects for charge carriers confined inside the small-size (radius of the order of several nanometers) clusters. At the same time the luminescence spectra of the same specimens, but excited with a xenon lamp at 77 K, had peaks at ~700 nm that approximately corresponded to the band gap of the crystalline CdS. The possibility of the crystallites existence follows from the size distribution of voids in the porous glass matrix and is confirmed by the X-ray spectra typical of the wurtzite structure. The peculiarities of the observed luminescence spectra are explained by the energetic diagram of CdS in the configurational space.

Keywords: porous glass, photoluminescence, CdS nanoclusters.

1. Introduction

This paper is a research of an opportunity to use porous silicate glasses as the model media for creation of semiconductor nano-clusters having specified sizes. The choice of a silicate porous glass as a matrix for impregnation by semiconductor clusters follows from the high-disperse distribution of interconnected pores typical of this material, in contrast to polymers [1] and gelatin [2]. The sizes of voids in silica porous glasses vary from several nanometers up to hundred nanometers, so that the sizes of formed semiconductor clusters are in the same limits.

It is necessary to distinguish the cases when the given chemical element initially exists in the glass matrix or it is introduced by an appropriate treatment. In the first case it is possible to create the clusters by a suitable processing of the matrix. As

the porous glass represents almost pure silicon dioxide, it is possible to create silicon clusters inside the pores by the so-called carbon processing [3, 4]. Nevertheless, other types of semiconductor inclusions are promising for practical applications, as well. New properties are expected for CdS nanoclusters having a different from silicon crystalline energetic structure [5–7].

2. Experimental procedure

Porous glasses of type β and δ , received from biphasic sodium-boron-silica glasses by chemical etching of the sodium-boron phase [8] with subsequent removal of secondary silica gel were used as a model media. The β -glasses contain small pores, while the δ -glasses contain only larger ones due to the absence of silica gel. Thus, there is a lot of place for forming clusters inside the pores of δ -glasses.

Differences in morphology of the used glasses were registered by absorption-desorption poroscopy. Water molecules having small sizes and capable to penetrate into the finest pores of the matrix were used as an adsorbent.

CdS clusters were formed inside the porous glass matrix by the chemical deposition from the liquid-gas phase [9]. Relatively small concentrations of the reactant were used not to allow the CdS film formed at the surfaces of pores to clog up the pore entrances. The sample was exposed to the deposition procedure several times. The changes of its properties were investigated after three treatments and after eight ones. The EDS technique was used for studying the elemental content of processed samples and investigating of CdS particles distribution in the specimen depth. The structure of particles was analyzed with the X'PERT X-ray diffractometer. The photoluminescence spectra were recorded using a Perkin-Elmer LS luminescence spectrometer at room temperature, and by excitation from various radiation sources (such as a 337 nm UV-laser and a 1 kW power xenon lamp) at 77 K.

In order to remove the adsorbed water, all samples were heated at 150 °C for 0.5 h prior to the measurements.

3. Results

Figure 1 shows the pore-size distributions for β - and δ -glasses. It is clear that there are mainly pores with the radius of about 15 nm in β -glasses and besides there are some pores with radii about 45 and 75 nm. For δ -glass, most pores have radius of about 50 nm though there is a significant number of pores with radii of 25 and 75 nm. A certain amount of fine pores having the radius of about 10 nm is typical of δ -glass as well. The analyses of the pore distribution in the range of big pores show that for δ -glass it is possible to detect pores of 80, 100, 125 and even 140 nm sizes.

The chemical analyses of the obtained clusters by EDS technique [9] show the presence of cadmium and sulfur in almost equal amounts both after the three treatments, and after the eight treatments. From the energetic considerations this

result confirms the fact that the CdS clusters were really formed inside the pores. The investigation of the CdS particle distribution as a function of depth from the specimen surface demonstrated a sufficient homogeneity of this distribution.

X-ray measurements [9] revealed a spectrum, typical of the wurtzite structure, superimposed with a peak at 23° , which is according to [10, 11] related to the silicate porous matrix. It is interesting to note that the discussed spectrum is registered only for glasses subjected to the eightfold treatment, when the size of the formed particles is sufficient for observation of the diffraction pattern.

Photoluminescence measurements with 235 nm wavelength excitation gave a number of peaks. Figure 2 shows these spectra for CdS nanoparticles in β -glass, and Fig. 3 shows similar results for the δ -glass. After the increase in the amount of treatments for the same type of samples, some peaks are shifted to the red side, some

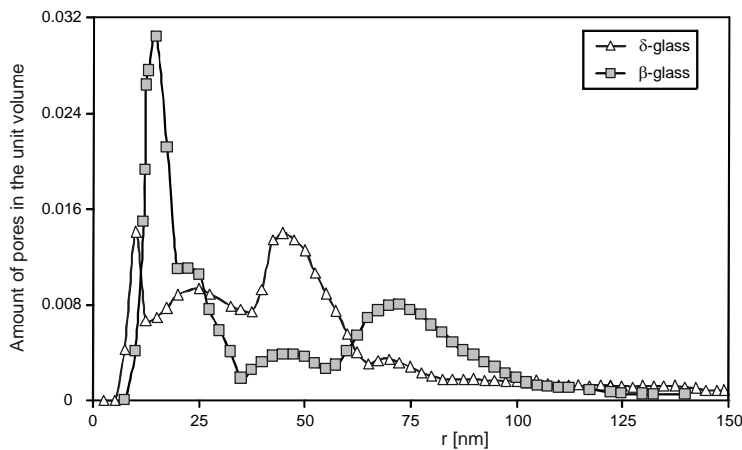


Fig. 1. Pore-size distributions for β - and δ -glasses.

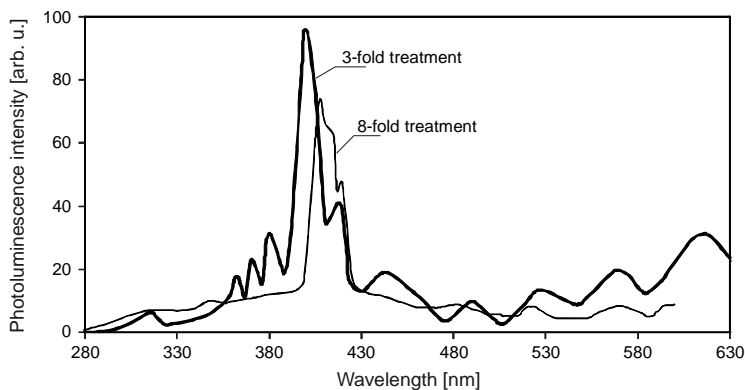


Fig. 2. Photoluminescence spectra of β -glass embedded with CdS (235 nm excitation wavelength).

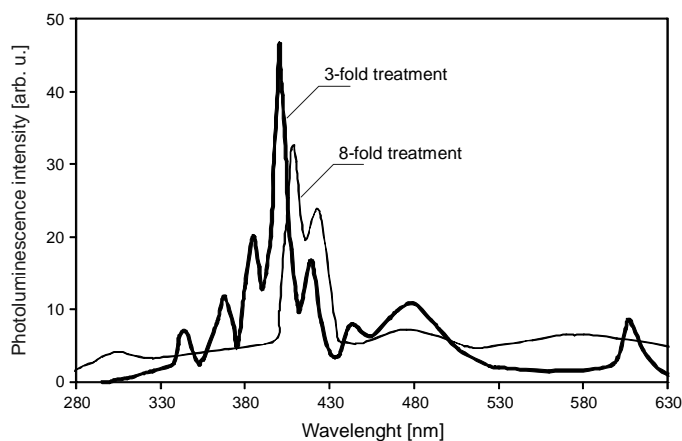


Fig. 3. Photoluminescence spectra of δ -glass embedded with CdS (235 nm excitation wavelength).

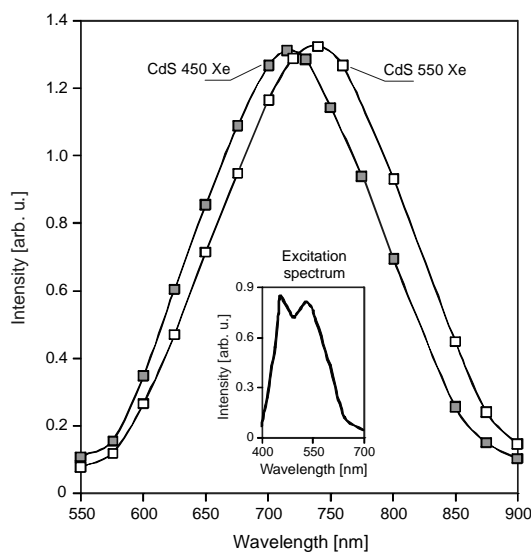


Fig. 4. Photoluminescence spectra of δ -glass embedded with CdS at 77 K (excitation with a xenon lamp). The inset shows the excitation spectrum.

peaks move into the violet directions, and some peaks disappear at all. This is consistent with quantum confinement effects, typical of small nanoparticles.

To investigate the contribution of big clusters into the photoluminescence, we changed the excitation source. Excitation of samples with the wavelength of 337 nm from the ultraviolet laser both at room temperature, and at 77 K did not result in the occurrence of photoluminescence. Excitation with 1 kW power xenon lamp at 77 K in the wavelength range of 450–550 nm allowed to register a photoluminescence peak at approximately 700–750 nm for the 8-fold processed sample (Fig. 4).

4. Discussion

The wurtzite structure is defined by the third coordination sphere: its atoms should be disposed so that the dihedral angle is equal to zero (the so-called shielded configuration). Thus this configuration should be repeated, at least ten times, to obtain the relevant reflexes at the X-ray pattern. So, the X-ray pattern obtained in [9] testifies that the clusters consisting of at least 40 coordination spheres (*i.e.*, their sizes are about 50 Å) are formed after the 8-fold treatments. Such clusters actually are large crystallites (the quantum confinement effect is negligible for them) [12]. After the 3-fold treatments, the clusters are too small, and the long-range order structure does not yet exist.

It is necessary to emphasize that there are both big and small pores inside both types of glasses (Fig. 1). The size of nanoformations is restricted to pore-sizes in the small pores and to a smaller degree depends on the number of treatments. Hence, while after the 3-fold treatments, the small clusters are formed both in big pores and in small ones, and after the 8-fold treatments clusters inside large pores can grow up to the sizes of relatively large crystals, thus explaining the results of X-ray investigations.

The quantum confinement effect predicts the shift of the peak, relevant to the edge luminescence, in the direction of short waves for the three-fold processing. For the 8-fold processing, the edge luminescence can almost coincide with that typical of bulk crystals.

The photoluminescence excitation spectrum for the studied specimens shows the in-turn role of nanoclusters of different sizes. Excitation photoluminescence with the 235 nm wavelength allows to register the sets of peaks (Figs. 2 and 3). The shift of some peaks to the red range of spectrum, and others to the violet range after an increase in the number of treatments for the same type of samples allows to understand the nature of different peaks. It is clear that semiconductor clusters formed after the 3-fold processing have smaller sizes than after the 8-fold processing. According to [13], the peak which is relevant to the edge luminescence should be shifted to the red range with the increase in the cluster sizes, while the peaks relevant to cluster surface defects should be shifted into the violet range: the surface of a big cluster is smaller than for several small ones with the same volume. Besides, the defects at the cluster surface tend to healing as the cluster size increases.

The figures show that the peak located approximately at 400 nm shifts into the red range of spectrum. Thus, this peak can be connected with the edge luminescence of small CdS nanoclusters. The triplet, shifted from this peak to the short-wave range, disappears after an increase in the number of treatments for both matrixes. This is typical of the exciton nature of peaks [14]. Other peaks are shifted into the violet range of spectrum and lose their intensity after an increase in the number of treatments. This is consistent with surface defects, as it was mentioned above. The luminescence connected with surface traps is due to the recombination of electrons trapped by sulfur vacancies and valence band holes inside the CdS nanoparticles [10].

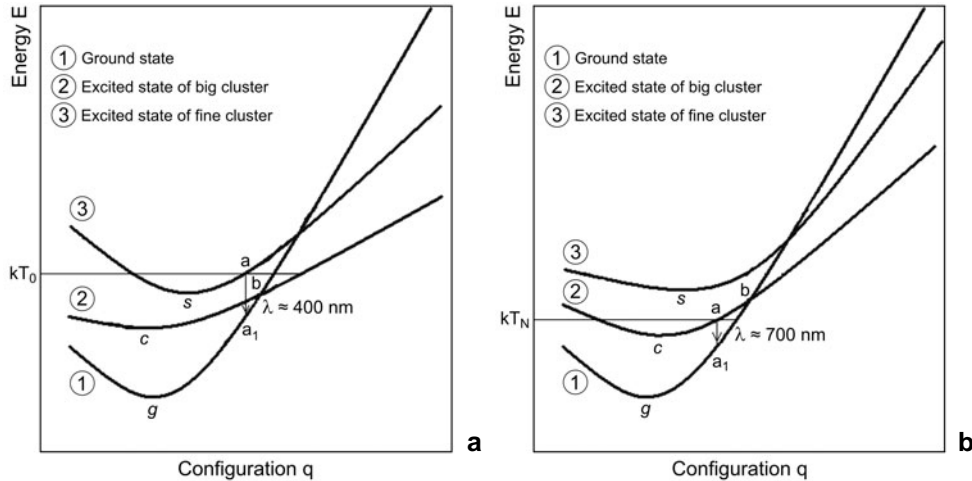


Fig. 5. Configuration diagram explaining the recombination processes in the porous glass matrix embedded with CdS.

The essential difference of luminescence spectra of the nanoclusters in δ -glass is their almost twice-smaller intensity in comparison with β -glass. This difference testifies that, though the volume of intraporous space is bigger for δ -glass, there are fewer pores with small diameter in this type of glasses (Fig. 1). Hence, the fine CdS-clusters, contributing to the luminescence intensity, are present to lesser extent. The big clusters, confirmed by the X-ray researches, do not contribute to the luminescence of both matrix types when excitation is by the 235 nm wavelength: apparently, the carriers in them recombine non-radiatively.

Nevertheless, contribution of large clusters to the photoluminescence spectrum is observed with excitation by a xenon lamp at nitrogen temperature. The photoluminescence peak at approximately 700–750 nm for the 8-fold processed sample (Fig. 4) almost corresponds to the edge luminescence of bulk CdS. The absence of photoluminescence for a sample after the 3-fold processing under the same conditions confirms the determining role of big crystallites for the occurrence of this specific peak.

It is possible to explain the observed effects with the help of a simple model in the configurational space (Fig. 5). The **a**-part of the figure corresponds to excitation by the ultra-violet laser. Different curves correspond to big clusters and small ones (curves 2 and 3, respectively). At room temperature T_0 , the excited carriers in the small clusters transfer into the ground state (curve 1) with the emission of light quantum with the wavelength $\approx 400 \text{ nm}$, while the carriers in the large clusters recombine non-radiatively (through the point *b* that shows intersection with the curve corresponding to the ground state). The **b**-part of Fig. 5, corresponding to smaller excitation quanta from the xenon lamp, illustrates the opposite effect: at nitrogen

temperature T_N , the excited carriers in big clusters transfer into the ground state with emission of light quanta having ≈ 700 nm wavelength, whereas carriers in fine clusters are not excited at all. Thus, the point of intersection b of the curve 2 with the curve 1 corresponding to the ground state, always disposes energetically below the minimal energy of the fine cluster excited state s . Therefore, at any temperature the recombination mechanism will not change: the luminescence will originate either from big or from small clusters. Thus, in order to stimulate radiative recombination inside big clusters, it is necessary to excite by lower energy sources at low temperature.

5. Conclusions

The comparison of the photoluminescence spectra in porous glass matrices embedded with CdS nanocrystallites for different temperatures and various excitation energies allowed to distinguish the contribution of small nanoclusters and big crystallites.

The features of recombination in large CdS clusters and small nanoclusters are explained by a simple model in configurational space. The observed shift of the photoluminescence peaks for different excitation energies is well understood within the suggested model.

References

- [1] KHANNA R.K., GOKHALE R.R., SUBBARAO V.V.V.S., SINGH N., JUN K.-W., DAS B.K., *Synthesis and optical properties of CdS/PVA nanocomposites*, Materials Chemistry and Physics **94**(2–3), 2005, pp. 454–9.
- [2] SMYNTYNA V.A., SKOBEVA V.M., MALUSHIN N.V., POMOGAILO A.D., *Influence of matrix on photoluminescence of CdS nanocrystals*, Photoelectronics **15**, 2006, p. 38.
- [3] GEVELYUK S.A., DOYCHO I.K., KOVALENKO M.P., SAFRONSKY E.D., RYSIAKIEWICZ-PASEK E., ROIZIN Y.O., *Carbon treatment as a method of the surface development of porous glasses*, Optica Applicata **30**(4), 2000, pp. 635–40.
- [4] GEVELYUK S.A., DOYCHO I.K., PROKOPOVICH L.P., RYSIAKIEWICZ-PASEK E., SAFRONSKY E.D., *Influence of carbon multiple treatments on the photoelectrical properties of porous glasses*, Radiation Effects and Defects in Solids **158**(1–6), 2003, pp. 427–32.
- [5] LU S.G., YU Y.J., MAK C.L., WONG K.H., ZHANG L.Y., YAO X., *Nonlinear optical properties in CdS/silica nanocomposites*, Microelectronic Engineering **66**(1–4), 2003, pp. 171–9.
- [6] REISFELD R., *Nanosized semiconductor particles in glasses prepared by the sol-gel method: their optical properties and potential uses*, Journal of Alloys and Compounds **341**, 2002, pp. 56–61.
- [7] BRUS L.E., *Electron-electron and electron-hole interactions in small semiconductor crystallites: the size dependence of the lowest excited electronic state*, Journal of Chemical Physics **80**(9), 1984, pp. 4403–9.
- [8] MAZURIN O.V., ROSKOVA G.P., AVIERIANOV V.I., ANYTROPOVA T.V., *Dwukhfaznyje stiolka: struktura, svojstva, primienienie*, Nauka, Leningrad 1991.
- [9] RYSIAKIEWICZ-PASEK E., ZALEWSKA M., POLAŃSKA J., *Optical properties of CdS-doped porous glasses*, Optical Materials **30**(5), 2008, pp. 777–9.
- [10] PAN A.L., MA J.G., YAN X.Z., ZOU B.S., *The formation of CdS nanocrystals in silica gels by gamma-irradiation and their optical properties*, Journal of Physics: Condensed Matter **16**(18), 2004, pp. 3229–38.

- [11] LI J.J., WANG A., GUO W., KEAY J.C., MISHIMA T.D., JOHNSON M.B., PENG X., *Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction*, Journal of the American Chemical Society **125**(41), 2003, pp. 12567–75.
- [12] LIPPENS P.R., LANNOO M., *Calculation of the band gap for small CdS and ZnS crystallites*, Physical Review B: Condensed Matter **39**(15), 1989, pp. 10935–42.
- [13] LEI Y., CHIM W.K., SUN H.P., WIDE G., *Highly ordered CdS nanoparticle arrays on silicon substrates and photoluminescence properties*, Applied Physics Letters **86**(10), 2005, p. 103106.
- [14] WANG C.R., IP K.M., HARK S.K., LI Q., *Structure control of CdS nanobelts and their luminescence properties*, Journal of Applied Physics **97**(5), 2005, p. 54303.

*Received September 23, 2007
in revised form March 29, 2008*