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Optical Spectroscopy of Opal Matrices with CdS Embedded in its Pores: Quantum Confinement and Photonic Band Gap Effects (*).

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Summary. — The spectra of transmission and reflection of synthetic opal which has 3-dimensional periodic structure were measured at different orientations of incident beam relative to the sample facets. It is shown that opal behaves as «semi-metallic» photonic band gap (PBG) material in the vicinity of photon energy 2.3 eV. The synthesis of CdS microcrystals embedded in the pores of opal was made for the first time in an attempt to form a system of quantum dots. Optical spectra (reflection and transmission, photoluminescence and Raman scattering) were studied. The results demonstrate good crystallinity of microcrystals embedded in opal matrix and exhibit well-pronounced quantum confinement effects in fundamental edge absorption spectra. The spectral overlap of the PBG of opal with electronic band gap of many of II-VI semiconductors seems to make opal/semiconductor system a promising media for experimental studies of such PBG-related effects as inhibition of spontaneous emission, microcavity polariton, etc.

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Introduction.

The methods of nanostructure fabrication connected with filling of mesoporous dielectric matrices (asbestos, MCM-41, zeolites, etc.) with various semiconductors have been intensively studied during last years [1]. One of the new porous dielectric matrices is synthetic opal [2] with highly ordered three-dimensionally periodic

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structure (closely packed cubic lattice of equal-diameter silica spheres) simulating the structure of natural precious opals [3]. Besides the possibility of pores filling this matrix possesses interesting optical properties defined by 3-dimensional modulation of refractive index. The propagation of light in such periodically modulated dielectric media is described by band theory including the idea of photonic band gap (PBG) [4]. The light wave from the PBG spectral region does not propagate through medium but is totally reflected as a result of interference on periodic structure. The opal lattice constant is about 0.2–0.4 μm that allows to expect the PBG in visible region of spectra. It is interesting to note that the energy of band-to-band transitions in semiconductor microcrystals embedded in the pores can overlap with PBG region. It can lead to significant modification of light-matter interaction that is the subject of intensive studies because of possible applications in optoelectronics [5].

In the paper presented we report on the first attempt of synthesis of CdS microcrystals inside the pores of opal matrix. Optical properties of the system determined by dielectric matrix as well as by CdS microcrystals are studied.

1. – Samples.

The synthetic opals used in this study were fabricated from the suspension of equal-diameter silica spheres that after sedimentation form closely packed face-centred cubic structure with two types of empty cavities between the touching spheres. Voids of 0.4 D diameter (cavities of «octahedron» configuration) and of 0.2 D diameter («tetrahedron» configuration) are interconnected via bottle-neck channels. The pores of opal matrix were filled with CdS using vapour phase synthesis with subsequent annealing in Cd or S atmosphere. The samples were characterised by X-ray diffraction, small-angle X-ray scattering, scanning transmission electron microscopy (STEM) and Raman scattering. The typical STEM micrograph of one of the opal/CdS samples is shown in fig. 1 displaying the regular package of silica spheres with diameter $D \approx 200$ nm. The lattice constant is reduced in comparison with unfilled opal down to ≈ 160 nm due to intrusion of silica spheres into each other during CdS synthesis and subsequent annealing. The CdS microcrystals can be seen

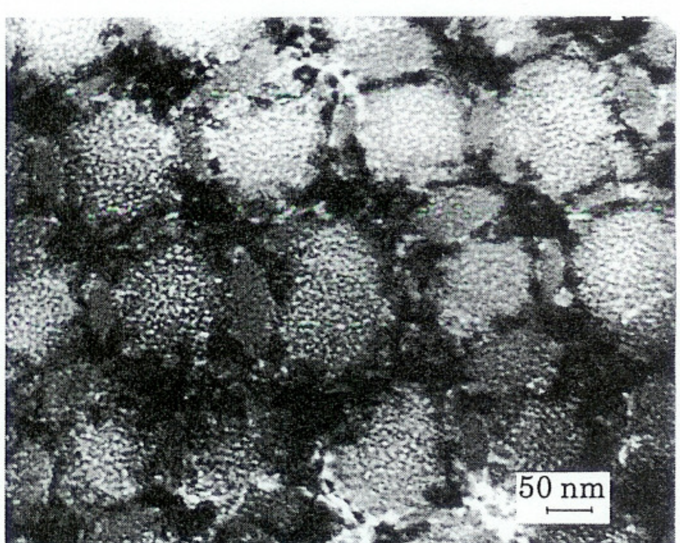

Fig. 1. – STEM micrograph of synthetic opal matrix filled with CdS.

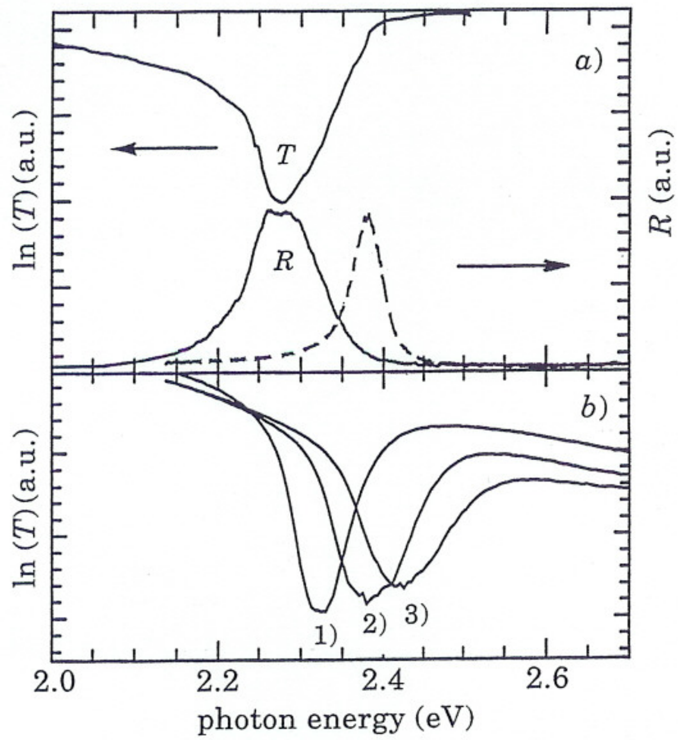

Fig. 2. – *a*) Transmission (T) and reflection (R) spectra of unfilled opal matrix measured at normal incidence. Reflection spectra were measured from the same facet as spectrum T (solid line) and from the perpendicular facet of the sample (dashed line). *b*) Transmission spectra measured at oblique incidence (spectra 1), 2), 3) correspond to the angles 5°, 15°, 30°).

as aggregates of dark grains decorating the spheres. The individual microcrystals can hardly be resolved that impedes the measurement of their sizes. However a crude estimate gives a value of the order of 10 nm. In Raman scattering spectra of opal/CdS the relatively narrow LO-phonon line was observed centred at the frequency (305.7 cm^{-1}) well corresponding to the bulk value that showed good crystallinity of semiconductor microcrystalites.

2. – Experiment and discussion.

2·1. *Photonic band gap effects defined by opal matrix.* – Transmission and reflection spectra of unfilled opal matrix are presented in fig. 2. In transmission spectrum measured at normal incidence on one of the sample facets (see spectrum T on fig. 2*a*)) the large drop can be clearly seen with minimum at 2.27 eV. In reflection spectra measured from the same facet at nearly normal incidence the intense line was observed (see spectrum R—solid line on fig. 2*a*)). The energy of its maximum and its width correspond well to those of the drop in transmission spectrum. A similar line was also observed in reflection spectrum taken from another facet of the sample perpendicular to the first one (see dashed line on fig. 2*a*)). Its spectral position is shifted from 2.27 eV to higher energies on the value comparable with the lines widths. The transmission spectra measured at oblique incidence (see spectra 1)-3) in fig. 2*b*)) showed that the drop undergoes an analogous shift also related with changing of the light propagation direction. It is interesting to note that the rotation of the sample by only 10–20° results in an increase of transmission at 2.27 eV by two orders of magnitude providing almost complete transparency.

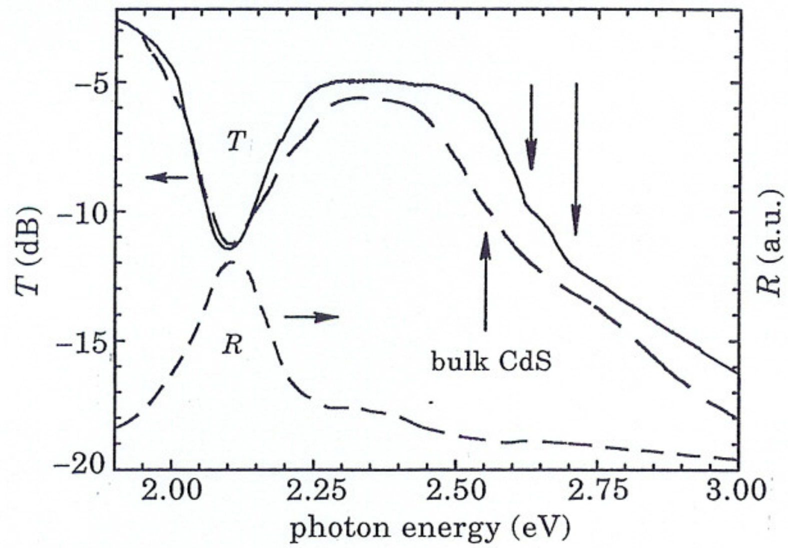

Fig. 3. – Transmission (T) and reflection (R) spectra of opal filled with CdS measured at normal incidence at $T = 2$ K (solid line) and $T = 300$ K (broken lines). Arrows show the excitonic transitions in CdS microcrystals.

The correlation of the spectral positions and the widths of peculiarities observed in transmission and reflection spectra taken at normal incidence shows that the attenuation of light in opal is defined not by absorption but by reflection due to interference of light on the grating formed by the periodic opal structure. This feature can be considered as photonic band gap [4] for a given light propagation directions (for corresponding photon wave vectors $\boldsymbol{k}$). The «valence» and «conduction» band edges of PBG can be defined as low-energy (≈ 2.2 eV in spectrum T of fig. 2a)) and high-energy edges (≈ 2.4 eV) of the drop in transmission spectra correspondingly. Thus the width of the band gap is about 10% of its central energy.

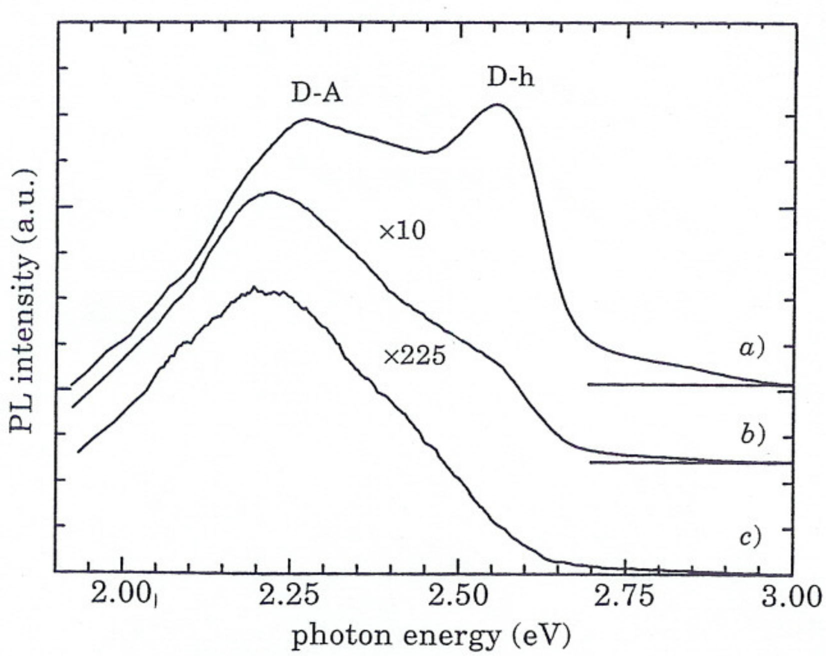

Fig. 4. – Photoluminescence spectra of opal/CdS measured as a function of time delay at $T =$ $= 2$ K under the pulsed excitation with N_2-laser. The time delay for spectra a), b), c) is 0, 50, 300 ns correspondingly.

The attenuation length $1/e$ within a PBG is of the order of 100 opal lattice constants. The shift of the PBG-related peculiarities in transmission and reflection spectra with changing of the propagation direction gives evidence on anisotropy of photonic band structure in reciprocal space. The fact that the magnitude of the shift is comparable to the spectral width of the observed peculiarities speaks well for energetic overlap of valence band in one section of the photonic Brillouin zone with conduction band in a different section of the Brillouin zone. Such «semi-metallic» photonic band structure is in agreement with the theoretical results [6] for face-centred cubic lattices with spherical «atoms» to which the opal structure belongs.

2·2. *Optical properties of* CdS *microcrystals embedded in the pores of opal.* – The transmission spectra of opal filled with CdS at energies below the absorption edge of the bulk CdS were found to be similar to that of unfilled opal. The PBG-related lines in transmission and reflection can be easily seen in fig. 3. The difference of the opal/CdS spectra from the spectra of unfilled opal consists in drastic decrease of transmission at the energies higher than the bulk absorption edge of CdS. This decrease is caused by absorption of light in CdS microcrystals that is confirmed by the blueshift (80 meV) of the absorption edge with decreasing temperature from 300 K to 2 K. At low temperature the well-defined oscillations in transmission spectrum at energies 2.62 eV and 2.71 eV (shown by the arrows on fig. 3) are observed. They can be attributed to excitonic transitions between the lowest quantum-confined electron and hole subbands h0,1-e0,1 (2.62 eV) and h1,1-e1,1 (2.71 eV). Average diameter of microcrystals calculated within the effective-mass approximation [7] was found to be about 6 nm.

The photoluminescence spectra of opal/CdS sample measured as a function of time delay at $T = 2$ K under the pulsed excitation with N_2-laser are shown on fig. 4. In spectra *a*) measured during the laser pulse ($\tau = 20$ ns) two broad lines can be seen with maxima at 2.57 eV and 2.27 eV. The measurements of luminescence decay kinetics showed the decay times $\tau \leqslant 20$ ns and $\tau \approx 150$ ns for the 2.57 eV line and 2.27 eV line correspondingly. Increasing of the delay time leads to the redshift of the low-energy line (see spectra *b*), *c*) in fig. 4). These observations allow to ascribe the lines to the impurity transitions: neutral donor-free hole D-h (2.57 eV) and donor-acceptor pair recombination D-A (2.27 eV). Note that observed peculiarities are similar to the PL properties of CdS microcrystals of analogous sizes in semiconductor-doped silicate glasses [8].

In conclusion it should be noted that the opportunity to fill the pores of opals with various semiconductors in principle opens the possibility to fabricate the material with photonic band gap in the energy range of near-edge radiative transitions in semiconductor microcrystals. It makes the synthetic opal a unique object for studying the theoretically predicted effects of light-matter interaction in 3-dimensional photonic crystal [5]: inhibition of spontaneous emission due to suppression of photonic density of states, formation of so-called cavity polaritons in photonic crystal with artificially introduced optical-impurity mode. In the samples studied only the low-energy tail of D-A recombination band is overlapped with PBG. However we believe that the task can be carried out by further technological efforts aimed at the choice of appropriate semiconductor as well as at the variation of opal photonic band structure due to changing of the spheres diameter, structure period and refractive index.

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REFERENCES

[1] Stucky G. D. and McDougall J. E., *Science*, 247 (1990) 669.
[2] Bogomolov V. N., Kumzerov Y. A., Romanov S. G. and Shuravlev V. V., *Physica C*, 208 (1993) 371.
[3] Sanders J. V., *Nature*, 204 (1964) 1151.
[4] Yablonovitch E., *Phys. Rev. Lett.*, 58 (1987) 2059; John S., *Phys. Rev. Lett.*, 58 (1987) 2486.
[5] For a review see Yablonovitch E., *J. Mod. Opt.*, 41 (1994) 2, 173 and references cited therein.
[6] Sözuer H. S., Haus J. W. and Inguva R., *Phys. Rev. B*, 45 (1992) 13962.
[7] Ekimov A. I. and Efros Al. L., in *Laser Optics of Condensed Matter* (Plenum Press, New York, N.Y.) 1988, p. 199.
[8] Ekimov A. I., Kudryavtsev I. A., Ivanov M. G. and Efros Al. L., *J. Lumin.*, 46 (1990) 83.