FORMATION OF NANO-STRUCTURED CdSe COMPOSITES IN POROUS SiO$_x$ LAYERS

YU.YU. BACHERIKOV, I.Z. INDUTNYI, I.YU. MAIDANCHUK, O.B. OKHRIMENKO, S.V. OPTASYUK, P.YE. SHEPELIAVYI

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V.E. Lashkaryov Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine
(45, Nauky Ave., Kyiv 03028, Ukraine; e-mail: yuyu@isp.kiev.ua)

A possibility to fabricate nanocomposite structures using various techniques–in particular, the implantation of CdSe nanoparticles into a por-SiO$_x$ matrix and the formation of CdSe nanoparticles in a por-SiO$_x$ matrix as a result of the chemical deposition–has been studied. The deposition of CdSe nanoparticles was shown to result in the formation of several fractions of nanoparticles in the porous near-surface layer Si–SiO$_x$, with nanoparticle dimensions being about 1.2 and 2.5 nm for their deposition from a colloid solution, and about 1.9 and 2.3 nm at the chemical deposition. The properties of nano-structured composites obtained by those two methods are found to be controllable by varying the regimes of additional treatments and the time of nanoparticle synthesis, respectively.

1. Introduction

The study of properties of substances composed of nanosized particles, as well as the working out of principles for the creation of nano-structured media on their basis, is a challenging direction of modern physics. Among nano-structured materials, of special interest are nanocomposites which are fabricated by inserting nanoparticles into a porous matrix made of a different substance. Those matrices can be either inert with respect to nanoparticles of a different material or capable to modify the properties of inserted nanoparticles. Nowadays, there are technologies that allow nano-structured compounds to be produced in various matrices which differ from one another by dimensions and topologies of their pores. Among matrix materials which are used for the creation of more complicated structures, it is necessary to distinguish porous semiconductors and insulators which are fabricated by removing some part of a material from the occupied volume or which are grown under special conditions [1]. The electric and optic properties of the structures formed in such a way can vary depending on the technique of initial material treatment [1]. The major factor that determines whether such nano-structured materials can be created or not is a size consistency between nanoobjects inserted into the matrix and separate structural elements of the nano-structured matrix; it is so owing to a confined geometry of a matrix volume (a pore), into which such nanoobjects are inserted.

The simplicity of the nano-structured matrix fabrication technique and a possibility to control the properties of given matrices by changing the regime of their formation make such substrates rather convenient objects for studying the physical phenomena that occur in nano-structured media. One of the methods for the fabrication of porous layers with given characteristics is the deposition of a substance in vacuum onto a substrate which is oriented at a definite angle with respect to the flux of the evaporated substance [2, 3]. In particular, with the help of such an oblique angle deposition of silicon monooxide (SiO), one can form porous layers of SiO$_x$ characterized by the given thickness and porosity [4].

This work aimed at studying the modifications of CdSe nanocrystals produced by different methods of nanoparticle deposition onto porous SiO$_x$ layers by examining their radiation characteristics.

2. Experimental Technique

CdSe nanocrystals were synthesized using a chemical method [5]. In this method, sodium selenosulphate Na$_2$SeSO$_3$ served as a source of Se^{2-} ions, and cadmium nitriletriacetate as a source of Cd^{2+} ones. Trilon B was used to bind Cd^{2+} ions, and decylamine CH$_3$(CH$_2$)$_9$NH$_2$ as a surfactant. After the particle growth had terminated, we obtained a colloid solution of CdSe nanoparticles in hydrocarbon [6].

A substrate with a porous surface layer (SL) in the form of a thin SiO$_x$ film was obtained by the thermal evaporation of silicon monooxide SiO of 99.9% purity (Cerac Inc.) in vacuum of $(1 \div 2) \times 10^{-3}$ Pa onto polished c-Si (100) substrates; the normal to the substrate surface was oriented at an angle of 75° to the direction toward the evaporator. The SiO$_x$ film thickness was 750 nm. For the etching of SiO$_x$ specimens, a weak solution of fluoric acid (HF) which acts selectively on the structure
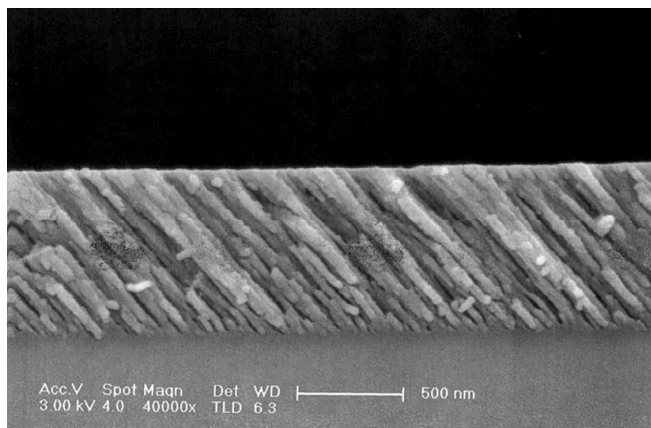
Fig. 1. Electron microscopy pattern of a SiO_x film cross-section. The film was fabricated by the method of thermal deposition in vacuum at an angle of $75°$
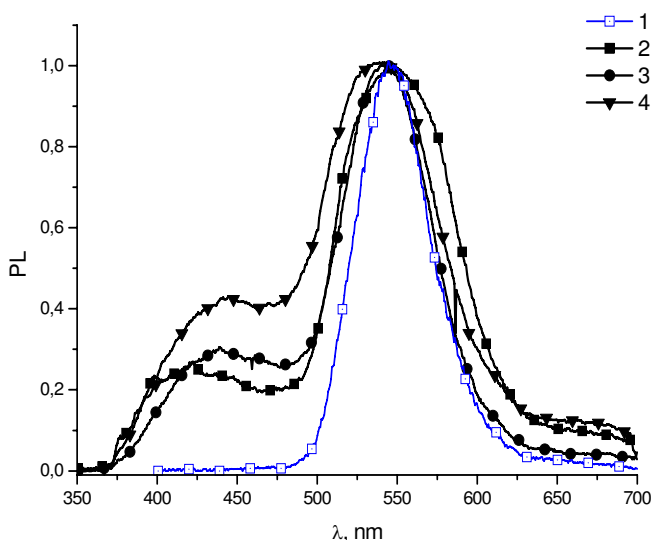

Fig. 2. (*1*) PL spectrum of CdSe nanoparticles in the colloid solution; PL spectra of CdSe nanoparticles deposited on Si–SiO_x SL: (*2*) after the evaporation of a hydrocarbonic solvent, (*3*) after the additional treatment by hydrocarbon, (*4*) after the repeated additional treatment by hydrocarbon. All spectra are normalized to the corresponding intensity maximum

concerned was used; namely, it dissolves SiO_2 and does not etch silicon.

In this work, we used two methods for depositing nano-sized CdSe onto the SL. The first method consisted of two stages. At the first stage, CdSe nanoparticles were fabricated using a chemical method [5] and deposited on the surface of Si–SiO_x structures in the form of a colloid solution; then hydrocarbon acting as a basis of the given solution was evaporated. After the hydrocarbon evap-

oration, the specimens were subjected to an additional treatment in hydrocarbon to activate the formation of a nanoparticle layer on the structured substrate surface.

The second method of nanoparticle deposition consisted in the direct formation of a nanoparticle layer on the specimen surface. Nanoparticles were chemically fabricated, as in the first case. At the chemical deposition of CdSe immediately onto the Si–SiO_x substrate, the rate and conditions of particle growth were maintained the same as they were at the formation of nanoparticles in the colloid solution. In this case, particles were deposited on the substrate without surfactants, in contrast to the first case where nanoparticles were contained in a shell with surfactants.

The SiO_x film structure was studied with the help of a ZEISS EVO 50XVP high-resolution electron microscope. The radiation of a nitrogen laser with $\lambda_{exc} = 337$ nm was used to excite PL spectra. The latter were registered on an SDL-2 installation. All measurements were carried out at room temperature.

3. Experimental Results and Their Discussion

In Fig. 1, the electron microscopy pattern of a SiO_x film cross-section is shown. The film was obtained by the deposition in vacuum at an angle of $75°$. As is seen from this figure, the film structure consisted of pronounced columns characterized by a definite growth orientation. The column diameters ranged from 10 to 100 nm. The dimensions of columns and their orientation, as well as the structure porosity, depended on the film deposition angle. For a deposition angle of $75°$, the film porosity (the relative pore volume), as was determined in work [7], amounted to 53%; the value of x in SiO_x was 1.48.

In Fig. 2, the PL spectra of CdSe nanoparticles deposited on the Si–SiO_x SL from the colloid solution (curves *2* to *4*) and the PL spectrum of CdSe nanoparticles in the colloid solution (curve *1*) are depicted. The PL spectrum of CdSe nanoparticles in the colloid solution is a symmetric band with a maximum at 548 nm. The shape and position of this PL band are typical of CdSe nanoparticles 2–3 nm in dimension [8]. The size of CdSe particles in the colloid solution was determined from the position of the absorption band maximum in the same manner as it was done in works [8, 9]; it was found to equal about 2.8 nm. The PL spectrum of Si–SiO_x substrate is a wide band with a low-intensity maximum at about 450 nm. The PL intensity of the nano-CdSe/Si–SiO_x structure which was formed after the deposition of CdSe nanoparticles from the colloid solution on the Si–SiO_x SL exceeds substantially the PL signal

intensity registered from the Si–SiO$_x$ substrate. Therefore, while discussing the experimental results, the substrate spectrum will be taken into consideration as a background.

As is seen from Fig. 2, the deposition of CdSe nanoparticles from the colloid solution onto the Si–SiO$_x$ SL is accompanied by considerable changes in the PL spectrum of the obtained nano-CdSe/Si–SiO$_x$ structure in comparison with that of the colloid solution. A small shift of the band with $\lambda_{\max} = 548$ nm toward the long-wave region to $\lambda_{\max} \approx 550$ nm is observed. In addition, an additional PL band appears in the spectrum in the interval from 420 to 440 nm. The subsequent treatment of specimens in hydrocarbon gives rise to an intensity redistribution between the 550-nm band and the band in the interval from 420 to 440 nm (Fig. 2, curves *3* and *4*) owing to a relative growth of the short-wave band intensity. A decomposition of the total PL contour into its components showed (Fig. 3) that the PL spectrum is a sum of two Gaussians with the following parameters (Tabl. 1).

For the colloid solution of nano-CdSe, $\lambda_{\max} = 548$ nm, and the band half-width (h.w.) is 47 nm. In case of nano-CdSe deposition, $\lambda_{\max 1} = 423$ nm, and the corresponding band half-width is 58 nm, $\lambda_{\max 2} = 550$ nm, and the corresponding band half-width is 75 nm. The intensity ratio $I_1/I_2 = 0.27$. After the first treatment, $\lambda_{\max 1} = 440$ nm, and the corresponding band half-width is 63 nm, $\lambda_{\max 2} = 544$ nm, and the corresponding band half-width is 60 nm, $I_1/I_2 = 0.3$. After the second treatment, $\lambda_{\max 1} = 431$ nm, and the corresponding band half-width is 56 nm, $\lambda_{\max 2} = 539$ nm, and the corresponding band half-width is 82 nm, $I_1/I_2 = 0.4$.

It should be noted that the PL spectrum, as well as the absorption spectrum of the nano-particle ensemble, is composed of discrete lines. The absorption for every line is proportional to the product between the reduced density of states of level pairs that are involved into the given optical transition in a given microcrystal and the total number of microcrystals. However, due to the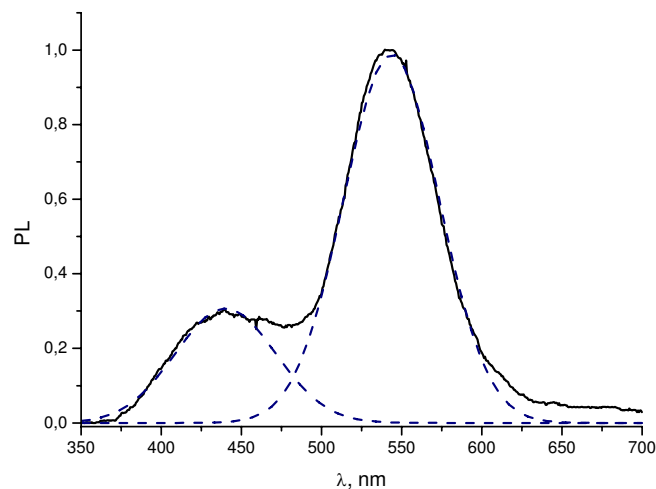 dispersion of microcrystal dimensions, the energy levels become smeared into bands, the density of states in which is proportional to the product between the concentration of microcrystals with a given radius r and the number of states in a definite energy interval. As the radius of microcrystals diminishes, the line width, which is associated with the spread of particles over their dimensions, broadens (this relation is described, e.g., by the Lifshits–Slezov formula [13]).

The spectral distribution of components in the nonuniformly expanded spectral line is connected with the distribution of the ground state of absorption centers over energetically nonequivalent configurations. In the case of a nano-crystal ensemble, these are the nonsphericity of nano-crystal shapes, the contribution of crystal–matrix interface, matrix heterogeneity, and so forth [13].

The appearance of PL bands with $\lambda_{\max} = 423$ and 550 nm in the PL spectrum of the nano-CdSe/Si–SiO$_x$ structure, which was formed after the deposition of CdSe nanoparticles from a colloid solution onto the Si–SiO$_x$ SL, evidences the existence of radiating centers of two types in this structure, which may probably be connected with the formation of two nanoparticle fractions with different dimensions. The variation of the CdSe nanoparticle dimension is known to result in a shift of the excitonic absorption peak position for a colloid solution of nanoparticles [10] and, hence, in a shift of the PL band maximum. In the case where the particle dimensions increase, the PL maximum moves toward larger wavelengths, whereas a reduction of the nanoparticle dimensions leads to a shift of the PL band maximum to the short-wave region. The positions of PL maxima can be

Fig. 3. Decomposition of the PL spectrum of nanoparticles deposited onto a Si–SiO$_x$ SL into band components. Solid curve is the experimentally registered PL spectrum, dotted curves are component contours

T a b l e 1. Parameters of a decomposition of the summary PL contour into components. Deposition of nanoparticles from a colloid solution

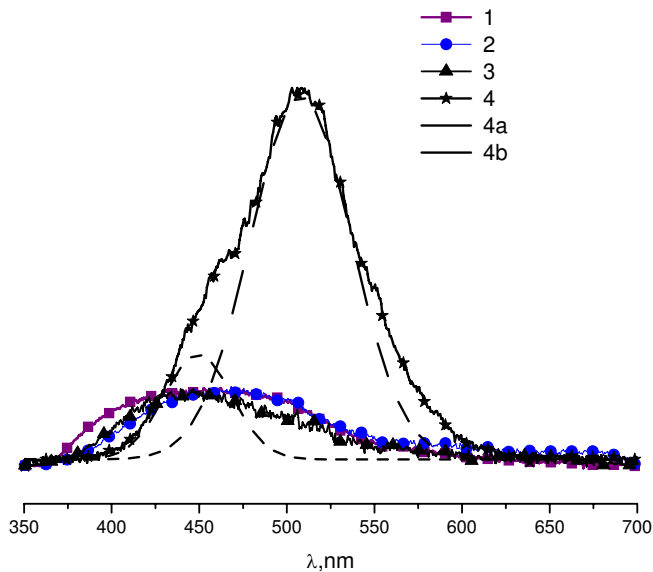| Peak	nano-CdSe	Deposition	1-st treatment	2-nd treatment
$\lambda_{\max 1}$, nm	–	423	440	431
$\lambda_{\max 2}$, nm	548	550	544	539
h/w$_1$, nm	–	58	63	56
h/w$_2$, nm	47	75	60	82
I_1/I_2	–	0.27	0.3	0.4

Fig. 4. PL spectra of nano-sized CdSe (the qualitative intensity ratio): (*1*) initial Si–SiO$_x$ specimen and after the chemical deposition of nano-CdSe onto the Si–SiO$_x$ SL for 2 min (*2*), 30 min (*3*), and 2 h (*4*). Curves *4a* and *4b* are the components of curve *4*

used to estimate the sizes of particles averaged over the ensemble which correspond to two PL bands in Fig. 2 (curve *2*). They are approximately equal to 2.5 and 1.2 nm.

For elucidating the peculiarities in the formation of a nanoparticle layer on a structured surface and their dependence on the method of nanoparticle deposition, we also synthesized nanoparticles chemically, directly on the substrate. At the chemical deposition of CdSe onto the Si–SiO$_x$ substrate, the rate and the conditions (the temperature, the reagent ratio) of particle growth were maintained the same, as they were at the formation of 2.8-nm nanoparticles in the colloid solution on the basis of hydrocarbon.

As is seen from Fig. 4, if the chemical deposition duration is short (less than 10 min), the substrate spectrum dominates the PL spectra, which testifies that, at such deposition time intervals, the nanoparticle layer has no enough time to be formed. If the time interval of the nanoparticle deposition onto the Si–SiO$_x$ substrate is less than 30 min, the corresponding PL spectra demonstrate a broad unstructured radiation band with a maximum at about 455 nm. A large half-width of this band testifies to the formation of CdSe particles with a wide dispersion of their dimensions on the Si–SiO$_x$ layer surface. In the case where the deposition time is 2 h, the PL spectrum is a rather intensive band with a maximum at about 510 nm, the shape of which points to the existence

of at least two PL bands with maxima located at about 550 and 449 nm and with half-widths of 38 and 58 nm, respectively (Fig. 4, curves *4*, *4a*, and *4b*, Tabl. 2).

Taking into account the fact that the emergence of those bands is caused by the formation of CdSe nanoaggregates on the SL, those bands can also be related to the formation of two fractions of CdSe nanoparticles. The dimensions of CdSe nanoparticles, averaged over the ensemble, were estimated from the PL spectra of the obtained nano-CdSe/Si–SiO$_x$ structure to equal 2.9 and 1.3 nm.

The formation of two nanoparticle fractions with the indicated dimensions can be caused by different localizations of nanoparticle growth centers. Some part of them are formed on the surface of SL, the others in the spatially confined volume of pores between SiO$_x$ columns. The restriction of the volume, in which nanoparticles grow, and the volume, which supplies Cd^{2+} and Se^{2-} ions, results in the formation, in substrate pores, of CdSe nanoparticles with dimensions smaller than those of particles formed on the SL surface. It is those two fractions of CdSe nanocrystals that favor the appearance of two bands in the PL spectrum (Fig. 4).

Similar processes occur, when the colloid solution is injected into the SL. Despite the presence of surfactant shells around those nanoparticles, the latter, forming a suspension in the colloid solution on the basis of hydrocarbons, exchange Cd^{2+} and Se^{2-} ions; however, this exchange does not affect particle dimensions [6, 12]. After the solution has been injected into the SL, the equilibrium conditions of ionic exchange become violated, especially in the case of particles that penetrate into pores between SiO$_x$ columns.

The violation of conditions governing the particle dimension stability induces the particle rearrangement into a number of new fractions (with new dimensions), for which the Gibbs free energy is minimal under given conditions of particle localization. The appearance of nanoparticle fractions characterized by several dimensions manifests itself in the PL spectra as a broadening of the major band at $\lambda_{\max} \approx 550$ nm and the appearance of an additional PL band at $\lambda_{\max} \approx 423$ nm (Fig. 2, curve

T a b l e 2. Parameters of a decomposition of the summary PL contour into components. Chemical deposition duration equals 2 h

Peak	nano-CdSe	Chemical deposition for 2 h
$\lambda_{\max 1}$, nm	–	449
$\lambda_{\max 2}$, nm	548	550
h/w$_1$, nm	–	38
h/w$_2$, nm	47	58

2). When the properties of the medium that plays the role of a nanoparticle carrier change due to an additional treatment, the integrity of the shell containing surfactants becomes violated. Moreover, the rearrangement of particle fractions continues and, as a consequence, brings about a modification of the band intensity ratio in the PL spectrum (Fig. 2, curves *3* and *4*). As follows from experimental data shown in Fig. 2, when the Si–SiO$_x$ surface with already deposited CdSe nanoparticles is subjected to an additional treatment with hydrocarbon – the treatment forces some part of deposited nanoparticles that are weakly coupled with the surface to transit into the colloid solution – a considerable modification of the half-widths of both PL bands is observed. It may probably be associated with the restoration of exchange processes between CdSe particles and clusters adsorbed on the specimen surface.

The data reported above testify that, when analyzing the nanoparticle deposition onto a nano-structured substrate surface, one has also to take into consideration that, since the substrate is a structure consisting of pronounced columns with a definite growth orientation, some part of nanoparticles deposited on such a surface will penetrate into a spatially confined volume between SiO$_x$ columns. The processes of CdSe deposition in this volume depend very strongly on the treatment conditions of nanoparticles and the integrity of a surfactant shell, because the finite-volume conditions act here together with the conditions of nanoparticle deposition and interparticle ionic exchange.

4. Conclusions

Hence, the analysis of both techniques aimed at the fabrication of nano-structured composites has shown that, in the both, a formation of several fractions of CdSe nanoparticles in the Si–SiO$_x$ SL is possible, with the average particle dimensions being about 2.5 and 1.2 nm for the deposition from a colloid solution and about 2.9 and 1.3 nm for the chemical deposition. The application of a structured surface as a substrate for the nanoparticle deposition allowed the process of nanoparticle synthesis to be realized in a confined volume. This provides an additional possibility to control the synthesis and allows several fractions of nanoparticles with different dimensions to be obtained, using, for this purpose, either a colloid solution of nanoparticles on the basis of hydrocarbons or an aqueous solution containing Cd^{2+} and Se^{2-} ions. The experimental data testify that the properties of the obtained nano-structured composites can be modified by varying the nanoparticle synthesis duration and the regimes of additional treatments. Monitoring can be carried out with the use of PL spectroscopy.

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ФОРМУВАННЯ НАНОСТРУКТУРОВАНИХ
КОМПОЗИТІВ CdSe В ПОРУВАТИХ ШАРАХ SiO$_x$

Ю.Ю. Бачеріков, І.З. Індутний, І.Ю. Майданчук,
О.Б. Охріменко, С.В. Оптасюк, П.Є. Шепелявий

Р е з ю м е

У даній роботі досліджено можливість створення нанокомпозитних структур різними методами: введенням у матрицю por-SiO$_x$ наночастинок CdSe, а також формуванням наночастинок CdSe у матриці por-SiO$_x$ внаслідок хімічного осадження. Показано, що осадження з колоїдного розчину наночастинок CdSe приводить до формування в пористому поверхневому шарі Si–SiO$_x$ кількох фракцій наночастинок із розмірами ∼ 1,2 і 2,5 нм, а при хімічному осадженні ∼ 1,9 і 2,3 нм. Встановлено, що властивості одержаних наноструктурованих композитів можна варіювати шляхом зміни режимів додаткових обробок і часу синтезу наночастинок для кожного методу відповідно.