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Luminescence of $In_xTl_{1-x}I$ Nanocrystals Embedded in Dielectric Matrixes

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The relaxation dynamics of the exciton resonances in the layer $In_xTl_{1-x}I$ semiconductor for its transition from bulk crystals to the quantum-size nanocrystals synthesised within the different matrices is analysed. The mordenite-type (Na-MOR) $Na_8[Al_8Si_{40}O_{96}]\cdot 24H_2O$ zeolite, beryl and porous silicon are used as matrices. As experimentally shown, the size-effects' influence affect the parameters of the band-to-band transitions and the genesis of exciton states in substitutional solid solution of $In_xTl_{1-x}I$.

На прикладі шаруватого напівпровідника $In_xTl_{1-x}I$ проаналізовано динаміку релаксації екситонних збуджень при переході від блочних монокристалів до нанокристалів, синтезованих у ріжних матрицях, таких як поруватий кремній, берил та природній цеоліт $Na_8[Al_8Si_{40}O_{96}]\cdot 24H_2O$ (морденіт). Експериментально виявлено вплив розмірного квантування на параметри зона-зонних переходів, а також генезис екситонних станів твердих розчинів заміщення $In_xTl_{1-x}I$.

На примере слоистого полупроводника $In_xTl_{1-x}I$ проанализирована динамика релаксации экситонных возбуждений при переходе от блочных монокристаллов к нанокристаллам, синтезированным в разных матрицах, таких как пористый кремний, берилл и цеолит $Na_8[Al_8Si_{40}O_{96}]\cdot 24H_2O$ (морденит). Экспериментально выявлено влияние размерного квантования на параметры зона-зонных переходов, а также генезис экситонных состояний твердых растворов замещения $In_xTl_{1-x}I$.

Key words: substitutional solid solution, indium and thallium iodide, quan-

tum-size effect, quantum dot.

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1. INTRODUCTION

Nowadays the control changing of fundamental characteristics and optical parameters of semiconductors remains important problem in microelectronics. Special attention devotes to operating of the fundamental and optical values such as: band gap energy E_g, energy characteristics of the exciton resonances (exciton band maximum energy, exciton band half-width) without crystal structure and chemical composition changing.

It is known that this problem may be solved if dimension of semiconductor crystal gradually decrease and bulk crystal transfers into quasi-zero-dimensional structure of 'quantum-dot' type. The reducing of quantum-dot size leads to dimensional quantization of the free carriers and causes a high-energy shift of the absorption edge.

In this work, the investigations of optical properties of $In_xTl_{1-x}I$ layered crystals synthesised into different matrices that establish desired conditions of nanocrystals sizes are reported. The mordenite-type $Na_8[Al8Si_{40}O_{96}]\cdot 24H_2O$ zeolite (Na-MOR), beryl and porous silicon are used as matrices.

2. MODELS AND FORMULATION

In reference [1], it was shown that for the given case the energy E of minimum phototransition is described by the following expression:

$$E = E_g^b - E_{ex} + \frac{\pi^2\hbar^2}{2\mu}\sum_{i=1}^{3}\frac{1}{\alpha_i^2}, \qquad (1)$$

where μ is an effective mass of electron and hole, E_g^b —band gap energy of bulk crystals, E_{ex} —exciton binding energy, α_i is effective size of the '*i*'-th quantum dot. It is clear that E is a function of the sizes 'α^{-2}', and the reducing of quantum-dot sizes leads to dimensional quantization of the free carriers and causes a high-energy shift of the absorption edge.

On the other hand, in the process of the size-dimensional quantization, the peculiar dynamics of the exciton states in semiconductor crystal will be revealed. There three different cases may occur: *1*—$\alpha_{ex} > \alpha_i$, *2*—$\alpha_{ex} \le \alpha_i$, *3*—$\alpha_{ex} << \alpha_i$, where α_{ex} is effective Bohr radius of the free exciton, α_i is effective size of nanocrystals,

$$\alpha_{ex} = \frac{h^2 n_{ex}^2 \varepsilon}{e^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)^{-1}.$$

The values of α_i are equal to one of the unit cell parameters, a, b, c, of crystal lattice.

In the first case ($\alpha_{ex} > \alpha_i$), where spatial distribution of the effective mass of quasi-particle exceeds the bounds of nanocrystals, free exciton states are absent. Energy of exchange (Coulomb) interaction between electron and hole will be as follows:

$$E_{ex} = \frac{\mu_{ex} e^4}{2\hbar^2 \varepsilon^2} = \frac{e^2}{2\varepsilon} \frac{1}{\alpha_{ex}}. \qquad (2)$$

If $m_e = m_h$, $\mu_{ex} = \dfrac{m_e m_h}{m_e + m_h} = \dfrac{m_e}{2}$. In conditions of $\dfrac{\pi^2 \hbar^2}{2\mu} \sum_{i=1}^{3} \dfrac{1}{\alpha_i^2} \geq \dfrac{e^2}{2\varepsilon} \dfrac{1}{\alpha_{ex}}$, the high-energy shift of exciton bands should be observed in optical spectra.

The third case ($\alpha_{ex} << \alpha_i$) is the classic bulk crystal, which was considered in [2]. Now, if believe that, for a real bulk crystal, $\alpha_i = 10^6$ nm and $\alpha_{ex} = 10$ nm, then we can neglect the last member in equation (1) and obtain the classic expression for free hydrogen-like exciton (without taking into account the exciton-zone dispersion).

Consequently, realising on experiment considered three models of quantum-size structures we can follow for the dynamics of the exciton states relaxation on the optic spectra in semiconductors.

3. RESULTS AND DISCUSSION

Layer semiconductors of InI and $In_xTl_{1-x}I$ substitutional solid solution (SSS) are considered as promising model materials for the studies of the problems above. Masses of the effective electron and hole in these materials are equal, [3], besides it is known that the model of the hydrogen-like Wannier exciton is valid for the bulk crystal [4, 5]. Since $E_{ex}^{n=1} = 0.005$ eV, $\alpha_{ex}^{n=1} = 2.7$ nm, bulk crystals of InI and $In_xTl_{1-x}I$ SSS are suitable for using as a model objects with $\alpha_{ex} << \alpha_i$.

The nanocrystals of indium and thallium iodide combined with SSS embedded into solid matrices of porous silicon with pore sizes of 1–50 nm are provided with a model for which $\alpha_{ex} \leq \alpha_i$. For third model ($\alpha_{ex} << \alpha_i$), the quantum-size microcrystals were incorporated into the natural zeolite Na-MOR ($Na_8[Al_8Si_{40}O_{96}] \cdot 24H_2O$). The natural mordenite has the one-dimensional emptiness with diameter of $\alpha_i = 0.7$–1 nm. $In_xTl_{1-x}I$ molecules were embedded into solid matrices by physical absorption.

The exciton photoluminescence spectra at different temperature are investigated in $In_xTl_{1-x}I$. The luminescence from the sample was measured with used the spectral complex SDL-2-1. The Ar-laser with $\lambda = 0.47$–0.51 μm was used for excitation of photoluminescence.

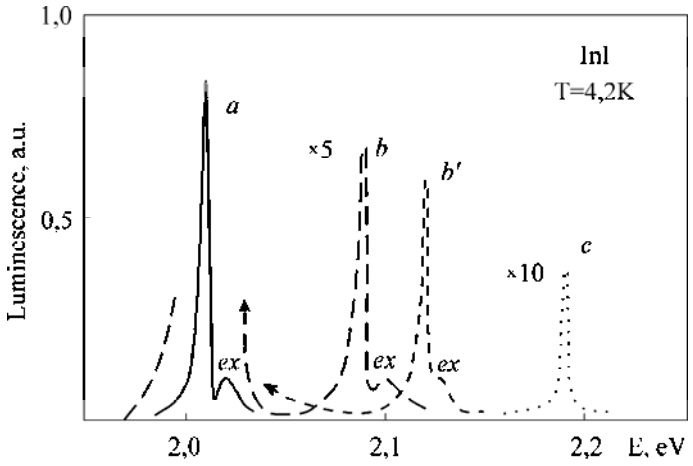

Fig. 1. The photoluminescence spectra of InI crystals: *a*—bulk crystals; *b*—nanocrystals incorporated into porous silicon ($\alpha_i = 0.01$ μm), *b*′—nanocrystals incorporated into glass cavities ($\alpha_i = 0.001$ μm), *c*—nanocrystals incorporated into natural zeolite Na-MOR ($\alpha_i = 1$ nm).

TABLE 1. Effective sizes of quantum dots in InI.

Crystal	$\alpha_i^{\text{experiment}}$, μm	$\alpha_i^{\text{experiment}}/\alpha_i^{\text{theory}}$
InI (*b*)	0.5	7
InI (*b*′)	0.01	2.5
InI (*c*)	0.0008	1.1
$In_{0.9}Tl_{0.1}I$ (*b*)	0.5	10
$In_{0.9}Tl_{0.1}I$ (*b*′)	0.01	3
$In_{0.9}Tl_{0.1}I$ (*c*)	0.0015	2.1
$In_{0.4}Tl_{0.6}I$ (*b*)	0.5	11.5
$In_{0.4}Tl_{0.6}I$ (*b*′)	0.01	5
$In_{0.4}Tl_{0.6}I$ (*c*)	0.001	1.4

Figure 1 shows the photoluminescence spectra of InI crystal. The line of recombination of free exciton with $h\nu_{ex} = 2.0194$ eV and line of localised exciton $h\nu_{ex} = 2.0174$ eV [6] is easily seen in photoluminescence spectrum of the bulk InI (*a*). Obtained results are in a good agreement with corresponding parameters of the exciton given in [4, 5]. Photoluminescence spectra for indium iodide incorporated into porous silicon are shown in Fig. 1, *b*, *b*′.

The violet shift of exciton photoluminescence is observed. Considering the value of the violet shift and regular parameters, α_{ex}, $E_{ex}^{n=1}$, μ_{ex}, the effective size α_i of quantum dot of InI embedded into porous silicon were calculated (Table 1).

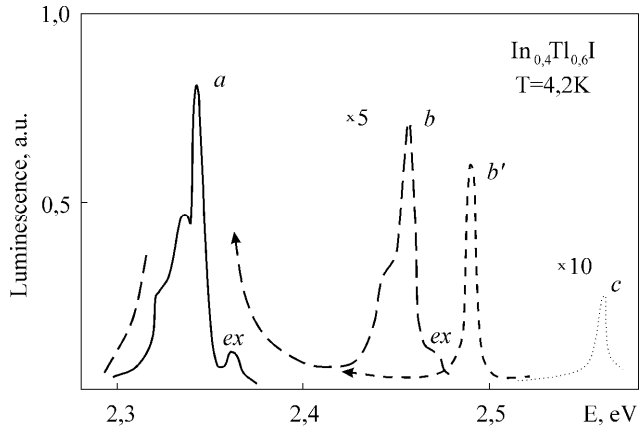

Fig. 2. The exciton photoluminescence spectra of $In_{0.4}Tl_{0.6}I$ crystals: *a*—bulk crystals; *b*—nanocrystals incorporated into porous silicon ($\alpha_i = 0.05$ μm), *b′*—nanocrystals incorporated into glass cavities ($\alpha_i = 0.001$ μm), *c*—nanocrystals incorporated into natural zeolite Na-MOR ($\alpha_i = 1$ nm).

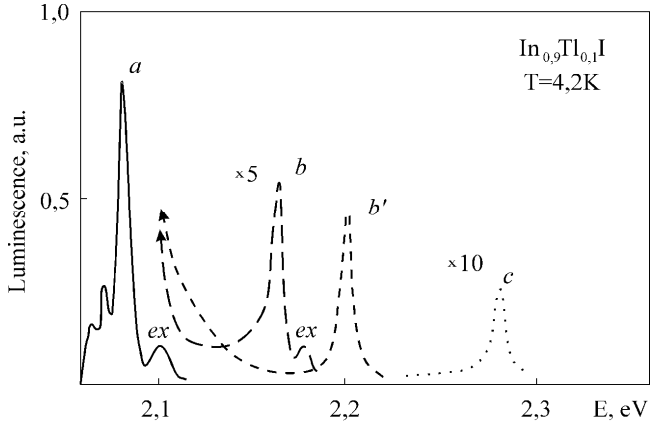

Fig. 3. The exciton photoluminescence spectra of $In_{0.9}Tl_{0.1}I$ crystals: *a*—bulk crystals, *b*—nanocrystals incorporated into porous silicon ($\alpha_i = 0.05$ μm), *b′*—nanocrystals incorporated into glass cavities ($\alpha_i = 0.001$ μm), *c*—nanocrystals incorporated into natural zeolite Na-MOR ($\alpha_i = 1$ nm).

The line *c* in Fig. 1 is experimental photoluminescence spectrum of indium iodide incorporated in solid matrices of natural zeolite Na-MOR type. Weak band with energy $h\nu_{ex} = 2.189$ eV are observed. Moreover, the band half-width is less than free-exciton photoluminescence bandwidth in two previous spectra. The temperature decay occurs at $T = 35$ K that suits the model of localised exciton well. The absence of the free-exciton band on photoluminescence spectra completely satisfies the con-

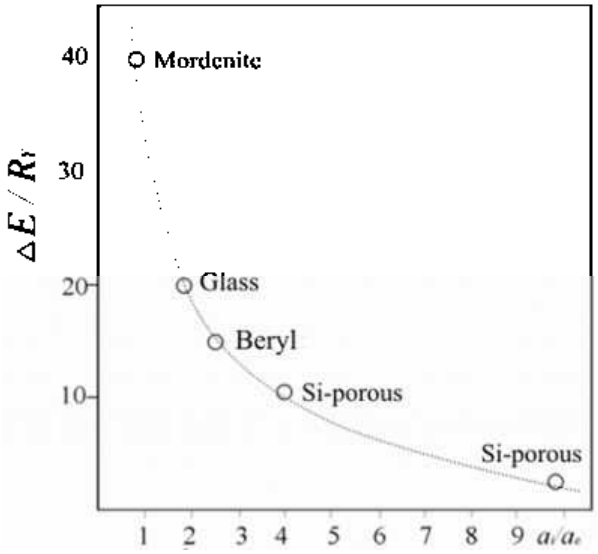

Fig. 4. The high-energy shift of exciton band as a function of ratio of nanocrystals' size to effective Bohr radius of the free exciton.

dition of $\alpha_{ex} << \alpha_i$.

The analogous experimental results (Figs. 2, 3) were obtained for $In_xTl_{1-x}I$ SSS. In substitutional solid solution, due to the regular fluctuations of a crystal lattice, the structure of localised-exciton band displays more distinct than in binary compounds.

The accuracy of band gap energy and binding energy of exciton determination decreases owing to structural disorder. This cause is an inaccuracy in evaluation of effective size α_i of nanocrystals. From experimental results, the dependence of high-energy shift value on the ratio of nanocrystals' size to effective Bohr radius of the free exciton was obtained (Fig. 4).

As seen from Fig. 4, the relative parameter of ground exciton state high-energy shift depends exponentially against the α_i/α_{ex} ratio. Moreover, strong quantum dimensional effect of exciton states appears within the range of $1 \geq \alpha_i/\alpha_{ex} \geq 4$. Taking into account small values of exciton binding energy in InI ($R_Y \approx 4.3$ meV) and relatively small value of effective Bohr radius ($\alpha_{ex} \approx 45$ Å), we can conclude that strong quantum dimensional effect in indium iodide takes place in a region where sizes of nanocrystals are comparable with lattice parameters.

4. CONCLUSIONS

Decrease of size of the semiconductor $In_xTl_{1-x}I$ crystals leads to size quan-

tization of the electron spectrum. This manifests in a form of the high-energy shift of exciton bands in photoluminescence spectra.

Synthesis of the semiconductor nanocrystals embedded into porous matrices with unknown size of emptiness is one of the experimental methods to determine an effective size of these microemptinesses.

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