Optical properties of quantum size nanocrystals $In_xTl_{1-x}I$ embedded in solid matrices.

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Abstract

The relaxation dynamics of the exciton resonance's in substitutive solid solution (SSS) of the layer semiconductor for the transition from bulk crystals $In_xTl_{1-x}I$ SSS to the quantum size microcrystals synthesised into different matrices are analysed. $Na_8[Al_8Si_{40}O_{96}]*24H_2O$ zeolite of the mordenite type (Na–MOR) and porous silicon in the matrices role have been used. It is experimentally shown that the size effects influence affect the parameters of the band–to–band transition and genesis upon exciton states in $In_xTl_{1-x}I$ SSS under the quantum-size effect are demonstrated.

Key words: Substitutive solid solution, quantum-size effect, quantum dot, indium and tallium iodide.

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Models and formulation

Nowadays the control changing of fundamental characteristics and optic parameters of semiconductor remains important problem in microelectronics. Special care is devoted to the fundamental and optic values such as: band gap energy E_g, energy characteristics of the exciton resonance's (exciton band maximum energy, exciton band half width) parameters which are searching without crystallinity and chemical composition changing.

It is known [1] that this problem may be solved if dimension of semiconductor crystal gradually decrease and bulk crystal transfers into quazi-zero-dimensinal structure of "quantum dot" type. In the reference [1] it was shown that for the given case the band gap energy E_g is described by the following expression:

$$E_g^a = E_g^b + \frac{\pi^2}{2\mu}\sum_{i=1}^{3}\frac{1}{\alpha_i^2} \qquad (1)$$

where μ is mass of effective electron and hole, α_i is effective size of the "i" quantum dot. From [1] it is clear that E_g^a is linear function of the sizes "α^{-2}". Thus reducing the sizes of quantum dot leads to dimensional quantization of the free carriers and cause high-energy shift of the absorption edge. On the other hand, in the process of the size-dimensional quantization peculiarity of, the dynamics of the exciton states in semiconductor crystal will be manifest. Three different cases may occur:

1 - $\alpha_{ex} > \alpha_i$

2 - $\alpha_{ex} \le \alpha_i$

3 - $\alpha_{ex} << \alpha_i$;

where

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

is effective Bohr radius of the free exciton, α_i is effective size of microcrystals. The values of α_i are equal to one of the unit cell parameters ***a, b, c*** of crystalline lattice. Thus in the first case ($\alpha_{ex}>\alpha_i$) the quasi-zero-dimensional crystal will appear, electron and hole energy states of which may be approximately described by the expression:

$$E_{e,h}=\frac{h^2n^2}{2\mu_{ex}\alpha_i^2\varepsilon} \quad (3)$$

Energy of exchange (Coulomb) interaction between electron and hole will be as follows:

$$E_{ex}=\frac{h^2n_{ex}^2}{2\mu_{ex}\alpha_{ex}^2\varepsilon} \quad (4)$$

When $m_e=m_h$, then $\mu_{ex}=\frac{m_e m_h}{m_e+m_h}$, and E_{ex} becomes much smaller than $E_{e,h}$ $E_{ex}<<E_{e,h}$ so that exciton mobility gets insignificant and free states are absent. Nevertheless, at localised or autolocalised states bulk excitons may emerge.

One can see from the expressions (3) and (4) together with the term of equality of effective carrier masses for microcrystals when $\alpha_{ex}<<\alpha_i$ could be wait for displaying on the optic spectra of the exception absorption bands or exciton photoluminescence in the states with n =1 at first and then n =2, 3 ... depend upon the correlation between α_i and α_{ex}. The third case ($\alpha_{ex}<<\alpha_i$) is the classic bulk crystal, which considered in [2]. For this case we have:

$$\hbar\omega=E_g-\frac{h^2n_{ex}^2}{2\mu_{ex}\alpha_{ex}^2\varepsilon}+\frac{h^2n^2}{2m_{e,h}\alpha_i^2\varepsilon}, \quad (5)$$

Now, if to believe that for real bulk crystal $\alpha_i=10^6$ *nm* and α_{ex} =10 *nm* then by the last term in equation (2) can neglect and the classic expression for free hydrogen-like exciton will be (without taking into account of the exciton zone dispersion). If α_i set off for α_{ex} then deposit from the last term in (5) will be increased and that must lead to the violet shift of exciton absorption band position.

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

Results and discussion

Layer semiconductors of InI and $In_xTl_{1-x}I$ 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 microcrystals indium and tallium iodide combined with SSS embedded in solid matrices of porous silicon with pore sizes 1-50 *nm* provided the model for which ($\alpha_{ex}\leq\alpha_i$). For the third model ($\alpha_{ex}<<\alpha_i$), the quantum-size microcrystals were incorporated into the natural zeolite Na-MOR ($Na_8[Al_8Si_{40}O_{96}]*24H_2O$). The natural mordenite has the one-dimensional emptiness with diameter of α_i = 0.7-1 *nm*. $In_xTl_{1-x}I$ molecules were embedded into solid matrices supercages 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 the used spectral complex SDL-2-1. The **Ar**-laser with λ=0.47-0.51 μm was utilised for excitation of photoluminescence.

Figure 1 shows the photoluminescence spectra of layer InI. The line of recombination of free exciton with $h\nu_{ex}$=2.0194eV 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 good agreement with corresponding parameters of the exciton given in [4,5]. Photoluminescence spectrum for indium iodide incorporated into porous silicon is shown in figure 1 (b,b').

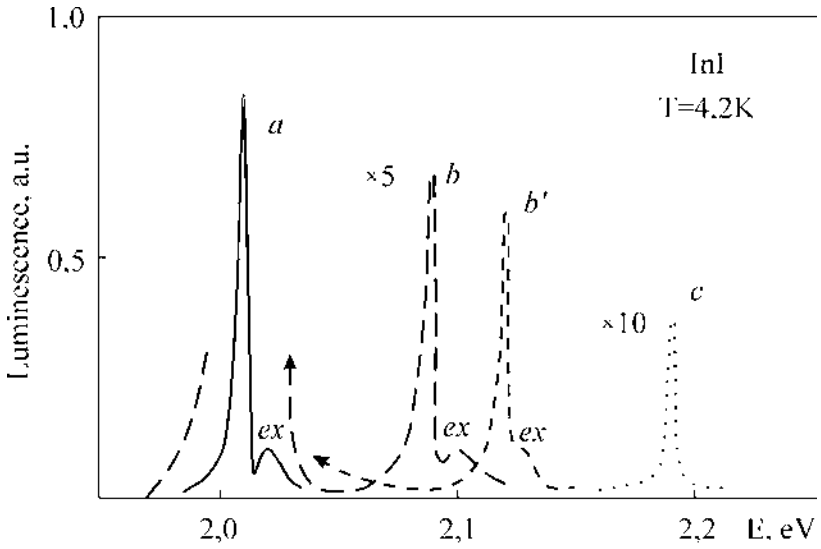

Fig.1. The exciton photoluminescence spectra of InI crystals.

The a-bulk crystals, b-microcrystals incorporated into porous silicon α_i =0,01μm, b'-microcrystals incorporated into porous silicon α_i=0,001μm, c- microcrystals incorporated into natural zeolite Na-MOR α_i=1nm.

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} and using equation (5) the effective size α_i of quantum dot of InI embedded into porous silicon were calculated. (Table 1)

Table 1.

Crystal		α_i^{exper}, μm	$\alpha_i^{expe}/\alpha_i^{theorr}$
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

The curve **c** in figure 1 is experimental photoluminescence spectrum of indium iodide incorporated in solid matrices of natural zeolite Na-MOR type. Weak band with the energy of $h\nu_{ex}$=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=35K that suits the model of localised exciton well. The absence of the free exciton band on photoluminescence spectra completely satisfies the condition of $\alpha_{ex} << \alpha_i$.

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

The a-bulk crystals, b-microcrystals incorporated into porous silicon α_i=0,05μm, b'-microcrystals incorporated into porous silicon α_i=0.001μm, c- microcrystals incorporated into natural zeolite Na-MOR α_i=1nm.

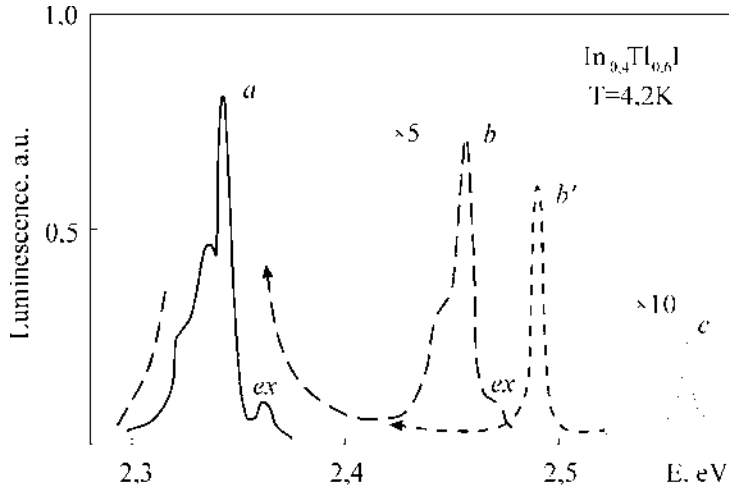

Fig.2. The exciton photoluminescence spectra of $In_{0.4}Tl_{0.6}I$ crystals.

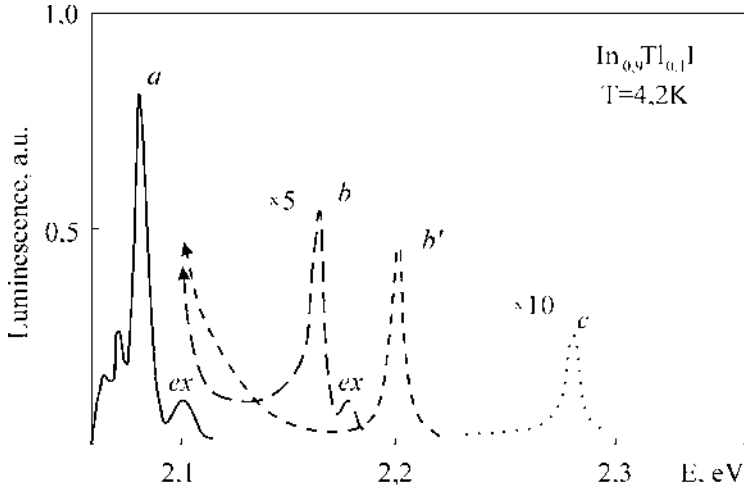

Fig. 3. The exciton photoluminescence spectra of $In_{0.9}Tl_{0.1}I$ crystals.

Conclusion

Decrease of size of the semiconductor $In_xTl_{1-x}I$ crystals leads to size quantization of the electron spectrum. This was manifested in the form of the high-energy shift of the exiton bands on photoluminescence spectra.

Synthesis of the semiconductor nanocrystals embedded into porous matrices with on unknown size of emptiness are one of the experimental instrument to determine effective size of these microemptinesses.

Reference

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