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EXCITONS AND EXCITON QUASIMOLECULES STATES IN NANOSYSTEMS OF SEMICONDUCTOR QUANTUM DOTS

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Within the framework of the modified effective mass method, a theory of an exciton quasimolecule (formed from spatially separated electrons and holes) is developed for nanosystems consisting of germanium quantum dots grown in silicon matrices. In an artificial quasi-molecule, the holes are located in the volumes of germanium quantum dots, and the electrons, moving in a silicon matrix, are localized above the spherical surface of germanium quantum dots. The variational method is used to derive the dependences of the total energy, as well as of the binding energy of the ground singlet state of the exciton quasimolecule, on the distance D between the surfaces of the quantum dots, as well as on the radius a of the quantum dot. It is shown that the main contribution into the binding energy of an exciton quasimolecule is made by the energy of the exchange interaction of an electron with holes, which substantially exceeds the contribution that causes the energy of the Coulomb interaction of an electron with holes. It has been found that the appearance of an exciton quasimolecule in a nanosystem has a threshold character, and possibly in a nanosystem where the distance D between the surfaces of quantum dots exceeds the value of a certain critical distance $D_c^{(1)}$. It is shown that an excitonic quasimolecule in a nanosystem can exist only at temperatures below a certain critical temperature T_c. At temperatures below the critical temperature $T<T_c$, the exciton quasimolecule splits into two artificial atoms (from space-separated electrons and holes). It has been found that the binding energy of the ground singlet state of an exciton quasimolecule, consisting of two quantum dots of germanium, is an essential quantity that exceeds the binding energy of biexciton in a silicon single crystal by almost two orders of magnitude.

Keywords: *spatially separated electrons and holes, binding energy, two germanium quantum dots*

INTRODUCTION

The Ge/Si heterostructures promising to create new elements for silicon infrared optoelectronics are self-assembled structures with Ge/Si nanoislands [1–3]. Ge/Si heterostructures with quantum dots (QDs) of Ge are II type heterostructures. In this nanosystem the lowest electronic level is in matrix, and the lowest hole level is within bulk of QD. A large shift of the valence band (610 meV) generates the localization of holes in the bulk of QD. A significant shift of the conduction band (about 340 meV) is a potential barrier for electrons [1–3]. The electrons move in the matrix and do not penetrate in the bulk of QD [1–3]. When investigate the optical properties of heterostructures Ge/Si with Ge QDs in experimental papers [1–3] it was found that the electron can be localized above the surface of the QD while the hole here moves in the bulk of the QD. In [1–3] using the method of electron-beam lithography, heterostructures are obtained which are linear chains of QDs germanium on Si substrates. The average sizes of the QD Ge is less than 60 nm. It was noted [4, 5] that, at such a QD content in the samples, one must take into account the interaction between charge carriers localized above the QD surfaces. In [5], a theory of an exciton formed by spatially separated electron and hole is developed (the hole moves in the bulk of a Ge QD and the electron is localized above the spherical interface between the QD and the Si matrix). It has been found that the binding energy of an exciton in such nanosystem is much higner (almost an order of magnitude) than the binding energy of an exciton in a Si single crystal.

At present, there are no theoretical studies of nanosystems containing significant concentrations of quantum dots. With such concentrations of quantum dots, it is necessary to take into account interactions between quantum dots. Therefore, in this work, a theory of an exciton quasimolecule formed of two interacting germanium quantum dots is developed. In such an exciton quasimolecule, electrons and holes are spatially separated –

the holes are located in the bulks of the germanium quantum dots, and the electrons, moving in the silicon matrix, are localized above the spherical surface of the germanium quantum dots.

ENERGY OF THE EXCITON QUASIMOLECULE GROUND SINGLET STATE

Let us consider a model of a nanosystem that consists of two spherical Ge quantum dots [6–8]: QD(*A*) and QD(*B*) with radius *a*, grown in a matrix of silicon with a dielectric constant $\varepsilon_1 = 11.7$ (*D* is the distance between the surfaces of the QD). The QDs contain a Ge with the dielectric constant of $\varepsilon_2 = 16.3$ in their volume. For simplicity, we assume that holes *h(A)* and *h(B)* with the effective mass $(m_h/m_0) = 0.39$ are located at the centers of QD(*A*) and QD(*B*), and electrons $e(1)$ and $e(2)$ with effective mass $(m_e^{(1)}/m_0) = 0.98$ are localized above the surfaces of QD(*A*) and QD(*B*) in a matrix of Si respectively (m_0 is the electron mass in free space). In the nanosystem the holes do not therefore escape from the bulk of the QD while the electrons do not enter the QD.

Let us now use this model to consider the possibility of the formation of an exciton quasimolecule from spatially separated electrons and holes (the holes are located at the centers of QD(A) and QD(B) and electrons are localized near their spherical surfaces). Using adiabatic approximation and the effective mass approximation, the Hamiltonian of the exciton quasimolecule (of spatially separated electrons and holes) can be written in the form [6, 7]:

$$\hat{\mathrm{H}} = \hat{\mathrm{H}}_{A(1)} + \hat{\mathrm{H}}_{B(2)} + \hat{\mathrm{H}}_{\mathrm{int}}, \qquad (1)$$

Where $\hat{\mathrm{H}}_{A(1)}$ and $\hat{\mathrm{H}}_{B(2)}$ are the Hamiltonians of the excitons of spatially separated hole *h(A)* and electron $e(1)$ and hole *h(B)* and electron $e(2)$, respectively. The contribution of the energy of polarization interaction with the surface of QD to the Hamiltonians of the excitons $\hat{\mathrm{H}}_{A(1)}$ and $\hat{\mathrm{H}}_{B(2)}$ can be, as the first approximation, neglected [4, 5]. In (1) E_g is the bandgap energy of the germanium ($E_g = 0.661$ eV). In the first approximation we can neglect the contributions to the Hamiltonian $\hat{\mathrm{H}}_{\mathrm{int}}$ of the interaction energies of the electrons $e(1)$ and $e(2)$ and the holes *h(A)* and *h(B)* with polarization fields induced by these charge carriers on the surfaces of QD(A) and QD(B) [6–8]. Thus the Hamiltonian $\hat{\mathrm{H}}_{\mathrm{int}}$ incorporates only the energies of Coulomb interaction of electron $e(1)$ with hole $h(B)$, and electron $e(2)$ with hole $h(A)$, as well as that between electrons $e(1)$ and $e(2)$, and holes *h(A)* and *h(B)*. Under the assumption that the spins of the electrons $e(1)$ and $e(2)$ are antiparallel, let us write down the normalized wave function of the ground singlet state of the exciton quasimolecule as a symmetric linear combination of wave functions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ [6–8]:

$$\Psi_S\left(r_{A(1)}, r_{A(2)}, r_{B(1)}, r_{B(2)}\right) =$$

$$= \left[2\left(1+S^2(D,a)\right)\right]^{-1/2}\left[\Psi_1\left(r_{A(1)}, r_{B(2)}\right) + \Psi_2\left(r_{A(2)}, r_{B(1)}\right)\right], \qquad (2)$$

where $S(D, a)$ is the overlap integral of single-electron wave functions. Assuming that the electrons $e(1)$ and $e(2)$ move independently from each other, let us represent the wave functions $\Psi_1(r_{A(1)}, r_{B(2)})$ and $\Psi_2(r_{A(2)}, r_{B(1)})$ (2) as a product of single-electron wave functions $\varphi_{A(1)}(r_{A(1)})$ and $\varphi_{B(2)}(r_{B(2)})$, as well as $\varphi_{A(2)}(r_{A(2)})$ and $\varphi_{B(1)}(r_{B(1)})$, respectively [6–8]. Let us also represent the single-electron wave functions as variational functions of Coulomb type [6–8]. In the framework of the variational method, the energy of the exciton quasimolecule ground singlet state, as a first approximation, is given by the mean value of the Hamiltonian $\hat{\mathrm{H}}$ (1) over the states described by the wave functions of the zeroth approximation Ψ_S (2) [6–8]. The total energy $E_0(\tilde{D}, \tilde{a})$ of the exciton quasimolecule ground singlet state takes the form [6–8]:

$$E_0(\tilde{D}, \tilde{a}) = 2E_{ex}(\tilde{a}) + E_b(\tilde{D}, \tilde{a}), \qquad (3)$$

where $E_b(\tilde{D}, \tilde{a})$ is the binding energy of the ground singlet state of the exciton quasimolecule ($\tilde{D} = \left(D / a_{ex}^{2D}\right)$), and $E_{ex}(\tilde{a})$ is the binding energy of the ground state of the exciton

(consisting of spatially separated electron and hole) localized over the surface of QD, which was worked out in [4, 5]. Fig. presents the results of the variational calculations of the binding energy $E_b(\tilde{D},\tilde{a})$ of the exciton quasimolecule ground state in a nanosystem with QD of Ge of the mean radius $\tilde{a}_1 = 12.8$ nm, grown in a matrix of silicon (the Bohr radius of the 2*D* exciton $a_{ex}^{2D} = 2.6$ nm).

The variational method that we used for the calculation of the exciton quasimolecule ground state binding energy $E_b(\tilde{D},\tilde{a})$ is applicable provided that it is much smaller than the binding energy of the exciton ground state $E_{ex}(\tilde{a})$, i.e. the following condition must be fulfilled: $(E_b(\tilde{D},\tilde{a})/E_{ex}(\tilde{a})) << 1$. The binding energy $E_b(\tilde{D},\tilde{a})$ of the exciton quasimolecule ground state in a nanosystem with QD of Ge of the mean radius $\tilde{a}_1 = 12.8$ nm has a minimum $E_b^{(1)}(D_1,\tilde{a}_1 \approx -6.1$ meV (at the distance $D_1 \cong 3.1$ nm) (corresponds to the critical temperature $T_c \approx 71$ K). As it follows from Fig., the exciton quasimolecule appears in the nanosystem at distances $D \geq D_c^{(1)} \cong 2.1$ nm between the surfaces of QD. The formation of such an exciton quasimolecule is of threshold character and may occur in a nanosystem with QDs of the mean radius $\tilde{a}_1$, where the distance *D* between the surfaces of QD exceeds a certain critical value $D_c^{(1)}$. The existence of such distance $D_c^{(1)}$ arises from quantum size effects in which the decrease in the energies of interaction between the electrons and holes entering into the Hamiltonian (Eq. (1)) of the exciton quasimolecule with decrease in the distance *D* between the surfaces of the QD cannot compensate for the increase in the kinetic energy of the electrons and holes. The binding energy of the exciton $E_{ex}(\tilde{a})$ amounts to $E_{ex}(\tilde{a}_1) \cong -64$ meV [5], with the energy of the exciton quasimolequle ground state (7) taking the value $E_0(\tilde{D}_1,\tilde{a}_1 \approx -134.1$ meV. It should be emphasized that the criterion of the applicability of the variational method for the calculation of the exciton quasimolecule binding energy $E_b(\tilde{D},\tilde{a})$ is fulfilled $\left(\left(E_b^{(1)}(D_1,\tilde{a}_1)/E_b^{(1)}(D_1,\tilde{a}_1)\right) \cong 0.09\right.$ meV).

At larger distances *D* between the surfaces of QD: $D \geq D_c^{(2)} \cong 4.4$ nm, the exciton quasimolecule breaks down into two excitons (consisting of spatially separated electrons and holes), localized over QD surfaces. Thus an exciton quasimolecule can be formed in a nanosystem where $D_c^{(1)} \leq D \leq D_c^{(2)}$ nm, (see Fig.). Furthermore, an exciton quasimolecule can exist only at temperatures lower than the critical temperature $T_c = 71$ K). In the Ge crystal with the binding energy $E_b = 0.34$ meV the exciton binding energy $E_b^{(1)}$ is almost two orders of magnitude.

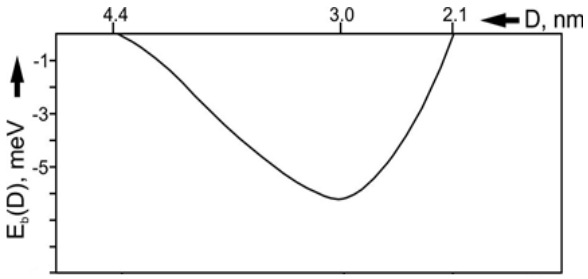

Fig. The dependence of the binding energy of the ground singlet state $E_b(D,\tilde{a}_1)$ of the exciton quasimolecule in a nanosystem made up of two spherical germanium quantum dots QD(A) and QD(B) with the mean radius $\tilde{a}_1 = 12.8$ nm on the distance *D* between the surfaces of QD(A) and QD(B)

This effect is a significant increase in the binding energy of the ground singlet state exciton quasimolecule due to the fact that due to the presence in nanoscale interfaces (QD-matrix), the energy of the exchange interaction of the electrons with the holes (renormalized Coulomb interaction between electrons and holes) in the excitonic quasimolecule should be much greater than the energy exchange interaction between electrons and holes in a single crystal. Apparently, the latter fact opens the possibility of observing such excitonic quasimolecules at room temperature. The energy of the exchange interaction between electrons

and holes mainly contributes to the binding energy of an exciton quasimolecule, which is significantly greater than that for the energy of the Coulomb interaction between electrons and holes (i.e., their ratio ≤ 0.11). The estimations of the binding energy $E_b(\tilde{D},\tilde{a})$ of the singlet ground state of a quasimolecule are variational and may give low values of the binding energy ($E_b(\tilde{D},\tilde{a})$ and $E_b^{(1)}(D_1,\tilde{a}_1)$).

CONCLUSIONS

The binding energies of the exciton quasimolecule consisting of two germanium QDs acquire an anomalously high value that exceeds the binding energy E_b of the biexciton in germanium by almost two orders of magnitude. This effect is a significant increase in the binding energy of the ground singlet state excitonic quasimolecule due to the fact that because of their presence at nanoscale interfaces (QD-matrix), the energy of the exchange interaction of the electrons with the holes (renormalized Coulomb interaction between electrons and holes) in the excitonic quasimolecule should be much greater than the energy exchange interaction between electrons and holes in a single crystal. Such an effect opens up the possibility of using the exciton quasimolecules as an active medium in nanolasers emitting in the infrared region and operating on exciton transitions at room temperatures in the elementary base of quantum nanocomputers. The results presented demonstrate a fundamental possibility of creating unique quasiatomic nanosystems in the form of exciton quasimolecules, including natural systems with new physical characteristics.

On this basis, it is possible to construct new nanosystems or quasicrystals in which control of the symmetry and lattice constant will make it possible to realize unique physical effects and phenomena and to create new principles in materials behavior. Such quasimolecule excitons are promising to create new elements silicon infrared optoelectronics, including new infrared sensors.

Екситонні і екситонної квазімолекули стани в наносистемах напівпровідникових квантових точок

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В рамках модифікованого методу ефективної маси розвинуто теорію екситонної квазімолекули (утвореної з просторово розділених електронів та дірок) в наносистемах, що складаються з квантових точок германію, вирощених в кремнієвих матрицях. У штучній квазімолекулі дірки розташовані в об'ємах квантових точок германію, а електрони, рухаючись в матриці кремнію, локалізуються над сферичною поверхнею квантових точок германію. Варіаційним методом отримані залежності повної енергії, а також енергії зв'язку основного синглетного стану екситонної квазімолекули, як функції відстані D між поверхнями квантових точок, а також радіуса a квантової точки. Показано, що в енергію зв'язку екситонної квазімолекули основний внесок дає енергія обмінної взаємодії електрона з дірками, який істотно перевершує внесок, що обумовлюється енергією кулонівської взаємодії електрона з дірками. Встановлено, що виникнення екситонної квазімолекули в наносистемах має пороговий характер, і можливе в наносистемах, в якій відстань D між поверхнями квантових точок перевищує значення деякої критичної відстані $D_c^{(1)}$. Показано, що екситонна квазімолекула в наносистемах може існувати тільки при температурах нижче деякої критичної температури T_c. При температурах нижче критичної $T<T_c$ екситонна квазімолекуа розпадається на два штучних атоми (з просторово розділених електронів та дірок). Встановлено, що енергія зв'язку основного синглетного стану екситонної квазімолекули, що складається з двох квантових точок германію, є суттєвою величиною, яка перевершує енергію зв'язку біекситона в монокристалі кремнію майже на два порядки.

Ключові слова: *просторово розділені електрони і дірки, енергія зв'язку, дві германієві квантові точки*

Экситонные и экситонной квазимолекулы состояния в наносистемах полупроводниковых квантовых точек

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В рамках модифицированного метода эффективной массы развита теория экситонной квазимолекулы (образованной из пространственно разделенных электронов и дырок) в наносистемах, состоящих из квантовых точек германия, выращенных в кремниевых матрицах. В искусственной квазимолекуле дырки расположены в объемах квантовых точек германия, а электроны, двигаясь в матрице кремния, локализуются над сферической поверхностью квантовых точек германия. Вариационным методом получены зависимости полной энергии, а также энергии связи основного синглетного состояния экситонной квазимолекулы, как функции расстояния D между поверхностями квантовых точек, а также радиуса a квантовой точки. Показано, что в энергию связи экситонной квазимолекулы основной вклад вносит энергия обменного взаимодействия электрона с дырками, который существенно превосходит вклад, вызванный энергией кулоновского взаимодействия электроном с дырками. Установлено, что возникновение экситонной квазимолекулы в наносистеме, носит пороговый характер, и возможно в наносистеме, в которой расстояние D между поверхностями квантовых точек превышает значение некоторого критического расстояния $D_c^{(1)}$. Показано, что экситонная квазимолекула в наносистеме может существовать только при температурах ниже некоторой критической температуры T_c. При температурах ниже критической $T<T_c$ экситонная квазимолекула распадается на два искусственных атома (из пространсвенно разделенных электронов и дырок). Установлено, что энергия связи основного синглетного состояния экситонной квазимолекулы, состоящей из двух квантовых точек германия, является существенной величиной, превосходящей энергию связи биэкситона в монокристалле кремния почти на два порядка.

***Ключевые слова**: пространственно разделенные электроны и дырки, энергия связи, две германиевые квантовые точки*

REFERENCES

1. Yakimov A.I. Spatial separation of electrons and holes of quantum dots Ge/Si. *JETP Lett.* 2001. **73**(10): 529.
2. Yakimov A.I. Effects of electron-electron interaction in the optical properties of dense arrays of quantum dots Ge/Si. *JETP.* 2001. **119**(3): 574.
3. Smagina G.V., Dvurechensky A.V. Linear chains of quantum dots Ge/Si. *Semiconductors.* 2015. **49**(6):749.
4. Pokutnyi S.I. On an exciton with a spatially separated electron and hole in quasi-zero-dimensional semiconductor nanosystems. *Semiconductors.* 2013. **47**(6): 791.
5. Pokutnyi S.I. Excitons based on spatially separated electrons and holes in Ge/Si heterostructures with germanium quantum dots. *Low Temperature Physics*. 2016. **42**(12): 1151.
6. Pokutnyi S.I. Biexcitons formed from spatially separated electrons and holes in quasi-zero-dimensional semiconductor nanosystems. *Semiconductors.* 2013. **47**(12): 1626.
7. Pokutnyi S.I. Biexciton in nanoheterostructures of germanium quantum dots. *Opt. Eng.* 2017. **56**(6): 067104.
8. Pokutnyi S.I. Biexciton in nanoheterostructures of dielectric quantum dots. *J. Nanophotonics.* 2016. **10**(3): 036008.

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