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Dependence of Quantum Yield for Periodic Array of Doped Semiconductor Nanocrystals

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ABSTRACT We have studied and calculated the fraction of empty semiconductor nanocrystals which controls the quantum yield as a function of the average number of donors per nanocrystal and the nanocrystal size. We have shown that if donor reached the critical value of 1.8 there are no empty nanocrystals in nanocrystal array due to electron redistribution between nanocrystals and consequently photoluminescence vanishes. The relative intensity of the photoluminescence is strongly correlated with the transport properties of these array. Which provides information about the redistribution of the charges between nanocrystals affecting both quantum yield of photoluminescence of an array of nanocrystals and its hopping conductivity. We have found that empty nanocrystals became extinct and photoluminescence was quenched abruptly at an average number of donors per nanocrystal. It turned out that doping resulted in transport properties which were typical for disordered semiconductors. The number of donors in different nanocrystals was random. In the ground state of the nanocrystal array many nanocrystals were charged. The charged nanocrystals leaded to the random coulomb potential and to the coulomb gap in the density of localized electron states that determined variable range of hopping conductivity. It was also found that an array of small nanocrystals due to the quantuization-gap induced redistribution of electrons among nanocrystals. The obtained results were found in good agreement with previous results.

KEYWORDS Semiconductor, Nanocrystal, Quantum Yield, Donor, Redistribution, Array, Transport, Doping.

INTRODUCTION

Shim et al.[1] Wang et al.[2] and Talapin et al.[3] studied that due to intrinsic difficulties of nanocrystal doping the impurity atoms[4] in the introduction of carriers into nanocrystals was reached by putting the electron donating molecules in the vicinity of the nanocrystal surface i.e. remote doping and applying external electric fields for electrochemical doping[5]. Brovelli et al.[6] and Kang et al.[7] demonstrated the carrier introduction into a nanocrystal via electronic impurity doping is done. In order to improve transport properties of a three dimensional array by doping it with electronic impurity is shallow donors, a donor electron be delocalized within a nanocrystal by the confinement potential. Ekinov et al.[8] presented that if the nanocrystal diameter D is smaller than six Bohr raddii of electrons $a_B = h^2 k_{NC} / me^2$, where e is the electron charge, k_{NC} is the dielectric constant and m is the effective electron mass of a semiconductor, the above conditions is satisfied. Moroz et al.[9] reported that the average number of donors per nanocrystal. Surface traps are constantly decreasing due to improved technology. The use of inorganic ligands drastically reduces the number of surface states. Semiconductor nanocrystals are used as building blocks for new solid materials with bulk properties which don not exist in conventional solids. From monodisperse spherical nanocrystals it is possible to assemble a closely packed nanocrystal solid a three dimensional periodic structure with spacing between nanocrystals much smaller than the nanocrystal diameter[10-12]. In bulk semiconductors doping is critical for nanocrystal solids which are electrically insulating. Adding charged carriers dramatically increases electronic mobility of ananocrystal array and opens new possibilities for many applications including field effect transistors, light emitting devices, photodetectors and solar cells[13-16]. Jee et al.[17] studied and calculated electronic bands density of states and charge transfer and related physical properties of gallium nitride with the use of linear combination of atomic orbital formalism. This calculation also carrying out selfconsistent calculations for gallium nitride using minimal basis set. Initial charge density for gallium nitride was calculated using atomic orbital of gallium and nitrite. The calculated energy conduction bands, band gaps and effective masses of carriers agreed with experimentally observed values. Aparajita et al.[18] studied electronic structure and optical properties of silicon nanocrystals by using density functional theory. The silicon nanocrystals of diameters 1.0 nanometer upto 4.6 nanometer using the Pseudopotential density functional theory were analysed. It was found that the concellation of many body effects and the excitons effects have given rise to density functional theory the highest occupied molecular orbital the lowest unoccupied molecular orbitals gaps comparable with the experimental optical gaps. They found that the narrowing of valence band states contributed to the blue shift of the band gap as a function of reduced size of nanocrystals. Kumari and Mishra[19] studied a phenomenological lattice dynamical model for the zinc blende and diamond structure crystals. The model incorporated the long range coulomb interaction for zinc blende crystals which are partially ionic bonding. They found that the obtained expectation for improving of interaction terms between bond stretching and bond bending internal coordinates are used. Skinner et al.[20] studied theoretically as function of the average number of donors and the nanocrystal diameter. Bae et al.[21] studied Auger recombination of a photo-excited electron hole pair. In such a process the annihilation energy of the electron-hole pair is transferred to an extra electron. The rate of non radioactive Auger processes is much larger than the rate of the radioactive recombination. Even one extra electron can quench photoluminescence from a nanocrystal with almost hundred percent probabilities. The obtained results were compared with previously obtained results.

METHOD

We have considered that if nanocrystals are neutral, the number of empty nanocrystals is equal to the number of nanocrystal with no donors. When donors are added randomly to each nanocrystal, the probability P(N) that a given nanocrystal has exactly N donors is given by the poisson distribution.

$$P(N) = \frac{v^N}{N!}\exp(-v)$$

$f(v)$ can be obtained at $N=0$. The poisson fraction is $f_p(v)=\exp(-v)$. $f(v)$ gives only the upper bound for $f(v)$, so that $f(v)<f_p(v)$, because electrons redistribute between nanocrystals in order to minimize their total energy. In order to calculate the fraction of empty nanocrystals we have assumed that nanocrystals are identical spheres of diameter D that form a three dimensional cubic lattice structure. We have assumed that the overlap of electron state of neighboring nanocrystals is so small that a small disorder originating from small fluctuations of diameters D and a random coulmb potential leads to Anderson localization of each electron in one of the nanocrystals. As a result each nano crystal has exactly an integer number of electrons. At the same time in the case $D<6a_B$, the wave function of a donor electron is delocalized within a nano crystal. Suppose that the wave function is close to zero at the nanocrystal surface due to large confining potential barriers created by the insulator matrix surrounding nanocrystals. Under these conditions the Kinetic energy $E_Q(n)$ of the nth electron added to a nanocrystal in the parabolic band approximation is

$$E_Q(n)=\frac{h^2}{mD^2}\times\begin{cases}0, & n=0\\ 19.74, & n=1.2 \quad (1S)\\ 4.38 & 3\le n\le 8 \quad (1P)\end{cases}$$

As a result, the first two electrons added to a nanocrystal fill is its (1 S) level, the next six fill its 1P level. The kinetic energy of electrons is only a part of the total energy of the nanocrystal. Calculating the total coulomb energy of the system is the positions of positive donors are random within the nanocrystals volume. For the solution of our problem a significant simplification is available because the internal dielectric constant k_{NC} typically is much larger than both the external dielectric constant k_i of the insulator in which the nanocrystals are embedded and the overall effective dielectric constant k of the array of nanocrystals. The large internal dielectric constant k_{NC} implies that any internal charge q is essentially completely compensated by the nanocrystal dielectric response, which leaded to homogeneous redistribution of the charge major part, $q(k_{NC}-k)/k_{NC}$, over the nanocrystal surface. In this way each semiconductor nanocrystal has been considered as a metallic one interms of its coulomb interactions, namely total coulmb energy i.e. self energy is equal to $\frac{(N-n)e^2}{kD}$. These approximation constant interaction models, which is individually used for quantum dots. We have neglected a donor position dependent correction to the Kinetic energy $E_Q(N)$ from coulomb interaction of an electron with a donor. This correction by the order of magnitude is equal to $\frac{e^2}{k_{NC}}D$. If $k<<k_{NC}$, this correction is always a smaller than charging energy and much smaller than the S – P gap energy, which induces redistribution of electrons. The gap $\delta(E)=E_Q(3)-E_Q(2)$ between the 1 S and 1 P levels of nanocrystal and the energy of adding one electron to a neutral nanocrystal $\frac{e^2}{kD}$, which is called the charging energy

$$\Delta=\frac{\delta E}{\frac{e^2}{kD}}=\frac{20.64k\hbar^2}{me^2D}=20.64\frac{k}{k_{NC}}\frac{a_B}{D}.$$

Which grows with decreasing nanocrystal diameter D. estimating this parameter, we have considered CdSe nanocrystals with $k_{NC}\approx 9.2$ and $D=5$nm arranged in a crystalline array with lattice constant $D'=6nm$. Assuming that $k_i=2$, the Maxwell-Garnet formula then gave $k\approx 3.2<<k_{NC}$. Using $m\approx 0.12m_e$, where m_e is the electron mass, we have $a_B\approx$ 4nm, $l^2/kD\approx$ 0.08eV and $\Delta\approx$ 5.7. In order to calculate $f(v)$ at any Δ we have taken out the coulomb interaction between charged nanocrystals. We have used the model of three dimensional arrays with the Hamiltonian

$$H = \sum_i \left[\frac{e^2 \left(N_i - n_i\right)^2}{kD} + \sum_{k=0}^{n_i} E_Q\left(k\right) \right] + \sum_{(i,j)} \frac{e^2 \left(N_i - n_i\right)\left(N_j - n_j\right)}{k r_{ij}}$$

Where $e\left(N_i - n_i\right)$ is the charge of the i^{th} nanocrystal. The first term of the Hamiltonian is the sum of self emergies of nanocrystals the second term is the total quantum energy of n_i electrons in the *i*th nanocrystal and the last term is responsible for the coulomb interaction between different nanocrystals. The interaction between two nanocrystals i and j at a distance r_{ij} is written as $\frac{q_i q_j}{k r_{ij}}$. This approximation is for large distance r_{ij}. Even for two nearest neighbor nanocrystals in a typical array this approximation well established. For parameters D = 5 nm and D=6 nm the energy of interaction of the two nearest charged metallic spheres has been approximated as the interaction of two central point charges $\frac{q_i q_j}{k r_{ij}}$ with an accuracy of 1 % . This is also applicable for two nearest neighbor nanocrystals if $k_{NC} >> k$.

RESULTS AND DISCUSSION

The function $f\left(v\right)$ obtained for $\Delta >> 1$ is shown in Figure (1). It shows that $f\left(v\right)$ vanishes at $v = v_c \approx 1.8$ and $f\left(v\right) = 0$ at $v > v_c$. The numerical result for $\Delta = 5$ is close to analytical result for $\Delta >> 1$. The long range random potential originating from the last term and have been ignored laeds to the avoided threshold in the vicinity $v = 1.8$. Curves for smaller Δ shows the 1P–1S gap induced carrier redistribution weakens and $f\left(v\right)$ approached $f_p\left(v\right)$. To quantify the charge redistribution we have considered nanocrystals in which $f\left(v\right) > \frac{f_p\left(v\right)}{2}$ while nanocrystal array obeying the opposite inequality $f\left(v\right) > \frac{f_p\left(v\right)}{2}$ which is shown in graph (1). The conductivity is described by the Efros-Shklovshii variable range hopping law for $\Delta \gtrsim 0.5$ and $v \gtrsim 0.7$ and the thermally activated nearest neighbor hopping law in other cases. Thus there is correlation between quantum yield and the conductivity of an array of nanocrystals. Graph (2) shows the function $g_p\left(v\right)$ in the range of $1 < v < 3$, $g_p\left(v\right)$ is close to 0.5R We have neglected the radioactive decay of chargd nanocrystal, assuming that the ratio R of the radioactive recombination rate to the Auger rate for a nanocrystal with and extra electron is very small, hence $R << 1$. At relatively large $v > 2$ the fraction of empty nanocrystals $f\left(v\right)$ became very small. We have taken into account photoluminescence from nanocrystals with electrons i.e. filled nanocrystals. We have assumed that the rate of the Auger process linearly increased with the number of electrons in a nanocrystal n, so that the quantum yield from this nanocrystal is proportional to $\frac{R}{n}$. Thus normalized to undoped nanocrystal array of quantum yield of all filled nanocrystal $g\left(v\right)$ is

$$g\left(v\right) = R \sum_{n=1}^{\infty} \frac{w\left(n\right)}{n}$$

where $w(n)$ is the function of nanocrystals which n electrons in the nanocrystal array. At small Δ there is no electron redistribution in the array of nanocrystals i.e. $n = N$, we have

$$g_p(v) = Re^{-v}\int_0^v \frac{e^x - 1}{x}dx$$

The function $g_p(v)$ is shown in Figure (2). The role of the redistribution of electrons at larger Δ, we have simulated the ground state of electrons as in an array of nanocrystals and computed the distribution function $w(n)$ averaged over ten realization of a $20\times 20\times 20$ nanocrystal array, we have calculated $g(v)$ for $\Delta = 0.5$ and $\Delta = 5$. These numerical results have been shown in graph (2). We have found that at small $\Delta = 0.5\, g(v)$ practically coincides with $g_p(v)$. Result for $g(v)$ for $\Delta = 5$ does not differ by more than 20%. The obtained results were compared with previously obtained results and were found in good agreement.

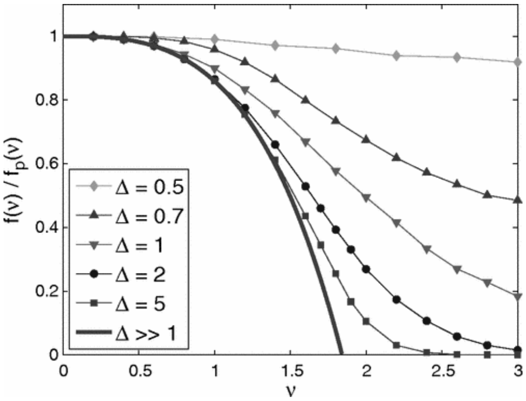

Figure 1: The dependence of the fraction of empty nanocrystals $f(v)$ in an array of doped nanocrystals on the average number of donors per nanocrystal *v.*

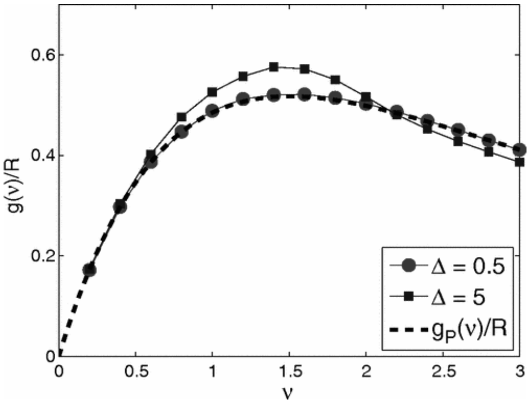

Figure 2: The dependence of the photoluminescence quantum yield of all filled nanocrystals $g(v)/R$, related to the quantum yield of an undoped array, on the average number of donors per nanocrystal *v*. The calculations were conducted for the ratios of the 1S -1 P gaps to the charging energies $\Delta = 0.5$ and 5.

CONCLUSION

We have studied dependence of the quantum yield for periodic array of semiconductor nanocrystals on the doping level and nanocrystal size. Computer simulation and analytical theory were used to find a fraction of such empty nanocrystals as a function of the average number of donors per nanocrystal and nanosize. For an array of small spherical nanocrystals the quantization gap between 1 S and 1 P levels leaded to transfer of electrons from nanocrystals with large number of donors to those without donors. We have found that average number of donors v per nanocrystals and the nanosize. If the v reached the critical value of 1.8 there are practically no empty nanocrystals and consequently photoluminescence vanished completely. It has provided that redistribution of charges between nanocrystals affected both quantum yield of photoluminescence of an array of nanocrystals and hopping conductivity. The obtained results were compared with previously obtained results of theoretical and experimental research woks and were found in good agreement.

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