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The Impact of the Colloidal Quantum Size Dispersion on the Absorption Coefficient of the Photodiode on their Base

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It was demonstrated within a simple theoretical model that the size dispersion of the colloidal quantum dots ensemble influence essentially on the absorption coefficient of the photodiodes on their base, and therefore is to be taken into consideration within the description of the operation of modern photodetectors for the Infra-Red range. The increase of dispersion of the nanoparticles ensemble in the photodetector leads to essential decrease of the absorption coefficient at the frequency, which corresponds the absorption in the nanoparticles of the mean size. The typical dependence of the absorption coefficient on frequency includes the sharp increase at the frequencies, close to the intrinsic absorption edge of the quantum dot, followed then by the decrease according to formula $1/\left(\hbar\underline{\omega} - E_g^{(b)}\right)^{3/2}$, where the denominator includes the gap value in the bulk material, and later – the further increase due to transitions including the upper energy levels of the nanoparticle.

Keywords: Colloidal quantum dots, photodiode, size dispersion, absorption coefficient.

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The transformation stage, connected with transition from bulk semiconductor materials to nanostructured systems, occurs in modern optoelectronics. A special place belongs here to colloidal quantum dots (CQD) – nanocrystals, synthesized by chemical methods, which permit to modulate the gap width by changing the particles size (see e.g. [1] and Refs. therein). This technology permits to fabricate cheap, flexible and highly effective photodetectors, especially for the short-wave Infra-Red range (SWIR), which are of crucial importance for the night vision systems, autonomous navigation (LiDAR) and bio-medical diagnostics.

The CQD's are treated, because of their unique optoelectronic properties, as the most perspective alternative to the traditional epitaxial materials (like InGaAs and HgCdTe) for the fabrication of photodetectors of the new generation, especially for the IR range. The evolution of photodetectors on the CQD's base had covered the way from the simple photoconductors, which ensure the high amplification factor due to the large lifetime of carriers, captured by the traps, but operate slowly (the bandwidth is < 100 Hz), up to fast acting photodiodes [2].

E.g., the modern photodiodes on PbS base reach the external quantum efficiency (EQE) over 80% and specific detectivity $8 \cdot 10^{11}$ Jones in the range up to 1550 nm, with the response time of 10 ns order [3]. These high figures of merit became possible due to the new strategies of surface passivation, including the substitution of the long organic ligands (the oleic acid) by the compact atomic ligands (halides: I, Br), which improve electronic bonds between nanocrystals and decrease the density of surface traps [3, 4, 5].

However, the consideration of the ensemble statistics remains a problem for a theoretical description of the real device on CQD's base. Despite all the achievements of colloidal chemistry, it is hardy possible to get the ensemble of nanoparticles of ideally the same size. The real films are characterized by the size distribution of nanoparticles, which is described usually by the Gauss function [6].

If the sizes of quantum dots are distributed according to the normal law, this yields to the corresponding distribution of the gap energy values, which are described

by the Brus formula and determine the absorption range of photodiode [1, 7]. Because of the non-linear dependence (the inverse quadratic one) the symmetrical distribution of sizes transforms into the asymmetrical distribution of energies.

The standard deviation for diameter is 5-10% for the typical ensembles of PbS quantum dots; this leads to energy dispersion of tens of meV order [3]. This parameter is crucial, because it is comparable with thermal energy at room temperature (26 meV), and it influence essentially the thermodynamics and kinetics of charge carriers.

At the same time, there are practically no theoretical investigations of the impact of the ensemble statistics on the parameters of real devices on the CQD's base (work [8] belongs to the rare exclusions). Therefore the goal of our work is to build a clear theoretical model, which would permit to describe an absorption coefficient (and thus the photocurrent) in the photodiode on the CQD's base, taking into consideration the size distribution in their ensemble.

A standard scheme of photodiode with CQD's is presented in Fig.1. It includes the internal energy barrier and the related Space Charge Region (SCR). This SCR is wide enough, and the quantum tunneling through it can be neglected. However, if there are CQD's in the SCR, with an energy of optical transition smaller, than the gap width in the dielectric or semiconductor matrix they are placed in, then the birth of an electron-hole pair can cause a current through the device.

The internal quantum efficiency of the photodiode can be high enough, if the life time of carriers, generated by light, is longer, than the time of the drift of these carriers through the SCR:

$$\tau \geq \frac{L^2}{\mu V_b} \qquad (1)$$

here L is the SCR width, μ is carriers mobility, V_b is energy of the internal potential barrier.

The mobility of carriers in the SCR is usually small, 10^{-3} – 10^{-2} cm^2 /V·s, and to increase it is one of the main challenges for the photodiode designers. Therefore for L of 100 nm order the drift time is not smaller than a few tenths of μs. Fortunately, the lifetime of excitons in these systems can be essential, longer, than 1 μs, and therefore the inequality (1) can be fulfilled. This enables high values of the internal quantum efficiency [2].

The electron and hole energies in the quantum dot (see Fig.1) in the effective mass approximation are described by Schrödinger equation for the particle in the spherical quantum well. The energy of the first excited state of the nanocrystal with R radius (the effective gap width $E_g(R)$) is determined by the Brus formula [7]:

$$E_g(R) \approx E_g^{(b)} + \frac{\pi^2\hbar^2}{2m_r R^2} - \frac{1{,}8e^2}{\varepsilon_1 R}, \qquad (2)$$

where $E_g^{(b)}$ is the gap width in the bulk semiconductor; $m_r = \frac{m_n m_p}{m_n + m_p}$ is the exciton reduced effective mass (m_n and m_p are the electron and hole effective masses); $\hbar$ is the reduced Plank constant; e is electron charge; ε_1 is the quantum dot permittivity.

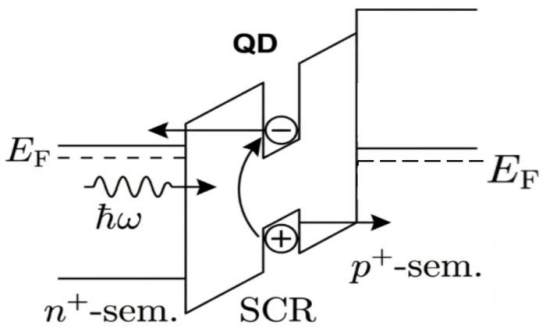

Fig. 1. Principal scheme of the photodiode on the CQD's base: the SCR, which consists from the dielectric with QD's placed into it, is situated between the strongly doped *n*- and *p*-type semiconductors. The absorption of photon induces a current through the device.

The first addend in the right part of (2) corresponds the gap width in the bulk material, the second one describes the kinetic energy of localization ("particle-in-a-box energy"), which increases the gap with the decrease of radius, the third one takes into consideration the Coulomb interaction between an electron and a hole, which decrease somewhat the energy of irradiative transition.

However, when we treat the energy of photon, which causes the up transition of electron between the two energy levels in the moment of time, when the electron-hole pair do not exist yet, this last addend in (2) should not be taken into consideration for the calculation of the absorption coefficient. The energy of the absorbed photon is determined by correlation:

$$\hbar\underline{\omega}_0 = E_g^{(b)} + \frac{\pi^2\hbar^2}{2m_r R_0^2} \qquad (3)$$

Therefore the last addend in (2) determines the energy of Stocks shift between the lines of absorption and irradiation in the quantum dot.

The absorption spectrum for a system without dispersion would consist from the clear definite peaks, which correspond the transitions between the discrete levels, among others, at frequency ω_o, which corresponds a transition between the principal quantum levels of an electron and hole in a spherical nanoparticle with radius R_o (3). However, an interaction with vibration modes at the finite temperature T leads to a smearing of energy levels and to a possibility of transitions in spectral range between ω_1 and ω_2, which are higher and lower than ω_o (see Fig. 2):

$$\hbar\underline{\omega}_{1,2} \approx E_b + \frac{\pi^2\hbar^2}{2m_r R^2} \pm 2kT. \qquad (4)$$

This causes at room temperature the smearing of line with frequency ω_o into a band with a width of 100 meV order.

The absorption coefficient α_a of the absorbing media in the SCR (Fig. 1) is usually presented as a product of the concentration of the quantum dots N_o and the cross-section α_a of the optical absorption of a separate quantum dot.

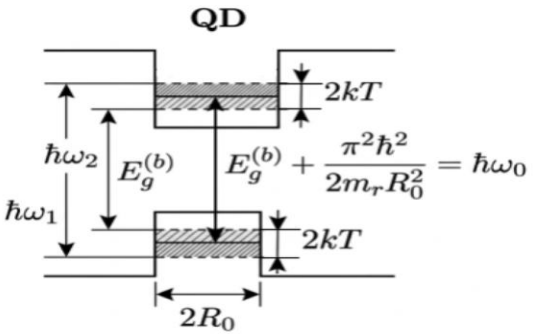

Fig.2. Energy ranges for the permitted transition in a CQD: $\hbar\underline{\omega}_0$corresponds the transition between the lowest quantum levels of electron and hole in the QD with radius R_o.

However, if we have the statistical ensemble of the quantum dots with the mean radius R_o and the standard deviation *s,* the absorption coefficient with allowance for dispersion would be written as:

$$\alpha_0(\hbar\underline{\omega}, R_0, s) = N_0 \int_0^\infty F(R_0, R, s)\sigma_\alpha(\hbar\underline{\omega}, R)dR \qquad (5)$$

The normal distribution function for the case R_o>>s needs no renormalization from the complete axis [-∞,+∞] to a half an axis [0,+∞] and can be written in standard form as:

$$F(R_0, R, s) = \frac{1}{\sqrt{2\pi}s} exp\left(-\frac{(R-R_0)^2}{2s^2}\right) \qquad (6)$$

The absorption cross-section for the spherical nano-particle within the Bruggeman effective media theory is usually written [9] as:

$$\sigma_\alpha(\hbar\underline{\omega}, R) = \frac{4}{3}\pi R^3 \frac{n_1}{n_2}\left|f(\hbar\underline{\omega})\right|^2 \alpha_b(\hbar\underline{\omega}) \qquad (7)$$

In eq.(7) $\alpha_b(\hbar\underline{\omega})$ is an absorption coefficient of the bulk material, $n_{1,2}$ are refraction indexes for a semiconductor material of a quantum dot and a dielectric material, which is a medium for this quantum dot. The local field correlation coefficient is presented as

$$f(\hbar\underline{\omega}) = \frac{3m_2^2}{m_1^2+2m_2^2} \qquad (8)$$

where $m_{1,2}$ are complex reflection indexes for semiconductor and dielectric. There is no absorption in the dielectric, therefore $m_2 = n_2$.

The restrictions, imposed on the absorbed photon energy by eq.(4), leads to the fact, that each photon energy $\hbar\omega$ from this band corresponds the range of the quantum dot radius values, for which the absorption is possible:

$$R_{1,2} = \frac{\pi\hbar}{\sqrt{2m_r\left(\hbar\underline{\omega} - E_g^{(b)} \pm 2kT\right)}} \qquad (9)$$

Outside the range $[R_1, R_2]$ the transition is forbidden, therefore the limits of this range are to be taken as integration limits in eq. (5). By introducing the new dimensionless integration variable and dimensionless parameters $r = R/R_0$, $r_{1,2} = R_{1,2}/R_0$, $b = s/R_0$, we get an expression for the absorption coefficient:

$$\alpha_\alpha(\hbar\underline{\omega}, R_0, s) = \frac{4}{3}\pi N_0 R_0^3 \frac{n_1}{n_2}\left|f(\hbar\underline{\omega})\right|^2 \alpha_b(\hbar\underline{\omega}) Int;$$

$$Int = \frac{1}{\sqrt{2\pi}b}\int_{r_1}^{r_2} r^3 exp\left(-\frac{(r-1)^2}{2b^2}\right) dr \qquad (10)$$

The dimensionless integral in eq. (10) can be easily calculated for the two limit cases.

A). If the standard deviation in (6) trends to zero (the case without the dispersion; in this case $r_2 - r_1 \gg b$, and the integration limits can be taken from 0 to ∞), we get:

$$Int \approx \int_0^\infty r^3\delta(r-1)dr = 1 \qquad (11)$$

B). If the dispersion is essential, $r_2 - r_1 \ll b$, then r in front of the exponent in (10) can be substituted by it's mean value 1 for a narrow interval between r_2 and r_1, and the value of the exponent itself is also close to 1. This yields

$$Int \approx \frac{r_2 - r_1}{\sqrt{2\pi}b} \equiv \frac{R_2 - R_1}{\sqrt{2\pi}s} \qquad (12)$$

After substituting (9) into (12) and carrying an expansion using a small parameter (this can be done, if the quantum dot mean radius is small enough, and the energy of optical transition is essentially greater than the gap width in the bulk material), we finally get:

$$Int \approx \sqrt{\frac{\pi}{2}}\frac{\hbar}{s\sqrt{2m_r\left(\hbar\underline{\omega} - E_g^{(b)}\right)}}\frac{2kT}{\left(\hbar\underline{\omega} - E_g^{(b)}\right)} \qquad (13)$$

For the general case this integral is presented in Fig.3 as a function of $r_2 - r_1$ for the different values of the dimensionless deviation b. It can be seen well from the figure, that for the values b= 0.2 and greater a transition to the case, described by formula (12), occurs.

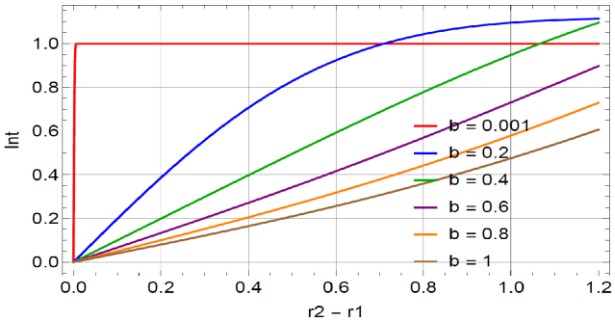

Fig. 3. Integral *Int* in (10) as a function of $r_2 - r_1$ for the different values of dispersion b (0.001, 0,2, 0,4, 0,6, 0,8, 1).

As we can see from eq. (12) in comparison with eq. (11), the increase of dispersion in the nano-particles ensemble leads to essential decrease of the absorption coefficient at the frequency, which correspond the absorption of nano-particles with mean radius (3). In this case the absorption coefficient (10) dispersion with frequency is determined by eq. (13) dominantly, because the dispersion of all the other quantities in eq. (10) at the frequencies from in the range (4) is not essential, because

these frequencies are far (due to the small size of nano-particles, see (3)) from the frequency of the internal absorption edge in the bulk. The strongest decrease of the absorption coefficient in the systems with dispersion occurs in the low temperature range, which corresponds (13).

Therefore the dependence of the absorption coefficient in the general case has a form, presented in fig.4: after the sharp increase at the frequencies, close to ω_1, the decrease according to the law $1/\left(\hbar\underline{\omega} - E_g^{(b)}\right)^{3/2}$ occurs, and then the further increase takes place, determined by the transitions with the participation of the upper quantum levels of the quantum dot. This corresponds qualitatively the result, obtained experimentally for the InP CQD's with the size 1 – 5 nm (see Fig. 1a in Ref. [10]).

So, it was demonstrated in our work on the base of a simple and transparent theoretical model, that the dispersion of sizes of the CQD's makes an essential impact on the absorption coefficient of the photodiode on these CQD's base and is to be taken in consideration within the modeling of the operation of modern IR range photodetectors.

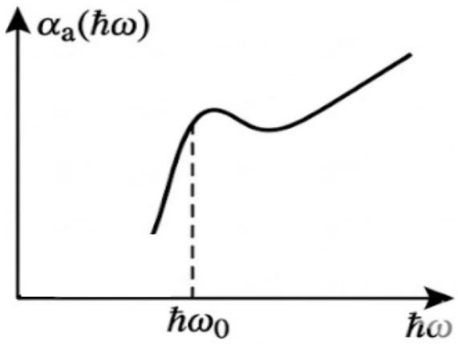

Fig. 4. Typical form of the absorption coefficient dependence on the photon energy for the photodetector on CQD's base.

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Вплив дисперсності колоїдних квантових цяток за розмірами на коефіцієнт поглинання фотодіода на їх основі

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На основі простої теоретичної моделі показано, що дисперсність ансамблю колоїдних квантових цяток за їх розмірами суттєво впливає на коефіцієнт поглинання фотодіодів на їх основі і має обов'язково враховуватися при описі роботи сучасних фотодетекторів для інфрачервоного діапазону. Зростання дисперсності ансамблю наночастинок у фотодетекторі призводить до помітного зменшення значення коефіцієнта поглинання на частоті, що відповідає поглинанню для наночастинок середнього розміру. Типова залежність коефіцієнту поглинання фотодетектора від частоти включає різке зростання на частотах, близьких до краю власного поглинання наноцятки, потім спад за законом $1/\left(\hbar\underline{\omega} - E_g^{(b)}\right)^{3/2}$, де до знаменника входить величина забороненої зони в об'ємному матеріалі, а потім – дальше зростання, обумовлене переходами з участю вищих квантованих енергетичних рівнів наноцятки.

Ключові слова: колоїдні квантові цятки, фотодіод, дисперсність, коефіцієнт поглинання.