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Current transfer in the tunneling microscope probe–tunnel gap–layer of A^3B^5 and A^2B^6 semiconductors quantum dots system under illumination

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Received December 29, 2024
Revised December 29, 2024
Accepted December 29, 2024

In this work, the features of current transfer in the system of a tunneling microscope probe–tunnel gap–layer of quantum dots of A^3B^5 and A^2B^6 semiconductors under the influence of external electromagnetic radiation of the visible spectral range are investigated. It is established, that the peaks on the normalized differential tunneling current-voltage characteristics corresponding to discrete levels of the energy spectrum of the studied quantum dots can disappear under illumination, which is due to the inclusion of photogenerated electrons in the current transfer process.

Keywords: semiconductor quantum dots, energy spectrum, photogeneration, tunnel current-voltage characteristics.

Introduction

Modern electronics is based on physical effects that manifest themselves in objects and systems, the sizes of active areas in which range from units of nanometers to tens of centimeters. Miniaturization of the sizes of electronic elements, devices and devices has been the most important trend in development of electronics globally for many years and decades [1–3].

Nanoscale particles and quantum dots are among the important and promising objects of research in these areas due to their unique properties. Among them, semiconductor quantum-dimensional objects are of particular interest for micro- and nanoelectronics [4–6]. For low-dimensional semiconductor systems, the issues of electronic states, electron behavior, and current transfer are relevant and most fundamental from the standpoint of electronic industry [7–11]. These issues require detailed theoretical and experimental research. In particular, much attention is paid to the study of tunneling current transfer through semiconductor quantum dots by measuring the current-voltage characteristics (CVC) on a scanning tunneling microscope due to the possibility of current flowing electronically [12–14]. The process of tunneling current transfer through semiconductor quantum dots can be influenced by various external factors, such as temperature or lighting, causing new effects or making changes in the process to be reviewed when further examining the measurement results.

Our studies of semiconductor quantum dots by method of normalized differential tunneling CVCs showed that the peaks on the differential CVCs correspond to the levels of energy spectrum of the studied quantum dots (QDs), which allows both determining the position of these levels and analyzing the conduction mechanisms of the studied structures, calculating some parameters of QDs and a number of other important characteristics of electronic processes in them [15–17]. The effect of temperature on the differential CVCs pattern of tunneling current transfer from a metal substrate to a metal probe STM through semiconductor QDs has already been shown [18]. Therefore, in this work, the influence of illumination in different parts of the optical range on the process of tunneling current transfer in a similar system was investigated.

1. Research methodology

Semiconductor QDs of InSb (A^3B^5) and CdSe (A^2B^6) compounds were selected as the objects of the study due to the fact that for many years they have been among the most relevant and interesting semiconductor materials from a practical standpoint, since they are straight-band, have a high quantum yield of luminescence and photo-stability, which is why they are widely used in optoelectronics. They also have very important characteristic features of the energy spectrum and extremely small values of the effective mass of conduction electrons.

The quantum dots represented a structure of a „shell-free nucleus“ of InSb and CdSe. The methods of synthesis of QDs studied in this work are described in detail papers [17,19–22]. Oleic acid for CdSe QD solution and trioctylphosphine (TOP) for InSb QD solution were used as stabilizers. The obtained solutions were preliminarily purified from an excessive amount of stabilizer, after which chloroform was added until a QD concentration of $(5-6) \cdot 10^{-3}$ M was obtained. The QDs used in the experiments were themselves the complex-shape objects, which, however, were still closer to cubic for InSb and spherical for CdSe (QD images obtained using transmission electron microscope (TEM) Libra 120 (Zeiss, Germany) are shown in Fig. 1).

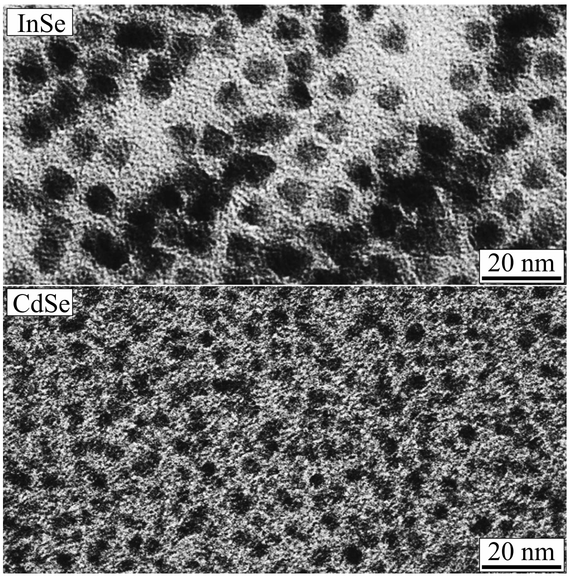

Figure 1. TEM images of the used QDs InSb and CdSe.

The absorption spectra of QD solutions are shown in Fig. 2.

For the formation of structures based on nanoscale objects that are convenient for investigation by various methods, including scanning tunneling microscopy, promising technologies are those that use the effects of self-organization, when structures of certain sizes form themselves under the influence of internal forces acting during growth, for example, Langmuir–Blodgett technology [23–25].

Using Langmuir–Blodgett methods the monolayers of selected QDs were formed, after which they were transferred to solid substrates for further investigation. Solutions of colloidal QDs with a concentration of $5 \cdot 10^{-3}$ M were added to the water surface in a volume of 50 l, after which the layer on the surface was compressed by barriers to a surface pressure corresponding to the state of a tightly packed monolayer without collapse or formation of a multilayer structure (12 mN/m for CdSe and 16 mN/m InSb, respectively). Next, the obtained monolayers were transferred to solid substrates, which themselves were a glass coated with indium-tin oxide (ITO). In this way, structures suitable for being studied by scanning tunneling microscopy were formed (Fig. 3).

The obtained samples were examined using a scanning probe microscope SOLVER NANO (NT-MDT, Russia). The method of measuring and analyzing the tunneling CVCs is similar to that described in jcite26, the distance between the QD and the probe was about 1–2 nm, and the electric field strength was more than $5 \cdot 10^6$ V/cm at voltages above 0.5 V. In the present study, the experiments were carried out with additional illumination of the samples in the optical range. The light from green LED (wavelength 530 nm, quantum energy 2.3 eV), blue LED (450 nm – 2.75 eV) and red LED (640 nm – 1.9 eV) was used. Radiation power in all cases was ~ 60 mW. The distance from the light source to the sample was of the order of 10–12 mm. The radiation power density on the surface of the samples was $\sim 5 \cdot 10^{-4}$ W/cm^2.

2. Results and discussion

In the system of the tunneling microscope probe –nanometer gap–layer of QD–substrate with a conductive electrode layer ITO, electrons are tunneled from filled electronic states near the Fermi level of ITO into the tunneling microscope probe at the appropriate polarity of the applied voltage. If the energy of the tunneling electron coming from the metal contact coincides with the energy of one of the QD levels, the probability of tunneling increases dramatically. The model representations of this process, considered in the works of authors jcite17,26,27, are schematically shown in Fig. 4 at an offset voltage of V corresponding to conditions for the process of electron tunneling from ITO into probe of microscope through the appropriate energy levels of QD.

The analysis of experimental data was carried out using the technique of normalized differential tunneling CVC — curves of $(dI/dV)/(I/V)$ versus voltage V (with a negative potential at ITO electrode). This technique is one of the most effective and information-rich to experimentally study the energy spectrum of the local density of electronic states in quantum dots [17,20,28].

The peaks on the normalized differential tunneling CVC correspond to discrete levels of energy spectrum of the studied QDs which are largely determined by the material, characteristic dimensions, and shape [17,29]. They are related to the change in conditions of current passage through the structure, as described above. Since the main current transfer is carried out primarily and predominantly through the first energy level of QD, in future it is this process that will be focused on in the analysis.

It is known that the mechanism of auto-electronic emission is the dominant mechanism of current transfer [30]. Approximate expression for the current density of auto-electronic emission rpoviding for the tunneling through the first level of a quantum dot (E_{c1}) in the system metal–quantum dot–nanometer gap–metal is represented by the formula [31]:

$$j_s \approx q(n_0 + n_1)\left(\frac{kT}{2\pi m_0}\right)^{1/2} \exp\left[-\frac{8\pi\sqrt{2m_0 A_s^3}}{3hqE}\,\theta\right], \quad (1)$$

$$n_1 \approx N_{\text{eff}} \exp\left[-\frac{E_{c1}}{kT}\right],$$

$$N_{\text{eff}} = \frac{1}{2\pi^2}\left(\frac{2m^* kT}{\hbar^2}\right)^{3/2},$$

where q — charge module and electron mass; θ — Nordheim function value; A_s — work function of electron leaving the semiconductor; E — local strength of electrical field; other symbols in (1) are standard.

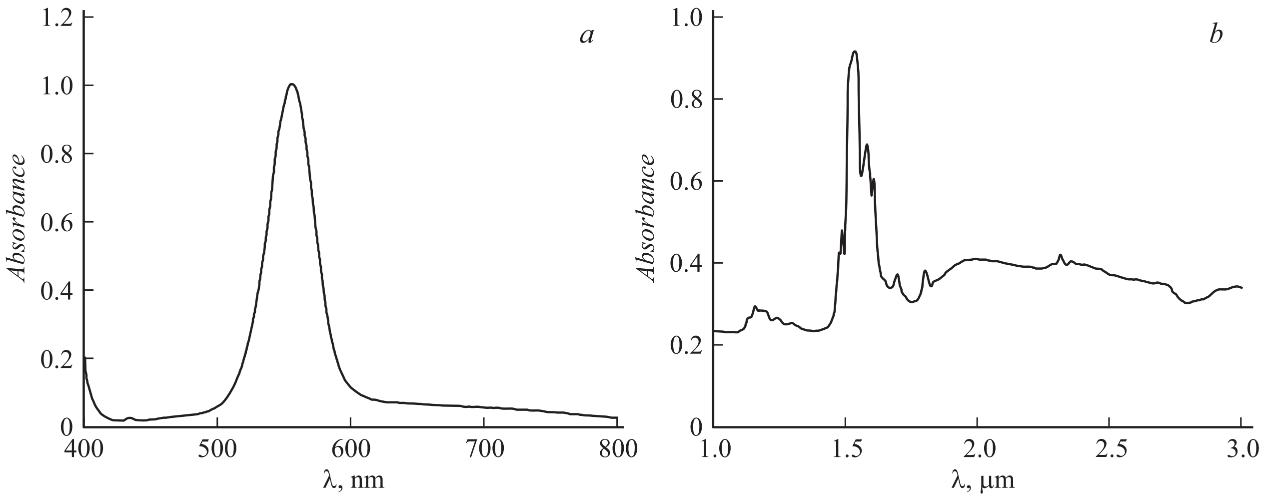

Figure 2. Absorption spectra of used QDs: *a* — CdSe, *b* — InSb.

To study the effect of electromagnetic radiation in the visible range on current transfer in this system, samples with QD were illuminated by radiation with different wavelengths. If the energy of the light quantum is sufficient to transfer an electron from level E_{v1} (the amount of energy of the first level of hole, measured from the bulk material's valence band top) to level E_{c1} (energy of the first level of the quantum dot electron, measured from bottom of the bulk material's conduction band), additional photo-generated electrons will appear and, accordingly, the photocurrent caused by them. This process will impact the current transfer in the system of tunnel microscope probe–nanometer gap– QD layer–substrate with the conductive electrode layer of ITO and, accordingly, in the way of normalized differential tunnel CVCs.

The quantum energy for the transition of electrons from level E_{v1} to level E_c, taking into account the band gap of the bulk material, was determined from the expression

$$E_{h\nu} = E_{g0} + E_{c1} + E_{v1}, \tag{2}$$

where $E_{h\nu} = h\nu$ — quantum energy in the absorption maximum, E_{g0} — width of the band gap of the bulk material, E_{c1} — energy of the first electron level of QD, measured from the bottom of the bulk material's conduction band, E_{v1} — energy of the first hole level, measured from the top of the bulk material's valence band. Because the effective mass of the electron is about 30 times less than that of holes ($0.014m_0$ and $0.43m_0$ respectively, m_0 — mass of free electron), the value E_{v1} in expression (2) may be neglected.

Since the studied QDs had almost cubic shape for InSb and almost ball shape for CdSe, to assess E_{c1} and E_{v1} for InSb QDs the model of a cubic edged shape of QD was used a (10–12 nm).

The levels energies may be evaluated from [32]:

$$E_i = \frac{(\pi\hbar)^2}{2m^*}\frac{1}{a^2}(l^2 + m^2 + n^2), \tag{3}$$

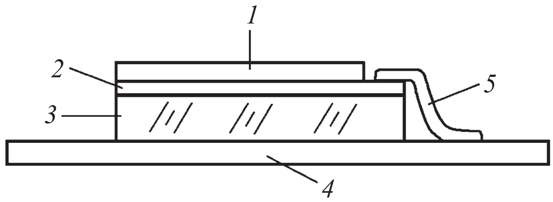

Figure 3. Structure of obtained samples with monolayers of QD: *1* — studied monolayer; *2* — ITO layer; *3* — glass; *4* — metallic substrate; *5* — adhesive conductive tape.

where $l, m, n = 1, 2, 3, \ldots$; m^* — effective mass of the bulk material's electron, a — specific size of QD (cube edge).

Analysis of the energy spectrum in accordance with the characteristic size a and shape of InSb QDs under study made it possible to estimate the amount of light quantum energy required for the electron transition from E_{v1} level to E_{c1}, which amounted to ~ 1 eV.

To evaluate E_{c1} and E_{v1} of CdSe quantum dots a ball-shaped model of QD was used with a radius $R = a/2$, where a — diameter of QD (5–6 nm). The levels energy was evaluated by [33]:

$$E_i = \frac{\hbar^2}{2m^*}\frac{k_{nl}^2}{R^2}, \tag{4}$$

where m^* — effective mass of electron and bulk material hole for calculation of E_{c1} and E_{v1} respectively, values k_{nl} are given in table [32,33].

Value k_{nl}

k_{nl}	$l = 0$	$l = 1$	$l = 2$	$l = 3$
$n = 0$	3.14	4.49	5.76	6.99
$n = 1$	6.28	7.73	9.1	10.42

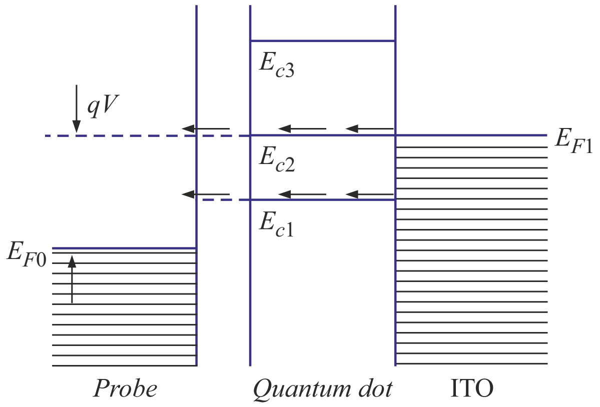

Figure 4. Diagram of the energy levels of QD, substrate, and probe of a tunneling microscope during electron tunneling through an air gap: E_{F0}, E_{F1} — Fermi level of metallic probe and ITO substrate, respectively, E_{c1}, E_{c2}, E_{c3} — energy of the 1-st, 2-d and 3-d level of QD electron counted from the bottom of the conduction band of a bulk material.

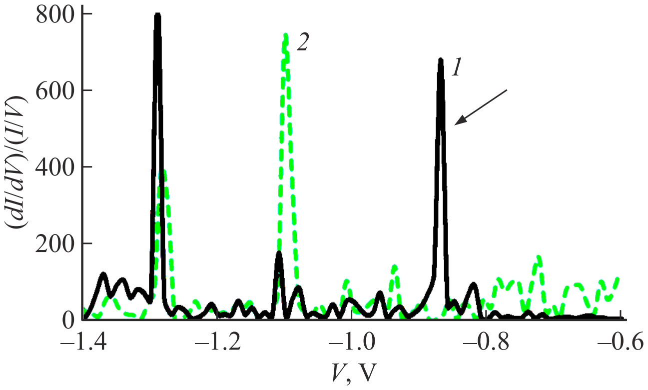

Figure 5. Normalized differential tunnel CVCs of InSb QDs: *1* — without light, *2* — with green light. The peaks analyzed in this paper are indicated by an arrow.

Taking into account the characteristic size and shape of the studied CdSe QDs, the energy of the light quantum required for the electron transition from E_{v1} to E_{c1} level was ~ 2.5 eV.

In the study the light from green LED (530 nm — for InSb QDs, (Fig. 5)), blue LED (450 nm — for CdSe QDs (Fig. 6)) and red LED (640 nm — for CdSe QDs (Fig. 7)) were used.

The results of the energy spectrum analysis using normalized differential tunneling CVC method for InSb QDs are shown in Fig. 5.

As follows from the analysis of experimental data, when illuminated with green light, the peak corresponding to the first level E_{c1} of InSb QD energy spectrum on the normalized differential tunnel CVCs (approximately 0.85 in Fig. 5), either disappeared or decreased to a value close to the measurement error (10–15 %).

Similar results were obtained for CdSe QDs, the most typical ones are shown in Fig.6. When illuminated with blue light, the peak corresponding to the first level E_{c1} of the electronic energy spectrum of CdSe QDs on the normalized differential tunneling CVCs (approximately 0.4 V in Fig. 6), decreased to the measurement error value.

To further substantiate the observed effect, some experiments were also conducted using illumination with red light with a quantum energy of 1.9 eV, which is greater than transition energy $E_{c1}-E_{v1}$ for InSb QDs and less than the corresponding energy for CdSe (2) QDs, therefore, for the experiment CdSe QDs were used. The results of experimental data analysis (Fig. 7) showed that in this case the peak corresponding to the first level of QD does not disappear.

As mentioned above, when irradiated with light quanta with the energy necessary for electron photo-generation (2), an additional photocurrent appears that is not associated with the auto-electronic emission of electrons from the metal electrode.

In this case, the peak on the normalized differential tunneling CVCs, due to the structure of QD energy

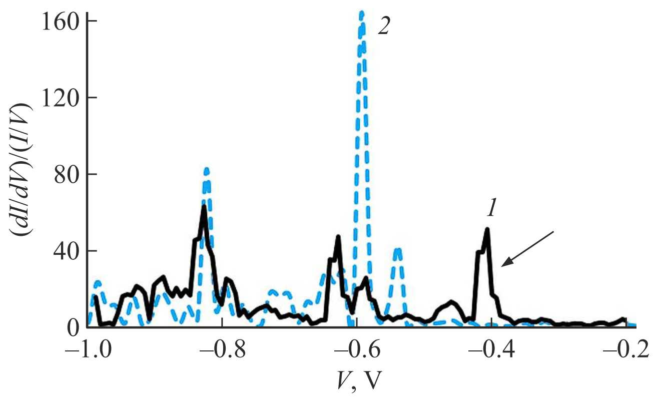

Figure 6. Normalized differential tunnel CVCs of CdSe QDs: *1* — without light, *2* — with blue light. The peaks analyzed in this paper are indicated by an arrow.

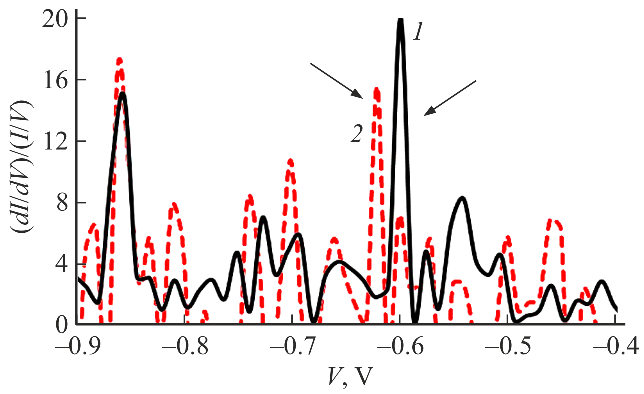

Figure 7. Normalized differential tunnel CVCs of CdSe QDs: *1* — without light, *2* — with red light. The peaks analyzed in this paper are indicated by arrows.

spectrum and current transfer conditions with a corresponding displacement, will be strongly blurred or may even disappear. If irradiated with light quanta having energy below the value found from (2), this effect will not be manifested.

It is obvious that in order for the 1st peak to disappear on the differential tunneling CVC under illumination, it is necessary not only that the quantum of irradiating light be at least $E_{h\nu} = E_{g0} + E_{c1} + E_{v1}$, but also that the irradiating light quantum flux be of sufficient intensity to provide the photoelectrons concentration comparable or greater than the dark concentration of electrons emitted from ITO on QD's 1st level.

In the stationary illumination mode, for the concentration of electrons excited by light at the level E_{c1}, one may write:

$$\Delta n_p = \alpha\beta\tau_l\Phi, \tag{5}$$

where α — absorption coefficient $\sim 5 \cdot 10^4$, β — quantum yield ~ 1, τ_l — lifetime of the photo-generated electrons in QD $\sim 2 \cdot 10^{-9}$ s (allowing for τ_l from [34]); Φ — light flux — 0.034, 0.018 and 0.025 lm for green, blue and red LEDs, respectively.

The estimated value of Δn_p for all three wavelengths of the irradiating light used in the experiments exceeded the concentration of electrons emitted from ITO to the 1st level of QD.

Conclusion

Thus, the paper describes the effect of light on the current transfer in the system of tunnel microscope probe–nanometer gap– QD layer of compounds A^2B^6 and A^3B^5–substrate with ITO electrode conducting layer when irradiated with light of various wavelengths. The proposed model concepts have been experimentally proved stating that the 1st peak of the normalized differential tunnel CVC, corresponding to the first discrete level of the electronic energy spectrum of the studied QD, may disappear or significantly decrease in magnitude when illuminated. The disappearance or significant decrease in the magnitude of this peak, at least to the noise level, is observed if the quantum energy and the intensity of the irradiating light excite a sufficient number of electrons from the 1st level of the valence quasi-band to the 1st level of the quasi-conduction band of the studied quantum dots. The observed effect has not been previously described in the literature. It shall be taken into account when interpreting experimental results on the tunneling CVC for the studied systems with quantum dots, as well as when using this method to characterize the properties of the quantum dots themselves. The work is of fundamental importance because, based on specially carried out experiments, it proves the basic model concepts of current transfer through QDs. The results and conclusions of the work allow us to further substantiate the details of QD characterization for the analysis of normalized differential tunnel CVCs. Given the promising results and interest in studying the quantum-size effects and systems the possibility of using the obtained experimental results in research of the current transfer in these objects is of specific scientific value.

Funding

This paper was supported by a grant from the Russian Science Foundation (project № 21-73-20057) and Saratov State University.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by T.Zorina