Method for analyzing the electrophysical properties of semiconductor quantum dots

A I Mikhailov, V F Kabanov, M V Gavrikov
Department of Nano and Biomedical Technologies, Saratov State University, Astrakhanskaya, 83, Saratov, 410012, Russia

Abstract. Some important properties of the InSb and CdSe quantum dots, such as size and energy spectrum, were studied by method of normalized differential tunneling current-voltage characteristics. The results of size evaluation are qualitatively and quantitatively consistent with the results obtained by TEM and analysis of spectral dependence of absorption coefficient and luminescence with an error less than 15%. During the study it was also shown, that method of normalized differential tunneling current-voltage characteristics also allows us to analyze the energy spectrum of semiconductor quantum dots (position of the first three energy levels).

1. Introduction
Quantum dots (QDs) are one of the most interesting objects for investigations in purpose of application in optoelectronics and nanoelectronics due to the presence of a number of characteristic features. Therefore, the choice of methods for studying them is also important. The main research methods, such as transmission electron microscopy (TEM), analysis of optical characteristics, etc., allow us to estimate the size, shape and composition of objects, however, they do not allow to evaluate the energy spectrum of QD, which can be a source of useful information about their optical and electronic properties. Therefore, the purpose of this paper was the substantiation and application of a method of analysis of normalized differential tunneling current-voltage characteristics, which allows to obtain this type of information about the objects, by using the semiconductor quantum dots of materials from groups A3B5 (InSb) and A2B6 (CdSe).

2. Samples obtaining technologies and measurement procedure
InSb quantum dots are of particular interest due to the unique properties of indium antimonide: ultra-high electron mobility, narrow forward band gap, small effective electron masses [1], a large de Broglie wavelength of ~ 55 nm compared to other materials. All this allows the use of this material in a variety of optoelectronic devices: transistors, sensors, IR detectors, etc. [2-4]. The CdSe material was chosen because it is one of the most promising and interesting semiconductor materials of the A2B6 group due to the high quantum yield of luminescence, photostability, and widespread use in optoelectronics [5–8].

In this paper we investigated monolayers of quantum dots that were formed on the surface of an aqueous subphase, using the Langmuir-Blodgett technology, and transferred onto solid substrates with a conducting layer of indium tin oxide (ITO) by self-organization of ensembles on the surface with subsequent controlled evaporation of the solvent and control of the layer parameters. The obtained samples were investigated by scanning tunneling microscopy (STM), transmission electron microscopy (TEM) and by analysis of spectral dependence of absorption coefficient.

For more complete analysis of electrophysical properties of the obtained film samples with QDs, in particular, the electronic spectrum, we used the STM technique. The studies were carried out using an
SPM SOLVER Nano scanning probe microscope. Before measuring the tunneling CVCs of an individual particle, we scanned the film surface by STM method in the stabilized current mode of measurements. After analyzing the STM image of the macrosample surface, we chose no less than 10 points for recording the CVCs. We automatically recorded no less than 10 CVCs per point. The measurements were carried out at current values in the range from $10^{-10}$ to $10^{-8}$ A and at voltages from 0 to 2 V. Taking into account the reproducibility of the result of measurements, we selected points with stable characteristics, after which we averaged the obtained characteristics. Model representations of the process of electron tunneling through discrete levels of a quantum-size objects in the structure for STM measurements were considered in [9-12]. For the analysis of experimental tunneling current-voltage characteristics we used the method of normalized differential current-voltage characteristics $(dI/dV)/(dI/dV)$ as the dependence on the voltage $V$ [13, 14].

3. Model representations and results

It is known that quantum-size effects in nanoparticles can be observed under the necessary conditions: 1) characteristic size of nanoparticle should be about the de Broglie wavelength (quantization of the energy spectrum of QD); 2) interval between discrete levels $\varepsilon_{i+1} - \varepsilon_i$ must be at least $3\div4$ of $kT$ value (for example, about 4 $kT$, which corresponds to 0.1 eV at room temperature).

The electron energy in QD can be represented as a three-dimensional infinitely deep potential well and if we use the cube-shaped QD model with the edge $a$, the position of the energy spectrum levels can be represented this way [15]:

$$\varepsilon_i = \frac{(\pi \hbar)^2}{2m^*} \cdot \frac{1}{a^2} \cdot \left( l^2 + m^2 + n^2 \right)$$

(1)

Here $l, m, n = 1,2,3,...$ are natural numbers corresponding to the QD level numbers; $m^*$ – is the electron effective mass; $a$ – is the characteristic size of the QD (cube edge).

In the case of using a sphere-shaped QD model with radius $a$ [16]:

$$\varepsilon_i = \frac{(\pi \hbar)^2}{2m^*} \cdot \frac{1}{a^2} \cdot \left( 4n + 2l + 3 \right)$$

(2)

Here $n = 0, 1, 2, ...$ is the radial edge number; $l = 0, 1, 2, ...$ is the orbital quantum number; $a$ – is the characteristic size of the QD (radius).

The electron energies calculated by formulas (1) for the first three allowed levels in an InSb QDs are shown in figure 1 (right). In the calculations, we used the electron effective mass in the conduction band of InSb $m^* \sim 0.013m_0$, where $m_0$ is the free electron mass.

Normalized differential tunneling current-voltage characteristics of the InSb QDs were obtained and analyzed at a negative bias potential on the substrate relative to the probe (figure 1 (left)). In this case, the tunneling of electrons from the ITO electrode occurs through the discrete levels of the quantum-dimensional object into the probe of the tunneling microscope. The discrete energy spectrum of QD electrons causes peaks at normalized differential CVCs. These peaks are characteristic of electron tunneling through the first three energy levels of quantum dot into a metal probe of a microscope. The voltage values (taken modulo) at peaks positions were aligned with the energy values on the previously obtained dependences of the levels of the energy spectrum of the QD on its size (figure 1 red lines). Thus, we determined the range of sizes of investigated objects (red area) and, accordingly, the position of the first three energy levels of the electron in them.

An analysis of the experimental data of the peaks position on differential normalized tunneling CVCs for the group of samples allowed us to estimate the linear size of the quantum dots in the range of 12–13 nm.
Figure 1. Typical differential normalized tunneling CVCs of InSb QDs in accordance with the calculated electron energies of the first three allowed energy levels in InSb QD as a function of the characteristic QD size $a$ (using the “cube” QD model).

Similar calculations and measurements were also made for CdSe quantum dots but in accordance with equation (2) and using a spherical model of a quantum dot. Results in figure 2. An analysis of the peaks position on differential normalized tunneling CVCs for the CdSe QDs group of samples allowed us to estimate the linear size of the quantum dots in the range of 3–4 nm.

Figure 2. Typical differential normalized tunneling CVCs of CdSe QDs in accordance with the calculated electron energies of the first three allowed energy levels in an CdSe QD as a function of the characteristic QD size $a$ (using the “sphere” QD model).

4. Results comparison
To confirm validity of the results, we carried out a series of control measurements of the quantum dots sizes by TEM and spectral analysis methods.
For InSb QDs we used analysis of spectral dependence of absorption coefficient that was performed in the range of 1.2–5 $\mu$m. Typical dependence of the absorption coefficient $\alpha$ on the wavelength is
presented in figure 3. The absorption peak corresponds to the energy value (0.83 eV) of the first level of quantum dot, measured from the bottom of the conduction band of the bulk material. Estimation of the size of InSb nanoparticles using the QD model of a cubic form showed values of the characteristic size (cube edge) of 10–12 nm.

![Figure 3](image1.png)

**Figure 3.** Typical spectral dependence of the absorption coefficient of InSb QDs.

The size estimation of CdSe QDs was carried out on the basis of the luminescence spectra. Typical CdSe QDs luminescence spectrum is shown in figure 4. Based on this spectra, the size of the CdSe QDs was estimated as 3–4 nm.

![Figure 4](image2.png)

**Figure 4.** Typical luminescence spectrum of CdSe QDs.

To confirm the validity of the obtained results, direct measurements of QDs sizes were performed using TEM. A typical TEM image of InSb and CdSe QDs is shown in figure 5 and typical TEM image of CdSe QDs is shown in figure 6.

The results show good agreement with the results calculated by other methods.
5. Conclusions

Thus, it can be concluded that the analysis of normalized differential tunnel current-voltage characteristics is an effective method to analyze the energy spectrum of QDs, which can be a source of useful information about their optical and electronic properties.

Size estimates of obtained samples using different approaches (analysis of the spectral dependence of the absorption coefficient and luminescence spectra, analysis by the method of differential normalized tunnel current-voltage characteristics and direct measurements using TEM) demonstrate qualitatively and quantitatively agreed results with an error less than 15%.

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