NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2019, 10 (6), P. 720–724

Methodology of analyzing the InSb semiconductor quantum dots parameters

A. I. Mikhailov, V. F. Kabanov, M. V. Gavrikov

Saratov State University, Department of Nanoand Biomedical Technologies,
Astrakhanskaya, 83, Saratov, 410012, Russia

maks.gavrikov.96@gmail.com

DOI 10.17586/2220-8054-2019-10-6-720-724

The investigation of indium antimonide quantum dots has been carried out by the methods of differential normalized tunnel current-voltage characteristics, electron microscopy, particle size analysis and spectral dependence of the absorption coefficient. Qualitatively and quantitatively consistent measurement results were obtained with an error less than 15 %. It is concluded that the analysis of normalized differential tunnel current-voltage characteristics is an effective method of express-analysis that can be used in investigation of quantum-sized objects properties.

Keywords: quantum dots, indium antimonide, differential tunnel current-voltage characteristics, energy spectrum.

Received: 12 September 2019

Revised: 1 November 2019

1. Introduction

In recent decades,semiconductor quantum dots (QDs) have caused great interest among researchers after the discovery of their quantum-size optical and electronic properties. The practical application of QD includes nanoelectronics, optoelectronics (displays, photovoltaics, light sources), visualization of biological objects, sensors, and etc. [1–6].

Indium antimonide (InSb) QDs causes particular interest due to the unique properties of indium antimonide: ultra-high electron mobility (up to 78000 cm^{2}V^{-1}s^{-1}), direct and narrow (0.18 eV) band gap, small effective masses ofconduction electrons($0.013m_0$, m_0 – mass of a free electron) [7] and large de Broglie wavelength of electrons – up to 55 nm.

The obtaining of various technologies has allowed us to solve problems of physical modeling of electronic processes in QD, investigate the influence of composition and structure on their properties and their interaction during segregation. This is especially important for colloidal QD, in which the crystalline and electronic structures are determined by self-organized nucleation during chemical synthesis, not forced, as during epitaxial growth.

The aim of this work is to develop and substantiate the methodology forinvestigation of InSbquantum dots electrophysical properties.

2. Samples obtaining technologies

Colloid synthesis of InSb QDs was carried out in anhydrous oleylamine using indium chloride $InCl_3$ and antimony tris [bis(trimethylsilyl)amide]($Sb[N(Si\text{–}(Me)_3)_2]_3$) as precursors according to the technique [8]. An additional modification of the technique was that a mixture of acetate and indium chloride in the ratio 4:1 was used as the indium precursor. The halide in this system is necessary for the reaction, and the addition of acetate allows to minimize the aggregation processes. QD were transferred from a colloidal solution to the glass substrates with indium – tin oxide (ITO) layer by self-organization of ensembles on the surface with subsequent controlled evaporation of the solvent and control of the layer parameters by optical constants control methods.

3. Research methods

The obtained samples were examined by scanning tunnel microscopy (STM) using SOLVER Nano, a laser particle size analyzer using Zetasizer Nano ZS, scanning electron microscopy (SEM) using a MIRA 2 LMU autoemission scanning electron microscope.

For more complete analysis of electrophysical properties of the obtained film samples with QD, in particular, the electronic spectrum, the STM technique was used. The studies were carried out using an SPM SOLVER Nano scanning probe microscope. Before measuring the tunnel I–V characteristic 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 I–V characteristics. We automatically recorded no less than 10 I–V characteristics per point. The measurements were carried out at currents ranging from

10^{-11} to 10^{-9} 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.

Tunneling CVC were measured between the probe and the ITO-deposited layer of InSb QDs. The characteristic size of the QDs was 10 – 20 nm, the distance between the probe and the QD was about 1 – 2 nm. The radius of the probe is determined mainly not by the macroscopic radius of curvature of the tip, but by its atomic structure, i.e. at the tip of the probe there is a high probability of one protruding atom or a small cluster of atoms (few nm) [9]. The stabilizer used in the synthesis of QDs does not allow them to aggregate among themselves and separates them. These two facts allow us to say that the current will mainly be determined by the flow of electrons from a single quantum-sized particle to nanoscale "protrusion" on the probe.

To analyze the experimental tunnel current-voltage characteristics, we used the method of normalized differential current-voltage characteristics $(dI/dV)/(I/V)$ as the dependence on the voltage V. In addition, as shown in [6, 10], this method can be used for analysis of conductivity mechanisms of obtained structures, calculations of their parameters and other important electronic processes.

4. 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 $3 \div 4$ of kT value (for example, about $4kT$, 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 QD cube-shaped model with the edge a, the position of the energy spectrum levels can be represented this way [11]:

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

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

The electron energies calculated by formula (1) for the first three allowed levels in an InSb QD are shown in Fig. 1. 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.

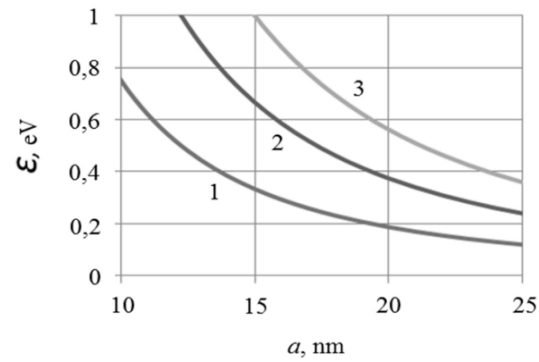

FIG. 1. Calculated electron energies of the first three allowed energy levels (1,2,3) in an InSb QD as a function of the characteristic QD size a (using the "cubic" QD model)

Realization of the necessary conditions for observing quantum-size effects is possible with characteristic sizes of InSb nanoparticles less than 30 nm (de Broglie wavelength is about 55 nm, interval between discrete levels $\varepsilon_2 - \varepsilon_1$ is morethan 0.1 eV). In this case, in the range of variable sizes of QD from 10 to 30 nm, the energy gap $\varepsilon_{c1} - \varepsilon_{v1}$ will vary from 0.3 to 1.0 eV considering the width of the band gapof bulk material (and the position of maximum absorption coefficient will vary from 1.2 to 4.1 μm). This allows us to reasonably assume the possibility of a significant effect of the characteristic size of the InSb QD on their optical and electrical properties overa wide range.

In this research, the normalized differential tunnel current-voltage characteristics were examined and analyzedata negative bias potential on the substrate relative to the probe. In this case, electrons tunnelfrom the ITO electrode to the probe of the tunnel microscope through the discrete levels of the QD. The discrete energy spectrum of conduction electrons of a quantum-size object definesthe peaks on the normalized differential I–V characteristic (Fig. 2(a) they are indicated by arrows). The experimentally obtained values of the applied voltage on the peaks were set in accordance with the calculated values of the electron energy levels of the QD (Fig. 2(b)). That way we determined the range of characteristic sizes of QD, which were compared with the available results. A schematic representation of the band structure with the corresponding energy levels when the potential on the substrate changes relative to the probe is presented in [12].

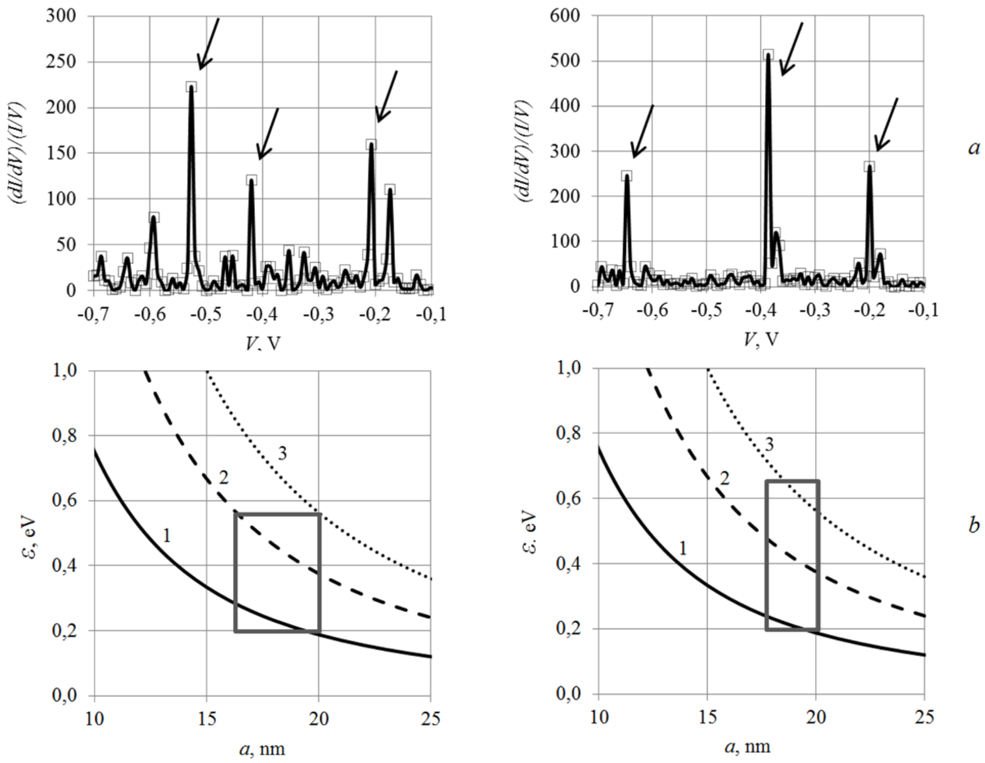

FIG. 2. (a) – typical normalized differential tunnel I–V characteristic of InSb QD samples; (b) – accordance with calculated levels of the energy spectrum. 1,2,3 – calculated electron energies of the first three allowed energy levels

This methodallow us to estimate the characteristic sizes of QD in the range from 16 to 20 nm with the measurement errors of the peak positions less than $2kT$.

To confirm the validity of obtained results, particle size analysis, spectral analysis and direct measurements using SEM were performed.

Spectral analysis of the obtained QD was performed in the range of 1.5 – 5 μm. Typical dependence of the absorption coefficient α on the wavelength is presented in Fig. 3

Size estimation of nanoparticles by the position of the maximum on the spectral dependence using the model of the QD cubic form showed characteristic values in the range of 14 – 17 nm.

The results of particle size investigation, using a laser particle size analyzer, is shown in Fig. 4. The obtained results were in the range of 17 – 22 nm.

To clarify the validity of these estimates, direct measurements were made using SEM. The results presented in Fig. 5 show good agreement with the estimated QDs sizes.

5. Conclusions

Thus, it can be concluded that the analysis of normalized differential tunnel current-voltage characteristics is an effective method of express-analysis that can be used in investigation of quantum-sized objects properties, in particular, InSb quantum dots.

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

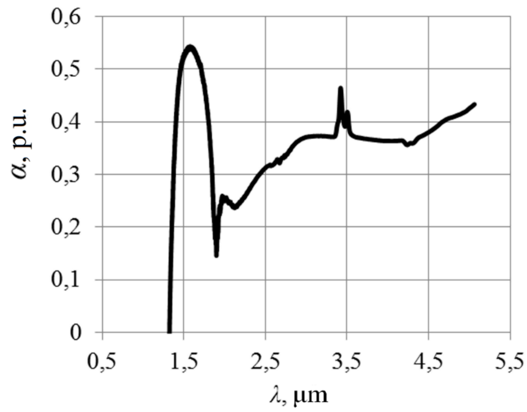

FIG. 3. Typical spectral dependence of the absorption coefficient of InSb QD

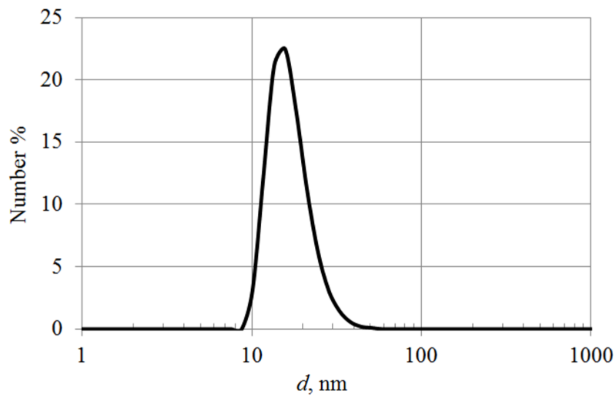

FIG. 4. InSb QD size estimating using a laser particle size analyzer

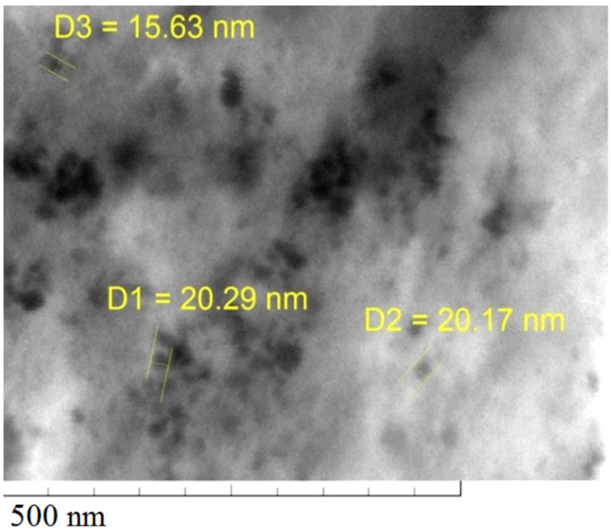

FIG. 5. Typical SEM images of InSb QDs

Acknowledgements

This work was supported by grants from the Russian Foundation for Basic Research Projects No. 19-07-00087 and No. 19-07-00086.

References

[1] Reiss P., Carriere M., et al. Synthesis of Semiconductor Nanocrystals, Focusing on Nontoxic and Earth-Abundant Materials. *Chem. Rev.*, 2016, **116** (18), P. 10731–10819.

[2] Yoffe A.D. Semiconductor quantum dots and related systems: Electronic, optical, luminescence and related properties of low dimensional systems. *Advances in Physics*, 2010, **50** (1), P. 1–208.

[3] Algar W.R., Tavares A.J., Krull U.J. Beyond labels: A review of the application of quantum dots as integrated components of assays, bioprobes, and biosensors utilizing optical transduction. *Analytica Chimica Acta*, 2010, **673** (1), P. 1–25.

[4] Brichkin S.B., Razumov V.F. Colloidal quantum dots: synthesis, properties and applications. *Russ. Chem. Rev.*, 2016, **85** (12), P. 1297–1312.

[5] Li N., Zhang X., Chen S., Hou X. Synthesis and Characterization of CdS Nanoparticles in the Presence of Oleic Acid as Solvent and Stabilizer. *Journal of Physics and Chemistry of Solids*, 2011, **72** (11), P. 1195–1198.

[6] Mikhailov A.I., Kabanov V.F., et al. Methodology of analyzing the A2B6 semiconductor quantum dots parameters. *Nanosystems: Physics, Chemistry, Mathematics*, 2018, **9** (4), P. 464–467.

[7] Abautret J., Perez J.P., et al. Characterization of midwave infrared InSb avalanche photodiode. *J. Appl. Phys.*, 2015, **117** (24), 244502 (1–6).

[8] Liu W., Chang A.Y., Schaller R.D., Talapin D.V. Colloidal InSb Nanocrystals. *J. Am. Chem. Soc.*, 2012, **134** (50), P. 20258–20261.

[9] Mironov V.L. *Principles of Scanning Probe Microscopy*. Tekhnosfera, Moscow, 2009, 110 p.

[10] Mikhailov A.I., Kabanov V.F., Zhukov N.D. Peculiarities of field electron emission from submicron protrusions on a rough InSb surface. *Technical Physics Letters*, 2015, **41** (11), P. 1065–1067.

[11] Dragunov V.P., Neizwestny I.G., Gridchin V.A. *Fundamentals of nanoelectronics*. Fizmatkniga, Moscow, 2006, 496 p.

[12] Mikhailov A.I., Kabanov V.F., et al. Electronic Properties of A2B6 Quantum Dots Incorporated into LangmuirBlodgett Films. *Bulletin of the Russian Academy of Sciences: Physics*, 2017, **81** (12), P. 1472–1475.