Investigation of indium antimonide nanoparticles, obtained by the method of liquid chemical etching

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Abstract. The possibility of obtaining indium antimonide nanoparticles by method of liquid chemical etching was analyzed. The dependence of obtained nanoparticles size on the etching time and composition of the etcher has been investigated. The nanoparticles were etched in solutions prepared on the basis of the peroxide-ammonia mixture; cetyltrimethylammonium bromide, a cationic surfactant, was used to stabilize the surface of the nanoparticles. The obtained quantum dots of indium antimonide were studied by the methods of differential normalized tunnel current-voltage characteristics, electron microscopy, particle size analysis and spectral dependence of the absorption coefficient.

1. Introduction
Nowadays practical application of quantum dots (QD) includes nanoelectronics, optoelectronics (displays, photovoltaics, light sources), visualization of biological objects, sensors, and etc. [1-6]. Indium antimonide (InSb) QD causes particular interest due to the unique properties of indium antimonide: ultra-high electron mobility (up to 78000 cm²V⁻¹s⁻¹), direct and narrow (0.18 eV) forbidden band, small effective electron mass (0.013m₀, where m₀ - mass of a free electron) [7] and large de Broglie wavelength of electrons – up to 55 nm.

The various obtaining technologies allows us to solve problems of physical modeling of electronic processes in QD, investigate the influence of composition and structure on their properties, their interaction during segregation. One of the ways of obtaining nanoparticles is using the approach, which is called «top-down» synthesis. In this case, monocrystalline plates of these materials are subjected to grinding, chemical (often electrochemical) etching and sedimentation, etc. In a result are nanoparticles - the raw material for quantum dots [8]. In this paper, InSb nanoparticles obtained by liquid chemical etching of InSb powders were investigated.

2. Model representations and evaluations
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 ε_{i+1} - ε_i must be at least 3÷4 of kT value (for example, about 4 kT, which corresponds to 0.1 eV at room temperature).

Realisation 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 ε_{i+1} - ε_i is bigger than 0.1 eV). In this case, in the range of variable sizes of QD from 10 to 30 nm, the energy gap ε_{i+1} - ε_i will vary from 0.3 to 1.0 eV considering the width of
the forbidden band of 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 in a wide range.

3. Samples obtaining technology
The initial InSb powders were obtained by grinding monocrystalline plates in a planetary ball mill PULVERISETTE (Fritsch, Germany). After that, the obtained powders were etched in a mixture of etchants similarly to [9].

To work out the technique of etching InSb powders, the most known in the electronics industry oxidative peroxide-ammonia mixture (pH = 11), consisting of deionized water, an aqueous solution of ammonia and hydrogen peroxide. Etching solutions were prepared with the volume ratios: \( \text{H}_2\text{O}, \text{NH}_4\text{OH}, \text{H}_2\text{O}_2 \) = 30: 6: 9. To improve the quality of the surface, a surfactant, that forming micelles in a water (cetyltrimethylammonium bromide), was used for etching, which also plays the role of a stabilizer, which prevents the aggregation of the resulting nanoparticles.

During the etching of InSb, an exothermic reaction was observed in the first few seconds when the temperature of the reaction mixture rose to \( t = 50^\circ\text{C} \). Then for 10 min the reaction mass cooled to room temperature. For a detailed study of the etching process, sampling for further analysis was carried out after 1, 5, 15, 30, 150 minutes and 24 hours after the start of the reaction.

4. Research methods and results
The particle size analysis was performed by using a laser particle size analyzer Zetasizer Nano ZS (the results are shown in Fig. 1 (a)), which showed typical nanoparticle sizes of about 20 nm, which is less than the de Broglie wavelength for an electron in InSb.

An analysis of the energy absorption spectrum for the obtained nanoparticles was performed using a Shimadzu Iraffinity-1 IR spectrometer (the results of the dependence of the absorption coefficient \( \alpha \) on the wavelength are shown in Fig. 1 (b); the absorption peak corresponds to the energy value (0.24 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 nanoparticles using the QD model of a cubic form [10] showed values of the characteristic size (cube edge) of 18–20 nm.

![Figure 1(a, b). (a) Size estimation of obtained nanoparticles; (b) Dependence of absorption coefficient on the wavelength for obtained nanoparticles.](image-url)
methods in the stabilized current regime was carried out. After analysis of the obtained STM image of
the surface at least 10 points were selected to obtain the CVC. In automatic mode, at least 10 CVC per
point were measured. CVC measurements were made within the current values from $10^{-11}$ to $10^{-9}$ A,
voltage - from 0 to 1 V. By reproducibility of the measurement results, points with stable
characteristics were selected, after which averaging of the CVC were performed.
For the analysis of experimental tunneling current-voltage characteristics, we used the method of
normalized differential current-voltage characteristics $(dI/dV)/(I/V)$ as a function of voltage $V$. In
addition, as shown in [6, 12], this method can be used for analysis of conductivity mechanisms of
obtained structures, calculations of their parameters and other important electronic processes.
In this research, the normalized differential tunneling current-voltage characteristics with a negative
bias potential on the substrate relative to the probe were examined and analyzed. In this case,
tunneling of electrons occurs from the electrode through discrete levels of a quantum-size object into a
probe microscope [10,11]. The discrete energy spectrum of conduction electrons of a quantum-size
object determines the peaks on the normalized differential CVC (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. The analysis of experimental data on the position of the peaks on the differential normalized
tunnel current-voltage characteristics also made it possible to estimate the linear size of a quantum
object in the range of 18–21 nm.

![Figure 2(a, b).](image)

(a) Typical differential tunnel CVC of InSb QD; (b) Compliance with calculated energy spectrum levels.

To clarify the validity of these estimates, direct measurements were made by scanning electron
microscopy (SEM) using a MIRA 2 LMU autoemission scanning electron microscope. The results
presented in Fig. 3 show good agreement with the estimated QD sizes.
Figure 3. Typical SEM images of InSb QD.

5. Conclusions
Thus, it can be concluded that the method of colloid synthesis of InSb quantum dots allows to obtain nanoparticles in a wide range of sizes up to few nanometers with the required reproducibility and accuracy, suitable for the production of semiconductor quantum dots. Also, the phase and structural composition of the obtained nanoparticles almost does not differ from the initial bulk monocrystalline material.

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

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