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Resonant reflection of light from a periodic system of quasi-two-dimensional layers of Bi nanoparticles in GaAs

© E.D. Polenok[1,2], V.V. Preobrazhenskii[3], M.A. Putyato[3], B.R. Semyagin[3], N.S. Potapovich[1], V.P. Khvostikov[1], V.I. Ushanov[1], V.V. Chaldyshev[1]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] ITMO University,
St. Petersburg, Russia
[3] Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences,
Novosibirsk, Russia

E-mail: Chald.gvg@mail.ioffe.ru

Received October 31, 2025
Revised October 31, 2025
Accepted November 1, 2025

We demonstrate the possibility of creating and have studied the optical properties of a structure, which is composed of an epitaxial GaAs matrix with an embedded periodic sequence of quasi-two-dimensional layers of Bi nanoinclusions. In the optical reflectance spectra of this structure, we reveal a resonant peak originating from the Bragg diffraction of electromagnetic waves scattered on the system of the nanoinclusions. The significant amplitude of the reflection peak (approximately 15% at normal light incidence) is due to the fact that the wavelength of the Bragg resonance is close to the wavelength of the localized surface plasmon resonance in the system of bismuth nanoparticles embedded in the gallium arsenide matrix.

Keywords: GaAs, Bi, optical properties, plasmon resonance, nanoparticles.

DOI: 10.61011/PSS.2025.11.62972.308-25

1. Introduction

The phenomenon of localized surface plasmon resonance (LSPR) makes it possible to focus the electromagnetic field in a subwavelength range and to considerably enhance the interaction between the light and the matter [1], which provides for its practical value. The key objects for the study in plasmonics are the systems of metal nanoparticles, which may demonstrate LSPR in a semiconductor medium [2–6]. They are used to develop biological sensors [6,7]; similar systems of plasmonic nanoparticles may increase the efficiency of solar cells [8,9]; the plasmon resonance makes it possible to enhance the Raman scattering signal by orders of magnitude [10–12]; it helps to achieve high-speed processing of information in quantum computers [13]; LSPR may drastically change the optical properties of the semiconductor, considerably expanding the range of applications of classical semiconductor materials [14–17].

The main difficulty in the development of the systems of plasmonic nanoparticles in semiconductors consists in the fact that most common plasmonic metals, such as gold, silver, copper, platinum etc., may be deposited onto the surface of the semiconductor in the form of thin films or nanoparticles [18], however, the formation of an array of such nanoparticles inside an epitaxial layer is not possible at this time. At the same time, some metals can form nanoparticles directly in the semiconductor medium. The elements of the fifth group — As, Sb and Bi are such plasmonic materials for semiconductors of type III-V, in particular for GaAs. According to the theoretical calculations of LSPR for nanoparticles of these materials in the GaAs matrix [19–21], bismuth is the best candidate for LSPR implementation within the GaAs transparency window. The LSPR energy corresponds to the photon energies outside the transparency window of the semiconductor matrix for a system of bismuth nanoparticles in gallium arsenide. Nevertheless, due to the large width of the resonance, LSPR should influence the optical characteristics of the material also in the long-wavelength part of the spectrum, where the GaAs matrix is considered transparent. To increase the effect from LSPR, the system may be made periodic, so that in the region of the plasmon resonance the constructive Bragg diffraction of electromagnetic waves occurs [22,23].

It should be noted that introduction of the considerable concentration of bismuth into the matrix of gallium arsenide that is necessary for the formation of the system of nanoinclusions, is a challenging technological task. It may be tackled using a method of molecular-beam epitaxy (MBE) [24]. It was demonstrated in study [25] that quasi-two-dimensional layers of bismuth nanoparticles in a GaAs matrix can be created using MBE. For this purpose the structure must be grown in nonstoichiometric conditions at lower temperatures, and then subjected to annealing at higher temperatures.

Previously we have already reported the experimental observation of Bragg resonance in the system of quasi-two-dimensional layers of Bi nanoparticles in the GaAs matrix [26], however, due to the disorder of the structure the resonance split into several quasi-Bragg peaks in the reflection. This circumstance however did not prevent us from building a numerical model that properly describes the experiment results. Based on these intermediate results, a new structure was developed, which provides Bragg resonance with a higher quality factor in this system.

The objective of this paper was to create and study the optical properties of the periodic structure based on quasi-two-dimensional layers of Bi nanoinclusions in the GaAs matrix providing for one mode of Bragg diffraction in the optical reflection near the edge of the GaAs band-gap. The article presents the results of experimental optical studies of such structure comprising 24 layers of Bi nanoparticles. A model was built to describe quantitatively all key features of the obtained reflection spectra.

2. Methods and materials

The studied sample was grown using the method of molecular-beam epitaxy on semi-insulating GaAs substrates with orientation $(001) \pm 0.5^\circ$. The processes were controlled on the growth surface using a reflection high-energy electron diffraction (RHEED) method. Density of the molecular fluxes of As_4 and Bi was measured using a manometer sensor of ionization vacuum gauge that was inserted in the growth region for the measurement period. The growth rate was measured using oscillations of specular reflex of the fast electron diffraction pattern. The substrate temperature was determined using the readings of a thermocouple calibrated by temperatures of transitions of surface structures on the surface of gallium arsenide.

After protective oxide layer removal a buffer layer GaAs $0.3\,\mu$m thick was grown on the substrate surface, with growth rate $1\,\mu$m/hour. The growth was performed at growth temperature $580\,^\circ$C under the conditions of superposition of surface superstructures $((2)(3) \times (4)(6))$. This provided growth conditions similar to stoichiometric conditions.

Upon completion of the buffer layer growth the substrate was cooled to temperature $200\,^\circ$C and a superlattice comprising 24 periods was grown at this low temperature (LT). The period consisted of 125 nm thick layers of LT GaAs and GaBi delta-layers with a thickness of one monolayer. The growth rate was $1\,\mu$m/hour. The fluxes of arsenic and bismuth in the growth zone were, respectively, $P_{As_4} = 3 \cdot 10^{-5}$ Torr and $P_{Bi} = 8 \cdot 10^{-8}$ Torr. After growth of layer LT GaAs the fluxes of gallium and arsenic were shut off, the shutter of the Bi source was opened and 1 bismuth monolayer was deposited. Deposition time was calculated by change of intensity of specular reflex of RHEED and was 45 seconds. Then the bismuth flux was stopped, and fluxes of arsenic and gallium were supplied.

At the initial stage of LT GaAs growth, a network of streaks of the main reflections was observed in the RHEED pattern, which indicates atomic smoothness and high crystalline perfection of the surface. The RHEED pattern during the growth demonstrated the diffuse scattering, which increased with increase in the thickness of growing layer. This phenomenon may be due to internal stresses increasing in growing heterostructure, caused by both capturing of excess arsenic, and effect of Bi delta-layers. No significant coarsening of the diffraction pattern was observed after growth completion.

After growth, the sample was subjected to high-temperature annealing to form a developed structure of Bi nanoinclusions. The processes of rapid thermal annealing were carried out in a quartz reactor in a continuous flow of hydrogen pretreated with a palladium filter. To prevent surface degradation, during temperature treatment the samples were covered with a GaAs wafer. Samples were heated with a tubular furnace to a temperature of $600\,^\circ$C with an accuracy of $\pm 1\,^\circ$C. The holding time at the annealing temperature was 15 min. Such thermal treatment provided a considerable drop in the concentration of intrinsic point defects in the LT GaAs and formation of quasi-two-dimensional layers of Bi nanoinclusions [25]. The electron-microscopic studies completed in the previous paper [25] demonstrated that Bi nanoinclusions are formed from the material of GaBi delta-layers, therefore the spatial position of the layers of Bi nanoinclusions and GaBi delta-layers coincide. The typical size of bismuth inclusions is 10–15 nm.

Optical examination of the sample was performed using optical reflection spectroscopy at various angles of incidence of light. A halogen lamp was the white light source. Fiber optic cables were used to transmit light. The light was polarized using a Glan–Taylor prism. We used the NIRQuest-512 and QE65000 mini-spectrometers, as well as the SpectraSuite software from OceanOptics to record the spectra. All studies were conducted at room temperature.

Optical spectra were modeled using a transfer matrix method. The Persson–Liebsch model was used to describe the interaction of an electromagnetic wave with a quasi-two-dimensional layer of bismuth nanoparticles [27]. The optical response of an individual nanoparticle was found using Mie theory. Since, as it was demonstrated in the previous paper [26], particles in such structures have a shape closer to spherical, their optical response may be described by polarizability of the following type:

$$\alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}, \qquad (1)$$

where a is the radius of the particle, ε_m is the dielectric constant of the metal, ε_d is the dielectric constant of the medium. The Adachi model [28] was used to describe the dielectric function of the GaAs matrix material. Data on the dielectric properties of Bi metal nanoinclusions were taken from the study of Ushanov et al. [21].

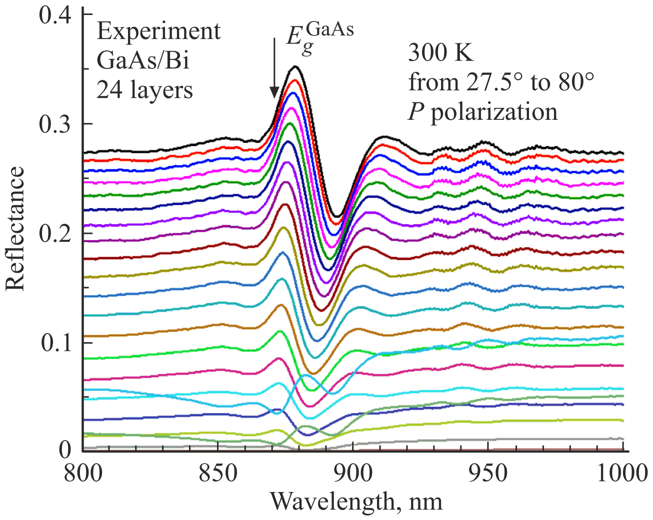

Figure 1. Experimental spectra of reflection from a periodic structure comprising 24 quasi-two-dimensional layers of Bi nanoparticles in the GaAs matrix, at incidence angles of P-polarized light from 27.5° to 80°. The spectra are recorded at room temperature with an angular step of 2.5°.

3. Experimental results

Figure 1 presents experimental spectra of reflection of the studied sample at incidence angles of P-polarized light from 27.5° to 80° with a step of 2.5°. An arrow marks the edge of the fundamental absorption of the GaAs matrix. It can be seen that in the spectral range 870–910 nm a sign-alternating resonance appears, which moves as the light incidence angle increases towards a short-wavelength region and to the fundamental absorption edge of the matrix. This shift is typical for Bragg systems, in which the position of the reflection maximum is described by the formula:

$$\lambda_{\text{Br}} = 2d\sqrt{\varepsilon_{\text{eff}} - \sin^2\theta}, \quad (2)$$

where λ_{Br} is the spectral position of the reflection maximum, d is the distance between reflecting interfaces, θ is the angle of incidence of light, ε_{eff} is the effective dielectric constant of the medium. In the long-wavelength region there are weak decaying side oscillations. It should be noted that at wavelengths greater than 1 μm bismuth nanoparticles lose their plasmonic properties [21]. No spectral features were observed in this long-wavelength region of the spectrum. In the short-wavelength region at photon energy $\hbar\omega > E_g^{\text{GaAs}}$ the GaAs matrix becomes opaque, and Bragg oscillations are no longer visible. The reflection coefficient beyond the resonance region corresponds to the values that may be obtained using Fresnel equations. As the P-polarized light incidence angle increases the reflection coefficient decreases, reaching the minimum at the Brewster angle that is around 74° in GaAs. At larger angles the reflection coefficient starts growing. In addition, the reflected light phase changes by π. In general, beyond the resonance region the reflection spectra correspond to those expected for conventional epitaxial GaAs.

The resonance reflection region requires a special review. Formula (2) makes it possible to qualitatively explain resonance shift when the incidence angle changes. For quantitative description, it is necessary to resort to the numerical modeling, the method of which was described in section „Methods and materials“.

4. Discussion of results

Figure 2 presents the calculated spectra of reflection for the structure consisting of 24 quasi-two-dimensional layers of bismuth nanoparticles in the gallium arsenide matrix, with a period equal to 122.7 nm, with diameter of the nanoparticles equal to 12 nm, and the filling factor inside a delta-layer (i. e. with the ratio of particle radius to the constant of the lattice), equal to 0.2. This configuration provides the most precise agreement between the calculated and experimental spectra. The obtained value of the period is close to the nominal value of 125 nm, and the derived diameter and the concentration of nanoparticles agree with the corresponding parameters found in the previous papers [25,26] using transmission electron microscopy.

From the comparison of Figure 1 and Figure 2 it can be seen that there is a good agreement between the experiment and the calculation. However, the calculation produces a sharper edge of GaAs absorption causing sharp peaks in the reflection spectra at photon energy equal to E_g^{GaAs}. In the experimental spectra such peaks are not observed, probably due to edge blurring and formation of the Urbach „tail“ in absorption. In LT GaAs such blurring is additionally

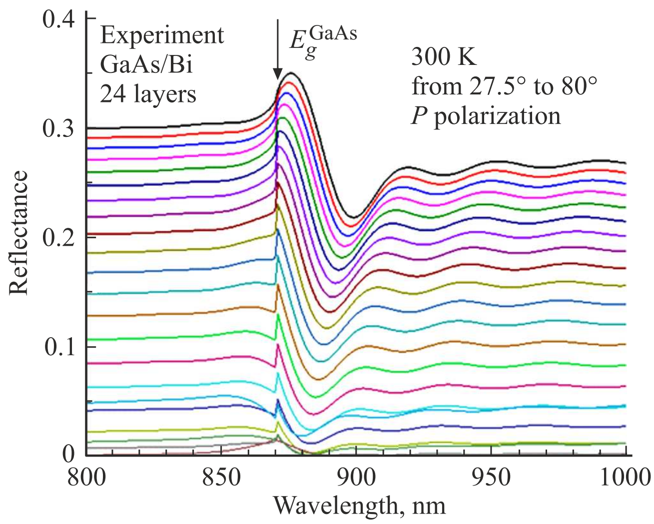

Figure 2. Calculated spectra of reflection from a periodic structure comprising 24 quasi-two-dimensional layers of Bi nanoparticles in the GaAs matrix, at incidence angles of P-polarized light from 27.5° to 80°. The spectra are calculated for room temperature with an angular step of 2.5°.

enhanced due to high concentration of point defects that are formed during low-temperature MBE [29,30].

Therefore, the modeling confirms that the experimental reflection spectra correspond to the optical response of the periodic structure comprising 24 quasi-two-dimensional layers of bismuth plasmonic nanoparticles.

5. Conclusion

Our studies demonstrated that formation of 24 periods of quasi-two-dimensional layers of bismuth nanoparticles makes it possible to form a prominent peak of optical reflection in the wavelength range 870−910 nm near the band edge of the fundamental absorption of the GaAs epitaxial matrix. Modeling of optical spectra with a transfer matrix method based on the data of structural studies and data on dielectric properties of bismuth and gallium arsenide confirmed that the physical reason for the observed reflection peak is the Bragg diffraction of electromagnetic waves induced by localized plasmonic excitations in Bi nanoparticles. It was found experimentally that the absolute amplitude of resonant optical reflection is as high as 15%. This result is provided at a concentration of Bi nanoparticles in delta-layers corresponding to the filling factor equal to 0.2.

Funding

This study was supported by grant of the Russian Science Foundation and St. Petersburg Science Foundation No. 24-22-20012, https://rscf.ru/project/24-22-20012/.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by M.Verenikina