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16

Bragg resonance in the system of layers of plasmonic Bi nanoparticles in GaAs matrix

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We have experimentally studied the optical properties of a structure that consists of a periodical system of quasi-two-dimensional layers of plasmonic bismuth nanoparticles embedded into the crystalline matrix of gallium arsenide. By using methods of transmission electron microscopy and X-ray diffraction, the spatial distribution of plasmonic nanoparticles was experimentally studied, and their characteristic size and concentration were determined. The transfer matrix method was used for modelling the optical reflection spectra. Geometric parameters of the model were determined on the base of the structural data. Optical response of the separate bismuth nanoparticles was calculated in terms of the Mie theory. The developed model quantitatively describes all the significant peculiarities of the experimental optical reflection spectra.

Keywords: non-stoichiometric GaAs, Bi nanoinclusions, localized surface plasmon resonance, Bragg diffraction, optical reflection.

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1. Introduction

Localized surface plasmon resonance (LSPR) makes it possible to concentrate the electromagnetic field on subwavelength scales and exponentially enhance the interaction of light with matter [1], which makes it attractive for practical applications. Metal nanoparticle systems capable of supporting LSPR in a semiconductor environment are one of the most promising objects of plasmonics studies [2–6]. Biological sensors are created on the basis of such systems [6,7], plasmonic nanoparticle systems are capable of improving the energy efficiency of solar panels [8,9], plasmonic resonance can significantly enhance Raman scattering [10–12], plasmons can be used to achieve high-speed information processing in quantum computers [13], LSPR is able to significantly change the optical properties of a semiconductor medium, allowing a significant expansion of the field of application of traditional semiconductor materials [14–16].

The problem with the formation of plasmonic nanoparticle systems in semiconductor media is that the most popular plasmonic metals, including gold, silver, copper, platinum, and others, can be deposited on the surface of a semiconductor in the form of thin films or nanoparticles [17]. However, the formation of a system of nanoparticles of these materials in the volume of epitaxial layer is not an achievable task today. However, there are metals that can form nanoparticles in a semiconductor environment. The elements of the fifth group, namely, As, Sb and Bi, are such plasmonic materials in the case of semiconductors of type $A^{III}B^{V}$, in particular GaAs. Theoretical estimates of LSPR for nanoparticles of these materials in the GaAs matrix show [18–20] that bismuth is the best candidate for LSPR implementation within the GaAs transparency window. The LSPR resonance energy is in the photon energy range outside the transparency window of the semiconductor matrix for a system of bismuth nanoparticles in gallium arsenide. However, due to the large width of the LSPR, it should also affect the optical properties of the material in the long-wavelength region of the spectrum, where the GaAs semiconductor matrix is nominally transparent. The system can be made periodic to further enhance the effect associated with LSPR so that the Bragg resonance [21,22] is also realized in the plasmon resonance region.

It is also important to note that the dissolution of a significant amount of bismuth in the gallium arsenide matrix, which is necessary for the formation of a system of nanoinclusions, is a difficult task. This problem can be solved using the molecular beam epitaxy (MBE) technology [23]. It was demonstrated in Ref. [24] that quasi-two-dimensional layers of bismuth nanoparticles in a GaAs matrix can be created using MBE. It is necessary to grow the structure under non-stoichiometric conditions at a low temperature for this purpose.

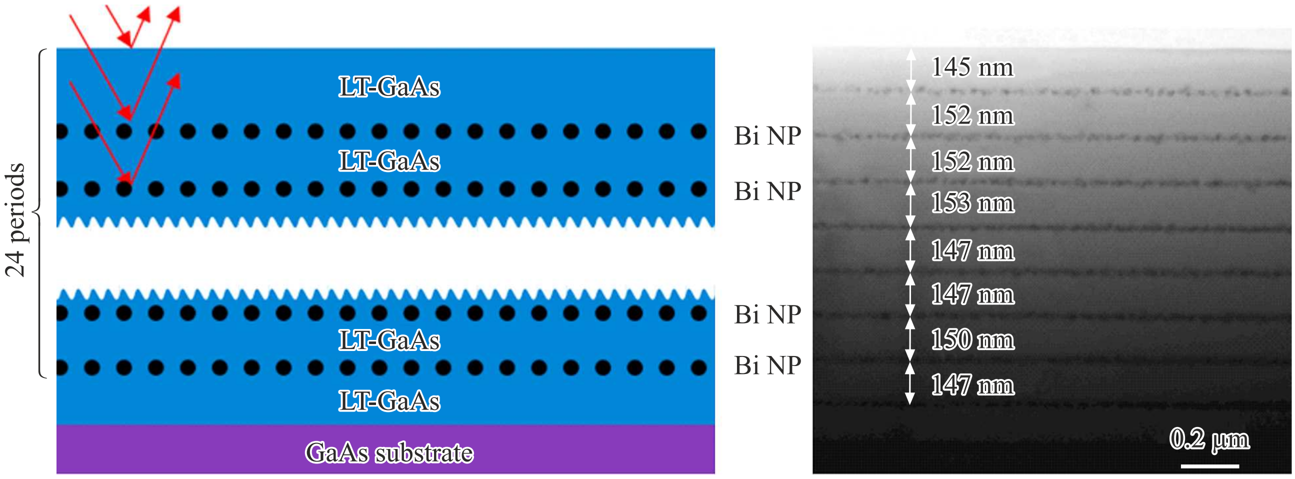

Figure 1. *a* — Schematic representation of the sample cross-section. The dark dots represent bismuth nanoclusions. The red lines with arrows represent the rays of incident and reflected light. *b* — A light-field cross-sectional image of a part of the sample obtained using transmission electron microscopy.

We report the results of experimental optical studies of a plasmon Bragg lattice consisting of 24 layers of Bi nanoparticles formed in a GaAs matrix in this article. A model has been constructed based on the structural research data that quantitatively describes all the essential features of the obtained spectra.

2. Samples and results of structural studies

The studied samples were grown by the MBE method. Semi-insulating gallium arsenide with orientation (001) was used as the substrate. At first, a GaAs buffer layer was built up on the substrate under normal conditions. Then the substrate temperature was lowered to 200°C. Layers of low-temperature gallium arsenide (LT-GaAs) with a thickness of about 145 nm and monolayers of bismuth were successively built up at this temperature, under conditions of excess arsenic. Thus, the structure consisted of 25 layers of gallium arsenide separating 24 delta layers of bismuth (see Figure 1, *a*). The growth process was periodically interrupted, after every five gallium arsenide layers, and during the interruptions the structure was annealed at a temperature of 500°C. The entire structure was also subjected to post-cold annealing at a temperature of 600°C for 15 minutes. As a result, a periodic system of quasi-two-dimensional layers of bismuth nanoclusions was formed. The process of growing samples and forming Bi nanoclusions in them is described in more detail in Ref. [24].

X-ray diffraction studies were performed to determine the bismuth content and geometric parameters of the structure. Diffraction reflection curves were obtained using D8Discover diffractometer from BrukerAXS (Germany) in two-crystal geometry using a Ge (022) quadruple slit monochromator. Studies have revealed a system of diffraction peaks corresponding to the periodic system of delta layers of bismuth. The average period of the resulting structure was equal to 147 nm. X-ray studies have also shown that there is some deviation from the exact periodicity in the structure. Diffraction curves and their detailed discussion are provided in our previous work in Ref. [24].

Transmission electron microscopy (TEM) was used to study the structure of the nanoinclusion system. Samples were prepared in cross section (110) according to standard procedure comprising preliminary mechanical thinning and ion sputtering. Electron microscope JEM-2100F (JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV was used for the measurements. Figure 1, *b* shows a light-field cross-sectional image of the sample. The image shows layers of particles with characteristic sizes from 5 to 15 nm. It was shown in Ref. [24] that these nanoparticles are inclusions of bismuth. It can be seen from Figure 1, *b* that the thickness of the gallium arsenide layers separating the quasi-two-dimensional layers of Bi nanoparticles varies from 145 to 153 nm within nine visible periods. TEM examination of other sections of the sample cross-section also shows variations in the thickness of the GaAs separation layers. The amplitude of thickness fluctuations relative to the average period of the structure does not exceed 10%. Thus, structural studies have shown that a system of quasi-two-dimensional layers of Bi nanoinclusions, close to periodic, was formed in the GaAs crystal matrix.

3. Optical research results

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

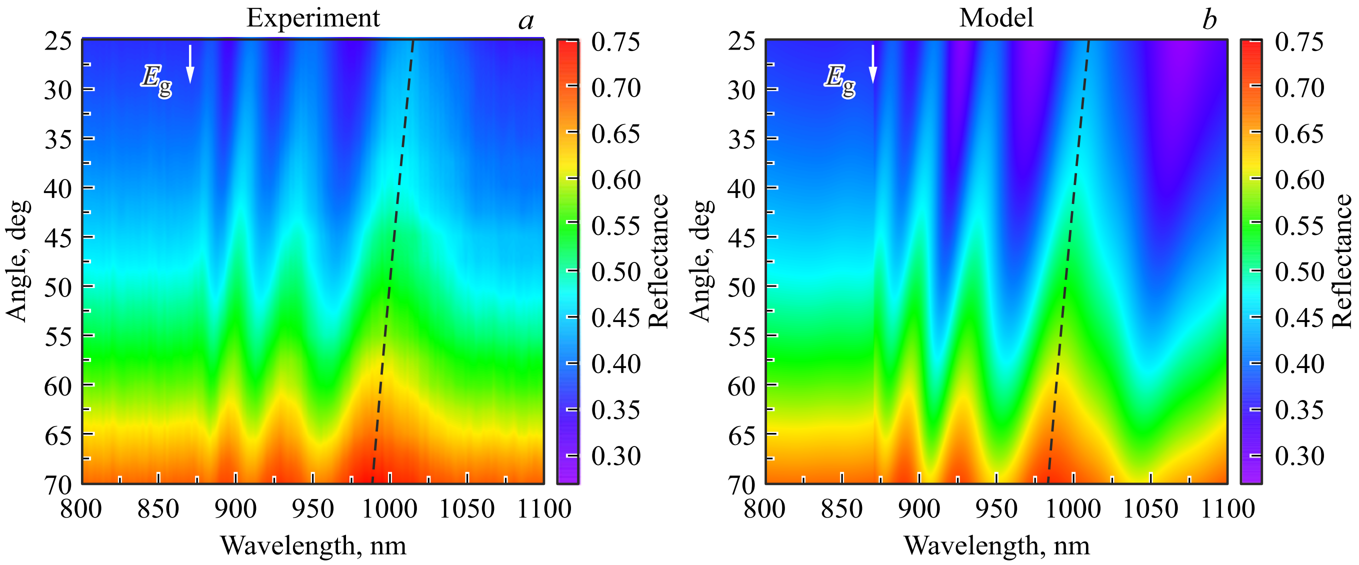

Figure 2. *a* — Optical reflection spectra of a sample annealed at a temperature of 600°C, with *S*-polarization of incident radiation for different angles of incidence, measured at room temperature. The dashed line connects the reflection maxima for each angle. *b* — Calculated optical reflection spectra under the same conditions.

the SpectraSuite software from OceanOptics to record the spectra. All studies were conducted at room temperature.

Figure 2, *a* shows the experimental reflection spectra of *S*-polarized light for various angles of incidence. The spectra show oscillations in the range of 870–1050 nm. The oscillation region is limited by the transparency window of the GaAs matrix on the short wavelength side which is determined by the value E_g. On the long-wave side, the oscillations also fade. It is worth noting that in addition to the main peak of the Bragg reflection in the spectra, there are additional peaks comparable to it in amplitude, which may indicate some violation of the periodicity of the sample.

The main reflection maxima in each spectrum are connected by a dashed line in Figure 2, *a*. It can be seen that the maximum energy shifts towards shorter wavelengths from 1025 to 1000 nm as the angle of incidence of light increases. This displacement is typical for Bragg diffraction, in which the position of the reflection maximum is described by the formula

$$\lambda = 2d\sqrt{\varepsilon_{eff} - \sin^2\theta}, \qquad (1)$$

where λ — spectral position of the reflection maximum, d — distance between reflecting interfaces, θ — angle of incidence of light, ε_{eff} — effective the dielectric constant of the medium.

The formula (1) provides a qualitative explanation of the displacement of the reflection maximum, but for a quantitative description of the diffraction pattern it is necessary to resort to more accurate numerical modeling. The first step in this simulation is to describe the interaction between an electromagnetic wave and a bismuth nanoparticle. This problem can be solved within the framework of Mi theory. Since bismuth nanoparticles have a shape close to spherical, their optical response can be described using the following polarizability:

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

where a is the radius of the particle, ε_m is the dielectric function of the metal, ε_d is the dielectric function of the medium. The well-known Adachi model [25] was used to describe the dielectric function of the GaAs matrix material. Data on the dielectric properties of Bi metal nanoclusions were taken from the study of Ushanov et al. [20].

The Persson-Liebsch model was used to describe the interaction of an electromagnetic wave with a quasi-two-dimensional layer of bismuth nanoparticles [26]. The optical reflection spectra were modeled using the transfer matrix method. When constructing the model, we took into account that five stops were performed during the growth process, during which intermediate annealing was carried out. Therefore, in the model, the entire structure was divided into five groups of layers, in each of which the thicknesses of GaAs separation layers and the parameters of quasi-two-dimensional layers of Bi nanoclusions were assumed to be the same. At the same time, the period in different groups ranged from 119 to 161 nm. The diameters of the metal nanoparticles ranged from 5 to 19 nm. In general, the magnitude of variations in the geometric parameters of the structure used in the modeling of optical spectra corresponded to the data of structural studies. Detailed model parameters are provided in the table.

Figure 2, *b* shows the calculated reflection spectra for different angles of incidence of *S*-polarized light with a wavelength from 800 to 1100 nm. It can be seen that the model used quantitatively describes all the features of the experimental reflection spectrum. The modeling has shown

Parameters of the model used in calculating the spectra shown in Figure 2, *b*

Number of groups	Period d, nm	Reciprocal filling factor R/a*	Particle radius a, nm
1	161	5.9	2.5
2	151	4.9	9.5
3	134	5.5	7
4	133	4.5	3.5
5	119	4.5	3.5

Note. *: Reciprocal filling factor is the ratio of the average distance between bismuth nanoparticles in the delta layer R to their radius a.

that the relatively small amplitude of the main Bragg peak is mainly attributable to the variability of the structure period over 25 layers. The dashed curve shows the displacement of the main peak of the Bragg reflection with a change in the angle of incidence of light, which corresponds to the formula (1) and experimental observations.

To confirm this conclusion, we performed calculations for virtual structures with a strictly periodic system of quasi-two-dimensional layers of Bi nanoinclusions and for the same system containing an extremely small number of nanoinclusions (a large inverse filling factor of quasi-two-dimensional layers). The calculation results are shown in Figure 3 for the angle of incidence of S-polarized light $\theta = 25^\circ$ with red and black lines, respectively. It can be seen from the figure that no significant resonant features are observed in the optical reflection spectra at a low concentration of plasmonic Bi nanoparticles. This spectrum (black curve) contains only weak Fabry-Perot oscillations in the gallium arsenide transparency window that occur during repeated reflection of light between media interfaces. A system of 25 equidistant quasi-two-dimensional layers forms a very strong main peak of Bragg diffraction, accompanied by weaker lateral oscillations, the amplitude of which decreases with distance from the resonant frequency (red curve). A comparison of the diffraction patterns in Figure 2 and Figure 3 shows that, firstly, Bi plasmonic nanoparticles play a crucial role in the formation of optical reflection spectra from the structure; and, secondly, the resonant optical response is very sensitive to deviations from the strict periodicity of the structure.

It should be noted that the dependence of optical resonance on deviations from periodicity is not a specific property of plasmonic nanostructures. A similar effect, for example, was observed for quasi-periodic systems of quasi-two-dimensional excitons [27–30]. A detailed analysis of the phenomena associated with spatial disorder is beyond the scope of this work. The Bragg oscillations in the optical reflection spectra obtained in the numerical model are limited from the short wavelength side by the beginning of the interband absorption band in the GaAs matrix. They are also attenuated by long waves greater than 1050 nm like in the experiment. This attenuation turned out to be related to the dispersion of the dielectric function Bi. Our calculations have shown that Bi nanoparticles cannot maintain localized plasmon resonance in the GaAs matrix in the long-wavelength spectral region. Namely, the resonant polarizability enhancement requires according to the formula (2) that the dielectric constant of the metal is negative, and its absolute value is close to twice the value of the dielectric constant of the dielectric medium. According to the data provided in Ref. [20], the dielectric function of bismuth cannot ensure that this condition is met for wavelengths of light greater than 1200 nm.

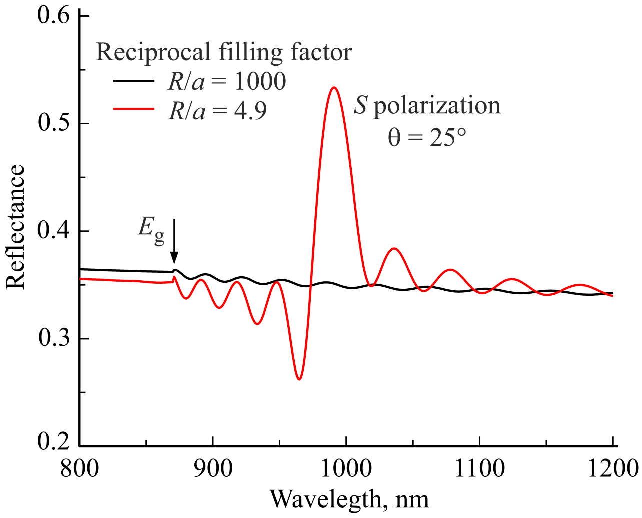

Figure 3. The results of modeling of optical reflection spectra from a structure with 24 equidistant quasi-two-dimensional layers of Bi nanoparticles with an inverse filling factor of 4.9 and a period of 139 nm (red line) and the same structure with an inverse filling factor of 1000 (black line). Calculations were performed for S-polarization and angle of incidence of light of 25°.

4. Conclusion

Optical reflection spectra from epitaxial gallium arsenide layers with an integrated system of quasi-two-dimensional layers of plasmonic bismuth nanoparticles were studied for the first time in this paper. Bragg oscillations of the intensity of light reflected from the layers of Bi nanoparticles were detected in the optical reflection spectra. A model has been constructed that quantitatively describes experimental optical reflection spectra and is consistent with data from X-ray diffraction and electron microscopy studies.

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Conflict of interest

The authors declare that they have no conflict of interest.

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