Technical Physics Letters, 2024, Vol. 50, No. 6

09.4

Formation of GaAs layers with Ag nanoparticles by ion implantation

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Received February 12, 2024
Revised March 9, 2024
Accepted March 9, 2024

The formation possibility of GaAs-based composite material containing Ag nanoparticles using ion implantation technology was studied. For this purpose, GaAs layers were irradiated with Ag^+ ions by an energy $E = 30$ keV at a current density of $J = 5\,\mu$A/cm^2 and a dose of $D = 6.2 \cdot 10^{16}$ ion/cm^2. To analyze the fabricated material, methods of electron microscopy and optical reflection spectroscopy were used. The experimental spectra were compared with the calculated ones of optical extinction obtained within the framework of the electromagnetic Mie theory. The formation of plasmon Ag nanoparticles ranging in size from 5 to 40 nm in the GaAs layer was demonstrated.

Keywords: GaAs, ion implantation, plasmon Ag nanoparticles.

DOI: 10.61011/TPL.2024.06.58480.19889

Layers of commonly used semiconductors (e.g., Si and Ge) containing plasmon noble-metal nanoparticles [1] are regarded as promising materials for fabrication of various types of electronic and optoelectronic devices. Other matrices, such as GaAs, also present some features of interest. Specifically, high-efficiency solar cell elements based on GaAs with plasmon Au, Ag, and Al nanoparticles are being investigated [2–4]. It was demonstrated that the integration of these nanoparticles with GaAs leads to an enhancement of total optical absorption of composite materials due to plasmon effects (collective oscillations of electrons in a metal), an increase in photoconductivity, and the manifestation of antireflective and light scattering properties. In addition, GaAs electrodes with Ag nanoparticles deposited onto them may be used as catalysts for decomposing methylorange dye in solutions during irradiation by ultraviolet and visible light [4]. Au:GaAs and Ag:GaAs substrates with Schottky contacts on them are regarded as promising sensors for polar gases CO and NO [5,6]. Layers of GaAs with island Au nanoantennas on the surface turned out to be efficient low-temperature photoconductive terahertz detectors [7].

Various techniques, such as synthesis of nanoparticles in solution with their subsequent centrifugal deposition onto the surface of GaAs substrates [2], electrochemical deposition of nanoparticles in solution [5], and evaporation in vacuum or RF sputtering of metal targets [7], were used for fabrication of composite materials from GaAs and plasmon metal nanoparticles.

In the present study, the method of low-energy high-dose implantation of metal ions, which has been applied successfully for ion synthesis of metal nanoparticles in semiconductor Si and Ge substrates [1,8], is proposed to be used for fabrication of layers with Ag nanoparticles in a GaAs matrix. Thus, the aim of this study is to evaluate the applicability of ion implantation for fabrication of GaAs layers with metal nanoparticles.

Smooth single-crystal GaAs layers with a thickness of $0.8\,\mu$m, which were formed by magnetron deposition on crystalline InGaP substrates in accordance with the procedure outlined in [9] with 30 min of subsequent thermal annealing at a temperature of 300°C, were used as substrates for ion implantation. Implantation was performed by an ILU-3 ion accelerator in vacuum (10^{-5} mm Hg) with Ag^+ ions with energy $E = 30$ keV, dose $D = 6.2 \cdot 10^{16}$ ion/cm^2 at current density $J = 5\,\mu$A/cm^2 and room temperature of the irradiated substrate. The sample surface morphology was examined with a Merlin (Carl Zeiss) scanning electron microscope (SEM) at an accelerating voltage of 5 kV and a current density of 300 pA. Specular optical reflection spectra of samples in the range of 230−1050 nm were measured with an AvaSpec-2048 (Avantes) waveguide spectrometer.

The DYNA computer code was used to evaluate the profiles of nonuniform depth distribution of implanted Ag^+ ions with $E = 30$ keV within the GaAs sample. The physical principles of calculation utilized in DYNA were discussed in detail the work [10]. This code relies on the approximation of binary collisions between accelerated ions and atoms of the irradiated matrix. These collisions induce a dynamic (dependent on irradiation time) change in the phase composition of the implanted substrate layer, the concurrent variation of which due to surface sputtering is also taken into account. The obtained results suggest that implanted Ag^+ ions are embedded in GaAs following a Gaussian statistical curve with its maximum at depth $R_p \sim 14.6$ nm and a straggle of $\Delta R_p \sim 6.9$ nm. The thickness of the near-surface doped layer (with surface sputtering during implantation taken into account) was estimated as $h = R_p + 2\Delta R_p$ i.e. 30 nm.

Figure 1 shows the SEM image of the surface of the initial GaAs layer and the Ag:GaAs sample. It is evident that the semiconductor surface prior to ion implantation appears to be smooth and free from any morphological features (Fig. 1, *a*). The irradiation with Ag^+ ions induced

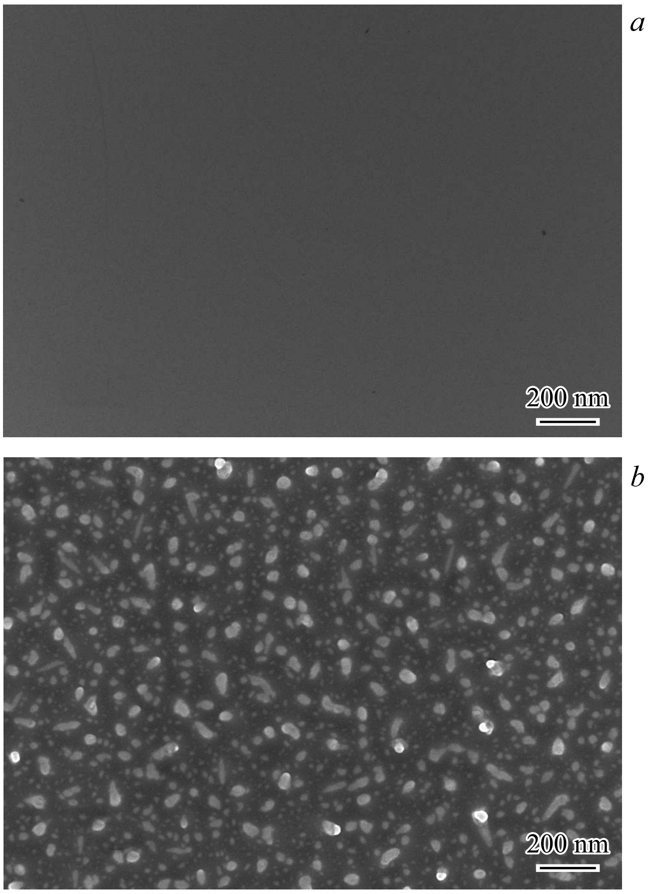

Figure 1. SEM image of the GaAs surface prior to (*a*) and after (*b*) implantation with Ag^+ ions at $E = 30$ keV, $J = 5\,\mu A/cm^2$, and $D = 6.2 \cdot 10^{16}$ ion/cm^2.

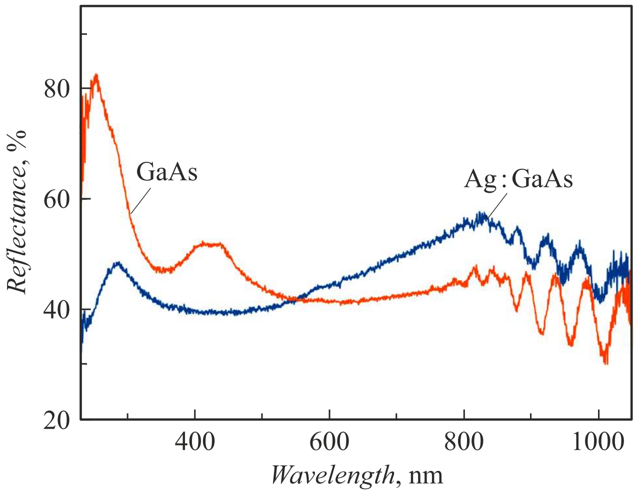

Figure 2. Spectra of optical reflection from the initial GaAs substrate and the implanted Ag:GaAs sample surface.

the formation of metal nanoparticles with sizes varying approximately from 5 to 40 nm, which appear in the SEM image in the form of bright spots distributed uniformly over the dark GaAs surface background (Fig. 1, *b*). A similar pattern was reported in experiments on implantation with metal ions into Si and Ge matrices [1,8]. The formation of pores, as in the case of Si^+ and Ge^+ ions [11], was not observed on the surface of GaAs irradiated with Ag^+ ions.

The optical reflectance of an ideal direct-band-gap semiconductor GaAs is characterized by bands with maxima at 242.2 nm (5.12 eV), 295 nm (4.2 eV), 427.6 nm (2.9 eV), 539 nm (2.3 eV), and 918.5 nm (1.35 eV), which are induced by intraband and interband electronic transitions [12]. The defect structure and the fabrication methods of GaAs crystals specify which of the above reflection bands are visible in actual experimental spectra. Notably, the intensity of the 242 nm band in the short-wavelength spectral region is the dominant one and is present in all types of GaAs, region is used in practice to characterize the degree of GaAs crystallinity.

The GaAs substrate used in this work in the short-wavelength region of the reflection spectrum demonstrates the presence of an intense band with a maximum at 242 nm, a shoulder near 295 nm, and a weaker double band at about 427 nm (Fig. 2). These bands vanished after irradiation with Ag^+ ions, indicating that the implanted layer was amorphized. A similar integral suppression of reflection upon amorphization of the surface for various semiconductors was demonstrated early in the work [1]. In the long-wavelength region of the reflection spectrum, GaAs and Ag:GaAs samples dempnstrate interference bands that emerge due to penetration of optical radiation through the deposited GaAs film and reflection from its substrate.

Figure 2 also reveals the emergence of an additional broad reflection band with a maximum around ~ 800 nm after ion implantation. Naturally, this band should be attributed to the formation of Ag nanoparticles in Ag:GaAs and the associated plasmon resonance effects. In order to verify this hypothesis, plasmon extinction spectra of Ag nanoparticles in a GaAs matrix were modeled with the use of the electromagnetic Mie theory, which was described in detail in the work [13]. Spectral values of permittivity of Ag nanoparticles and the GaAs medium for modeling of extinction spectra in the visible range were taken from the work [14].

Figure 3 shows the resonance extinction spectra calculated within the Mie theory for Ag nanoparticles of various diameters (from 10 to 40 nm) consistent with the SEM data (Fig. 1, *b*). It is evident that plasmon extinction bands with maxima positioned in the spectral interval from 750 to 850 nm correspond to metal nanoparticles. The spectral positioning of these bands is in close qualitative agreement with the experimental reflection spectrum for the Ag:GaAs layer (see Fig. 2). Note that this spectral positioning of extinction spectra for Ag nanoparticles modeled using the Mie theory is also consistent with the results of calculations for a similar structure performed within the Maxwell–Garnet effective medium theory [15].

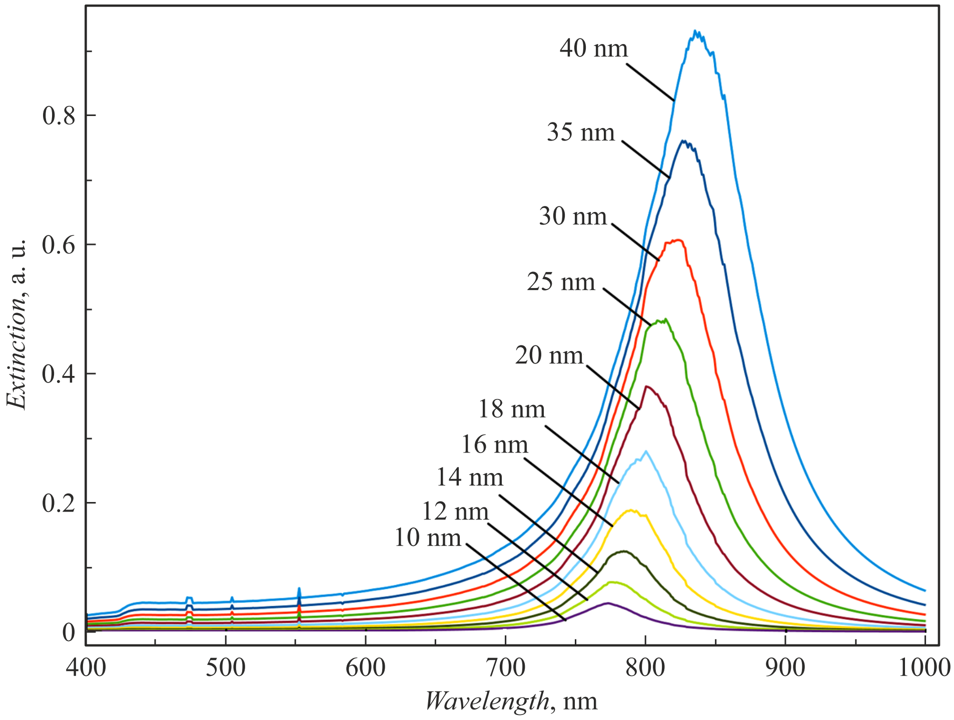

Figure 3. Calculated extinction spectra of Ag nanoparticles of various sizes in GaAs.

Thus, a composite material (Ag:GaAs) was formed for the first time by low-energy high-dose implantation of Ag^+ ions into a GaAs substrate. The formation of Ag nanoparticles in a GaAs layer was confirmed via electron microscopy and optical spectroscopy. The presence of ion-synthesized Ag nanoparticles in Ag:GaAs was verified by the results of modeling of plasmon resonance spectra within the Mie theory. It was demonstrated that the clean vacuum technology of ion implantation is suitable for fabrication of a thin-layer composite GaAs material with Ag nanoparticles, which may be regarded as a candidate material for solar cells and GaAs-based photodetectors.

Acknowledgments

The authors wish to thank V.I. Nuzhdin and V.F. Valeev for their help with ion implantation.

Funding

This study was carried out as part of the state assignment of the Federal Research Center „Kazan Scientific Center of Russian Academy of Sciences.“

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by D.Safin