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Features of isovalent doping of gallium arsenide with bismuth ions

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Abstract. The work shows the possibility of doping gallium arsenide with bismuth during ion implantation and the effect of rapid thermal and pulsed laser annealing on these structures. The results of a study of bismuth depth distribution profiles are presented in comparison with theoretical calculations. The influence of bismuth on the optical properties of gallium arsenide was investigated using transmittance and reflection spectroscopy methods. It has been shown that the introduction of bismuth leads to a decrease in the band gap of gallium arsenide.

Keywords: gallium arsenide, bismuth doping, ion implantation, pulsed laser annealing, rapid thermal annealing

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Материалы конференции
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Особенности изовалентного легирования арсенида галлия ионами висмута

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Аннотация. В работе показана возможность легирования арсенида галлия висмутом методом ионной имплантации, а также влияние быстрого термического и импульсного лазерного отжига на эти структуры. Представлены результаты исследования профилей распределения висмута по глубине в сравнении с теоретическими расчетами. Влияние висмута на оптические свойства арсенида галлия исследовано методами спектроскопии пропускания и отражения. Показано, что введение висмута приводит к уменьшению ширины запрещенной зоны арсенида галлия.

Ключевые слова: арсенид галлия, легирование висмутом, ионная имплантация, импульсный лазерный отжиг, быстрый термический отжиг

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Introduction

Bismuth is an element of Group V of the Periodic Table and, accordingly, is isovalent to arsenic atoms. The introduction of Bi atoms into the crystal lattice of gallium arsenide leads to the formation of a substitutional solid solution $GaAs_{1-x}Bi_x$. Due to the fact that Bi is heavier than arsenic (209 and 75 a.m.u., respectively), doping GaAs with it leads to a significant change in the properties of this semiconductor.

Thus, the introduction of bismuth leads to a decrease in the band gap (Eg) of this material. It was shown in [1] that the value of E_g at room temperature decreases monotonically from 1.42 eV for gallium arsenide to 0.8 eV for GaAs with ≈ 11 at.% of bismuth.

Also, in GaAs:Bi, even at low concentrations of bismuth, the energy of spin-orbit splitting (Δ_{SO}) increases. It was shown in [2] that Δ_{SO} increased from 0.34 eV for GaAs to ≈ 0.46 eV in GaAs:Bi with a bismuth content of about 1.8 at.%.

The influence of bismuth on electric transport properties is also noted in the literature. The addition of bismuth to nominally undoped gallium arsenide leads to the formation of the hole conductivity associated with the appearance of a shallow acceptor level at 26.8 meV, and, as shown in [3] and [4], an increase in the bismuth concentration in the $GaAs_{1-x}Bi_x$ solid solution leads to an increase in the hole concentration. The effect on electric transport in doped GaAs:Bi layers is shown in [5]. Thus, at bismuth concentrations up to 1.6 at.%, the electron mobility changes insignificantly, while the hole mobility decreases by more than an order of magnitude. Moreover, a decrease in the hole concentration in acceptor GaAs:Bi was observed, which the authors associate with the formation of bismuth clusters in GaAs, leading to the appearance of hole trap states.

As an alternative to the epitaxial methods usually described in the literature for obtaining GaAs:Bi, this work uses bismuth doping by ion implantation.

Materials and Methods

Bismuth ions were implanted into i-GaAs(001) substrates at the Raduga-3M accelerator, while the accelerating voltage (30 or 80 kV) and the dose of implanted ions were varied. The main feature of the accelerator is a vacuum arc source, which makes it possible to create intense ion beams using solid precursors. The source operates in a pulse-periodic mode with a pulse duration of ≈ 200 μs and a repetition rate of 50 pulses/s. Another feature of the accelerator is that the ion beam contains several charge fractions, and the distribution among the fractions depends on the specific metal. In particular, for Bi, the beam contains, according to [6], 83% Bi^+ and 17% Bi^{++} fractions. The implantation dose was chosen in such a way that, according to calculations using the SRIM 2013 code, the average bismuth content in the implanted layer varied from 0.5 to 1.0 and 1.5 at. %. For an accelerating voltage of 30 kV, these doses were $7\cdot10^{14}$, $1.4\cdot10^{15}$ and $2.1\cdot10^{15}$ cm^{-2}, respectively. For an accelerating voltage of 80 kV, the implantation doses were $8\cdot10^{14}$, $1.6\cdot10^{15}$ and $2.4\cdot10^{15}$ cm^{-2}. Since the ion mass is large (M_1 = 209 a.m.u.), the large sputtering coefficient (S = 16.0 atoms/ion for a Bi ion energy of 80 keV) must be taken into account when calculating distribution profiles.

After implantation, one part of the samples was subjected to pulsed laser annealing (PLA) with a KrF excimer laser with a pulse duration of 30 ns at different energy densities (P) per pulse (240 mJ/cm^2 for structures irradiated at 30 kV; 250, 300 and 400 mJ/cm^2 for 80 kV), and for comparison, the other part of the samples was subjected to rapid thermal annealing (RTA) in ultra-pure argon at T_a = 800 °C for 20 s. At this process the working surface of the samples was placed on a Si substrate plate, which prevented the evaporation of As atoms from the surface layer. The distribution of bismuth in the resulting layers was studied using the method of secondary ion mass spectrometry (SIMS) on the TOF.SIMS 5 installation during sputtering of GaAs with a beam of Cs ions. For comparison with experimental profiles, theoretical profiles of bismuth distribution were calculated using the SRIM 2013 code, taking into account ion sputtering of the structure surface in accordance with [7]. The properties of the resulting structures were studied using transmission and reflection spectroscopy in the wavelength range from 0.18 to 1.8 μm using a Cary 6000i dual-beam spectrophotometer (Varian).

Results and Discussion

The profiles of the distribution of bismuth atoms over the depth of the structures obtained by the SIMS method are shown in Fig. 1. For comparison, the calculated profiles are also given there. Note that for the Bi ion energy of 80 keV, the maximum of the distribution is located outside the boundary of the figure (the average projected range was 24 nm). It can be seen that, in comparison with the calculation, the profiles of Bi atoms after implantation are pulled towards the surface (see curves *2* in Fig. 1, *a* and Fig. 1, *b*). After thermal (curve *3* in Fig. 1, *b*) and laser annealing (profile *3* in Fig. 1, *a* and profiles *4* and *5* in Fig. 1, *b*), an increase of the bismuth concentration is observed in the near-surface region and a decrease in deeper regions. This suggests that during annealing, bismuth atoms move from the bulk to the surface. It is interesting that during laser annealing with $P < 300$ mJ/cm^2 of samples irradiated with both accelerating voltages of 30 and 80 kV, a second maximum is observed at a depth of about 5 nm, which disappears during annealing with a higher PLA energy. The height of the surface peak of bismuth atoms increases with increasing energy density of pulsed laser annealing.

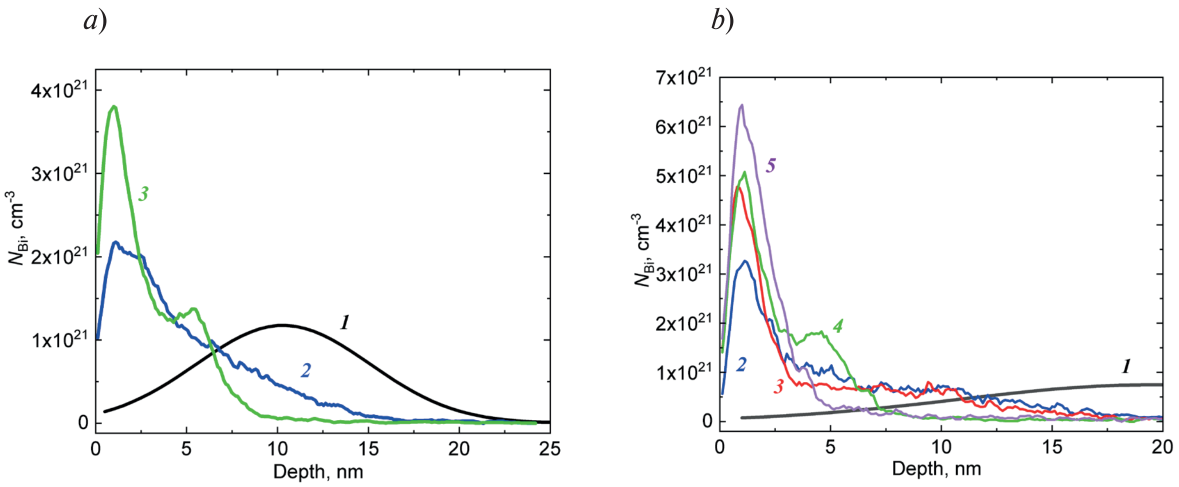
a) *b*)

Fig. 1. Calculated (curves *1*) and experimentally determined bismuth depth distribution profiles: (*a*) implantation with an accelerating voltage of 30 kV, a dose of 1.4×10^{15} cm^{-2} before annealing (curve *2*) and after PLA with P = 240 mJ/cm*2* (curve *3*); (*b*) implantation with an accelerating voltage of 80 kV, a dose of 1.6×10^{15} cm^{-2} before annealing (curve *2*), after RTA (curve *3*) and after PLA with an energy density of 250 (curve *4*) and 400 mJ/cm^2 (curve *5*)

The optical properties of GaAs samples irradiated with Bi ions were studied. Reflection spectra for structures implanted at 30 kV are shown in Fig. 2.

The reflection spectra of single-crystal GaAs contain characteristic features in the form of a doublet maximum at photon energies of 2.90 and 3.14 eV and a maximum at ~ 5 eV. After implantation, the reflection spectrum is a structureless dependence on the quantum energy, which indicates a complete loss of long-range order (amorphization) in the near-surface region of irradiated GaAs. After both thermal and laser annealing, the crystal structure is almost restored; only insufficient resolution of peaks near 3 eV indicates residual radiation defects.

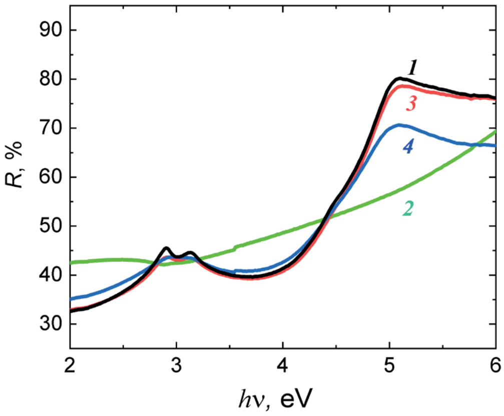

Fig. 2. Reflection spectra: single-crystal GaAs (curve *1*) and GaAs samples irradiated with Bi ions with an accelerating voltage of 30 kV: after ion implantation (curve *2*), RTA (curve *3*) and PLA (curve *4*) with *P* = 240 mJ/cm²

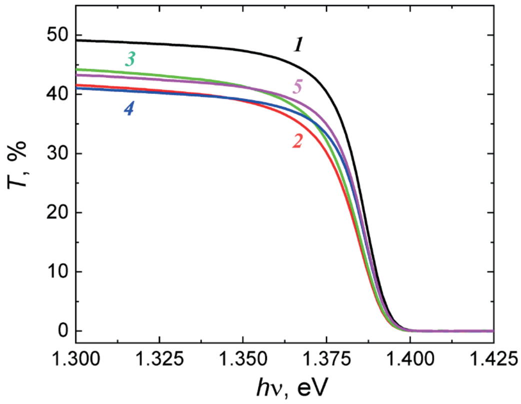

Fig. 3. Transmission spectra of single-crystal GaAs (curve *1*) and GaAs samples irradiated with Bi ions with an accelerating voltage of 80 kV: doses of $8{\cdot}10^{14}$ cm^{-2} (curve *2*) and $2.4{\cdot}10^{15}$ cm^{-2} (curve *3*) after RTA, a dose of $2.4{\cdot}10^{15}$ cm^{-2} after PLA with *P* = 250 mJ/cm² (curve *4*) and *P* = 400 mJ/cm² (curve *5*)

Fig. 3 shows the transmission spectra of GaAs(001) irradiated with Bi ions. Double-sided polished substrates of GaAs were used in these experiments.

It can be concluded that when bismuth is introduced, the absorption edge shifts to longer wavelengths. The band gap values for GaAs with bismuth estimated from the spectra give $E_g \approx 1.398$ eV at room temperature, which is less than 1.42 eV for single-crystal GaAs. An estimate based on data from [1] of the effective bismuth concentration, which affects the absorption edge, gives a value of ~ 1 at.%. This value coincides well with the average concentration of bismuth atoms in the layer up to approximately 15 nm, excluding the near-surface region with a thickness of 3 nm (see Fig. 1).

When discussing the presented results, it is first necessary to understand the reasons for the deviation of the implanted Bi profiles from the calculated ones. Let us pay attention to the similarity in the behavior of the impurity (pulling the Bi profile to the surface) during annealing and during the implantation process. This may indicate that, during pulsed ion irradiation, melting of the near-surface layer occurs, followed by recrystallization from the single-crystal substrate when the sample is cooled. In this case, the recrystallization front moves from single-crystal GaAs to the surface, leading to segregation and accumulation of bismuth near the surface. A similar process can occur during PLA. It is unlikely that Bi atoms in the subsurface layer 3 nm thick after implantation occupy GaAs lattice sites. Apparently, they enter into a chemical interaction with atmospheric oxygen and are included in the form of oxides in the transparent native oxide GaAs.

Conclusion

The work experimentally demonstrated the possibility of doping gallium arsenide with bismuth in the process of ion implantation. The effectiveness of using pulsed laser and rapid thermal annealing for restoring the crystal structure of the obtained samples has been shown, as evidenced by the reflection spectra. In a study of transmission spectra, it was experimentally shown that bismuth reduces the band gap of GaAs. In this case, the effective concentration of bismuth, which affects the shift of the absorption edge, is about 1 at.%. This may be due to heating processes occurring during implantation, which is a feature of the ion source which we used, as confirmed by secondary ion mass spectrometry data.

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