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Application of Ar⁺ ion implantation for obtaining nanocontacts on the GaP (111) single crystals surface

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Ultrathin ohmic contacts were fabricated on GaP(111) single crystals using argon ion (Ar⁺) implantation at an energy of $E_0 = 2$ keV and a dose of $D = 2 \times 10^{17}$ cm⁻², under high vacuum conditions (10⁻⁷ Pa). Post-irradiation analysis revealed a significant enrichment of the surface with gallium, reaching a concentration of approximately 90 at.%. Subsequently, a nickel (Ni) film with a thickness of about 1000 Å was deposited onto the GaP(111) surface to form the contact. This metallization step led to a three- to fourfold reduction in the total thickness of the contact layer compared to conventional approaches. Upon thermal treatment at $T = 850$ K, the initially disordered GaP(111) layers recrystallized, resulting in a polycrystalline contact structure. After annealing, the thickness of the contact layer increased by approximately 1.5 times, reaching 400–450 Å, which is still around 2.5 times thinner than the characteristic thickness (d_n) in the Ni/pure-GaP system. These findings demonstrate that ion implantation, followed by controlled metallization and annealing, provides an effective route for producing ultrathin, thermally stable ohmic contacts for GaP-based semiconductor devices.

Keywords: GaP(111), Ion implantation Ar⁺ ions, Ohmic contact, metal–semiconductor interface.

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Introduction

Binary A^{III}B^V semiconductors and multicomponent heterostructures based on them are widely used in the development of various opto-, micro-, and nanoelectronic devices. In particular, multilayer structures with layers of GaP, GaAs, GaInP, and AlGaInP are applied and show promising potential for the fabrication of laser diodes, solar cells, and photoelectric and optoelectronic devices [1-7]. When developing MIS (metal-insulator-semiconductor) and Schottky barrier structures, special attention is given to forming reliable ultrathin ohmic contacts on the surfaces of these semiconductors. Producing an ultrathin metal–semiconductor ohmic contact is challenging and depends on many factors, such as surface morphology, conductivity type of the semiconductor, degree of doping and oxidation, Schottky

barrier height, and others. Moreover, in many cases, such a contact becomes rectifying, and due to mutual diffusion of atoms, the penetration depth of metal atoms into the semiconductor can reach 500-600 Å. After thermal annealing, this depth may increase even further.

To fabricate ultrathin contacts in nanoscale structures, several methods are employed, including phase separation techniques, low-energy ion doping, deposition of multilayer compositions, and continuous heating of metal–semiconductor contacts [8-16]. These methods have mainly been used for Si and Ge. Each of them has certain advantages but also inherent limitations.

In [5], to form reliable ohmic contacts on Si, a method of Ba⁺ ion implantation was used, with energy E_0 varying from 5 to 0.5 keV. In all cases, the ion dose was approximately 6×10^{16} cm⁻². Post-implantation annealing at $T \approx 100$ –1100 K was performed to crystallize the ion-

implanted layers and form barium silicides. The resulting BaSi₂ films exhibited a specific resistivity ρ of approximately 50–100 $\mu\Omega\cdot\text{cm}$. Subsequently, a layer of nickel atoms was deposited onto the silicide surface. The penetration depth of Ni into Si was reduced by a factor of 5–6, down to ~ 100 Å. Only fragmentary studies of this type have been conducted for binary III–V semiconductors. In this work, we attempted to form a thin ohmic contact on the surface of a GaP single crystal using a method of irradiation with Ar⁺ ions.

I. Experimental details

The objects of study were monocrystalline GaP (111) samples. These samples were mounted in a universal ultrahigh-vacuum (UHV) chamber with a base pressure of approximately 10^{-7} Pa, where all technological operations— including heating, nickel (Ni) atom deposition, and ion implantation— were conducted, along with the analysis of the samples' composition and structure.

Nickel deposition was performed by thermal evaporation of high-purity Ni wire. Prior to deposition, the Ni wire was degassed for 5–6 hours under a vacuum of no worse than 10^{-6} Pa. The Ni film deposition rate was pre-calibrated and set at approximately 5 Å/min.

To fabricate ultrathin contacts, the surfaces of the GaP(111) samples were pre-treated by argon ion (Ar⁺) implantation. The principle of Ar⁺ ion generation is based on the ionization of argon atoms through collisions with fast-moving electrons. The ion source consisted of a filament and an anode, both placed in a magnetic field generated by a solenoid. Argon gas was introduced into the UHV system through an all-metal leak valve. Electrons emitted from the heated filament were accelerated by an electric field between the filament and the anode. Under the influence of the solenoidal magnetic field, these electrons followed a spiral trajectory within the anode, significantly increasing the probability of Ar ion generation. The geometry of the ion gun was designed to ensure a sufficient pressure gradient between the ion source and the sample analysis chamber. The ion source operated at an argon pressure of 10^{-2} Pa, while the pressure in the analytical section of the system did not exceed 5×10^{-7} Pa.

The elemental and chemical composition of the sample surfaces was examined using an Auger electron spectrometer (AES) equipped with a four-grid analyzer. Depth profiles of atomic distribution were obtained by AES in combination with stepwise ion etching using Ar⁺ ions at an energy of $E_0 = 2$ keV, incident at angles ranging from 5° to 10° relative to the sample surface. The etching rate was approximately 5 Å/min.

The crystalline structure of the sample surfaces was investigated by reflection high-energy electron diffraction (RHEED) using a EMR-102 setup. The surface resistivity was measured using the four-point probe method with a Jandel RM3000+ system. The surface morphology was examined using a scanning electron microscope (SEM) of the JSM-7200F type.

II. Results and Discussion

Prior to ion treatment, GaP(111) samples were degassed at a temperature of 900 K for approximately 4 hours under a vacuum of $P \approx 10^{-7}$ Pa. Analysis of the SEM images revealed that, after annealing, the GaP (111) surface exhibits atomic-level smoothness [6]. Figure 1 presents Auger electron spectra of pristine GaP(111) and GaP surfaces implanted with Ar⁺ ions at $E_0 = 2$ keV and a dose of $D = 2 \times 10^{17}$ cm⁻². To suppress channeling effects, the ion beam was directed at an angle of 5° – 60° relative to the surface normal. Further increasing the ion dose beyond this value did not lead to significant changes in surface composition, indicating that this dose corresponds to the saturation threshold (D_n). In the AES spectrum of the as-prepared GaP(111) surface, characteristic peaks of gallium (Ga) at 54, 79, and 103 eV, along with a phosphorus (P) peak at 121 eV, were observed, corresponding to the Ga-P compound.

Following Ar⁺ implantation, intense Ga peaks associated with elemental gallium appeared, while the phosphorus signal decreased sharply. This indicates that the GaP(111) surface becomes fully enriched with Ga atoms, effectively resulting in surface metallization.

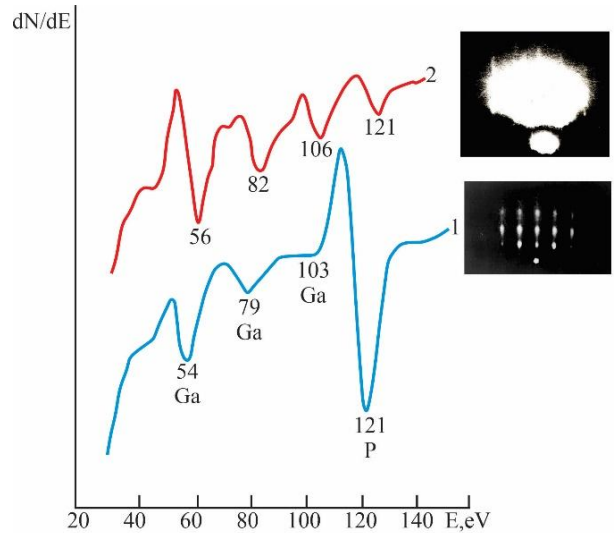


Fig. 1. Auger electron spectra of GaP(111) before (1) and after Ar⁺ ion implantation at $E_0 = 2$ keV with a dose of $D = 8 \times 10^{16}$ cm⁻² (2). The inset shows RHEED images of the GaP(111) surface before and after Ar⁺ ion irradiation, illustrating the transition from a crystalline to a disordered structure.

The concentrations of gallium (Ga) and phosphorus (P) at the surface and at various depths of Ar⁺-implanted GaP(111) were estimated by analyzing changes in Auger peak intensities using the following expression:

$$C_X = \frac{I_X/S_X}{I_i/S_i} \cdot \alpha,$$

where I is the Auger peak intensity, S is the elemental Auger sensitivity factor, and α is a matrix correction factor. For phosphorus, the LMM transition peak at $E = 121$ eV was used, while for gallium, the LMM peak at $E = 1071$ eV was applied (not shown in Figure 1).

The inset of Figure 1 shows RHEED patterns for GaP(111) before and after Ar⁺ ion bombardment. In the case of pristine GaP(111), the RHEED image clearly displays reflections characteristic of a single crystal with a cubic lattice structure. Calculations indicated that the lattice constant of GaP(111) is approximately 5.45 Å. After ion bombardment with Ar⁺ ions at E₀ = 2 keV and a dose of approximately 2 × 10¹⁷ cm⁻², these reflections disappear and are replaced by a broad white halo, typical of an amorphous structure. This confirms that under these conditions, the surface of GaP(111) becomes completely disordered.

Figure 2 presents the depth distribution profile of gallium atoms (C_{Ga}) in GaP(111) following Ar⁺ ion implantation at E₀ = 2 keV and a dose of D = 2 × 10¹⁷ cm⁻².

The data show that within the near-surface region up to a depth of approximately 60 Å, the Ga concentration remains nearly constant at ~90 at.%. In the depth range of x ≈ 60–100 Å, C_{Ga} gradually decreases to ~45–50 at.%, approaching the stoichiometric composition characteristic of GaP. At the same time, the surface was found to contain a certain amount of unbound phosphorus atoms (~5–6 at.%) and a non-stoichiometric Ga + P compound (~2–3 at.%). The sheet resistivity (ρ_s) of the GaP surface was measured using the van der Pauw four-point probe method, both before and after ion implantation. Prior to treatment, the resistivity was approximately 2.8 Ω·cm, whereas after Ar⁺ irradiation, it was reduced to ~5 × 10⁻³ Ω·cm, indicating a significant improvement in surface conductivity due to metallization.

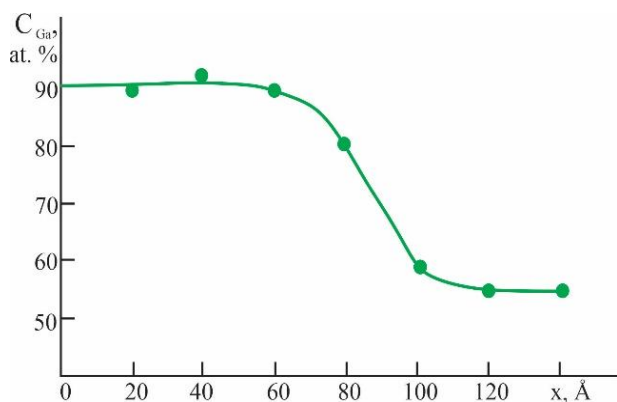


Fig. 2. Depth profile of gallium concentration (C_{Ga}) as a function of depth (x) in GaP(111) implanted with Ar⁺ ions at E₀ = 2 keV and a dose of D = 2 × 10¹⁷ cm⁻².

From the C_{Ga} profile in Figure 2, it is evident that the chemical composition of GaP is altered to a depth of approximately 95–100 Å, suggesting that the ion penetration depth for Ar⁺ at E₀ = 2 keV is around 100 Å. Calculations further indicate that the thickness of the amorphized surface layer is 2–2.5 times greater than the ion range, amounting to approximately 250 Å.

To enhance the crystallinity of the disordered GaP layer and improve film uniformity, rapid thermal annealing (RTA) was performed at T = 525 °C for 30 seconds. Following annealing, a nickel film of ~1000 Å thickness was deposited onto the surface under vacuum conditions of ~10⁻⁶ Pa.

Figure 3 presents the depth distribution profiles of Ni

atoms in three cases: (1) pure GaP(111), (2) Ar⁺-implanted GaP before annealing, and (3) after annealing at T = 800 K for 30 minutes. It is evident that the penetration depth of Ni into pure GaP reaches approximately 600–650 Å, whereas in the Ar⁺-implanted sample it is significantly reduced to ~100–120 Å.

Preliminary analysis has shown that at T = 850 K, the near-surface disordered layers of GaP undergo complete recrystallization, and the Ni–GaP(111) interface forms a polycrystalline structure. Therefore, post-deposition annealing of the ion-implanted GaP samples was conducted at 850 K.

Following thermal treatment, the penetration depth of Ni increases to ~220–250 Å, and the total thickness of the contact region (d_n) reaches ~350–370 Å. For comparison, in the case of Ni on pure GaP, the value of d_n is approximately 1050–1100 Å.

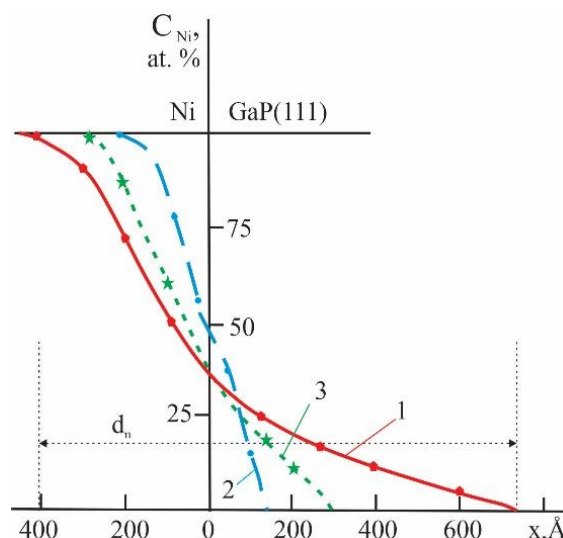


Fig. 3. Depth profiles of Ni concentration for: (1) pure GaP(111); (2) Ar⁺-implanted GaP before annealing; and (3) Ar⁺-implanted GaP after annealing at T = 800 K for 30 min.

Despite the variation in d_n, the specific contact resistivity in all cases was measured to be (5–8) × 10⁻⁴ Ω·cm, indicating stable and efficient electrical contact performance across configurations. It is worth noting that during the mutual diffusion of Ni atoms into the Ga layer and Ga atoms into the Ni layer, i.e., within the interfacial transition region, no formation of intermetallic compounds of the Ga–Ni type was observed, even at temperatures up to T = 850 K.

Conclusions

It was established that Ar⁺ ion implantation of GaP(111) single crystals at E₀ = 2 keV leads to the formation of a gallium-rich surface layer with a thickness of approximately 60 Å. The presence of this thin Ga layer significantly reduces the penetration depth of the contacting metal (Ni) into GaP by a factor of 3–4 compared to non-treated samples. The specific contact resistivity of the metal–semiconductor interface was measured to be approximately (5–8) × 10⁻⁴ Ω·cm,

indicating good ohmic behavior. Thus, this study demonstrates that preliminary Ar⁺ ion implantation of GaP(111) enables the formation of ultrathin ohmic contacts with a total thickness of ≤ 300 Å, suitable for advanced micro- and nanoelectronic applications.

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Застосування імплантації іонів Ar⁺ для отримання наноконтактів на поверхні монокристалів GaP (111)

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Ультратонкі омичні контакти сформовано на поверхні монокристалів GaP(111) із застосуванням імплантації іонів аргону (Ar⁺) з енергією $E_0 = 2\text{keV}$ та дозою $D = 2 \times 10^{17}\text{ cm}^{-2}$, в умовах високого вакууму (10^{-7} Па). Після опромінення виявлено суттєве збагачення поверхні галієм, концентрація якого досягала приблизно 90 ат.%. Надалі на поверхню GaP(111) осаджували плівку нікелю (Ni) товщиною близько 1000 Å для формування контакту. Застосування такого підходу до металізації забезпечило зменшення загальної товщини контактного шару у 3–4 рази порівняно з традиційними методами.

Після термічної обробки за температури $T = 850\text{K}$ первинно розупорядковані приповерхневі шари GaP(111) рекристалізувалися, що призвело до формування полікристалічної контактної структури. Після відпалу товщина контактного шару зросла приблизно у 1,5 рази і становила 400–450 Å, що все ще приблизно у 2,5 рази менше за характерну товщину (d_n) у системі Ni/чистий GaP. Отримані результати свідчать, що іонна імплантація з подальшою контрольованою металізацією та відпалом є ефективним підходом до створення ультратонких, термічно стабільних омичних контактів для напівпровідникових приладів на основі GaP.

Ключові слова: GaP(111), імплантація іонами Ar⁺, омичний контакт, інтерфейс метал–напівпровідник.