

Ferroelectric properties of (Al,Ga)InP₂ alloys

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Spontaneously ordered AlGaInP₂ layers with CuPt_B structure and ordering degree $\eta = 0.16$ – 0.46 were obtained by MOVPE epitaxy on GaAs substrates. Using the Kelvin probe microscopy method, the dependence of the layer surface potential on η was found. Comparative analysis of the behavior of CuPt_B-AlGaInP₂- and CuPt_B-GaInP₂-alloys under mechanical stress showed the presence of a martensitic transition and the associated change in the surface potential in both materials. The effect of Al on increasing the value of the built-in electric field in the stressed state of the crystal lattice and reducing the recovery time (relaxation) of the layer was found.

Keywords: Piezoelectric effect, martensitic transition, AlGaInP₂, Kelvin probe microscopy.

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1. Introduction

In modern optoelectronics, solid solutions based on phosphides of compounds of Ga_{1-x}In_xP and (Al_yGa_{1-y})_{1-x}In_xP have become widespread due to the possibility of lattice matching with GaAs substrates ($x = 0.47$ – 0.48 with a change in the content of Al (y) from 0 to 1, respectively) and a large band gap in the range of 1.9–2.1 eV (hereinafter GaInP₂ and AlGaInP₂). GaInP₂ solid solution is the most striking and well-studied representative of semiconductor materials in which spontaneous ordering into a monolayer superlattice of GaP₁/InP₁ is observed along the directions (111)_B which corresponds to the structure of CuPt_B in the cationic sublattice [1]. This structure has a trigonal C_{3v} symmetry group, which leads to the appearance of piezoelectric fields in the epitaxial layers of CuPt_B-GaInP₂ [2], which were studied in detail by us in Ref. [3,4] and are used to control electronic states in semiconductor nanoheterostructures such as InP/GaInP₂-quantum dots and transition metal dichalcogenides [5].

Studies using Kelvin probe microscopy (KPM) in combination with structural and optical measurements have shown the dependence of the piezoelectric fields of GaInP₂ epitaxial layers having an ordering degree of $\eta \sim 0.5$ and a thickness of $d = 70$ – 1500 nm on mechanical (cleavage) and thermal (annealing) action, which is caused by the martensitic transition, i. e., the switching of the crystal lattice between the stressed and relaxed states of the CuPt_B-structure [3]. The measured values of the fields E_{PE} were ± 100 kV/cm (positive for stressed and negative for relaxed states) and showed a strong decrease in $|E_{PE}|$ with increasing layer thickness (up to ± 7 kV/cm), due to the fixation

of the Fermi level and piezoelectric alloying. A decrease of $|E_{PE}|$ (to values of ± 2 kV/cm) and suppression of relaxation of the crystal lattice with a decrease in the degree of ordering were also detected [4].

In this paper, we present similar studies of ordered CuPt_B-AlGaInP₂ layers with an aluminum content of $y_{Al} \sim 0.35$, in order to study the effect of Al on the martensitic transition and the magnitude of E_{PE} and to expand the control capabilities of piezoelectric properties of these materials.

2. Experiment

2.1. Epitaxy

(Al_yGa_{1-y})_{1-x}In_xP solid solutions were grown by epitaxy from metal-organic compounds (MOVPE) on the Aixtron AIX-200/4 installation. The growth temperature was 690 °C. GaAs(001) substrates with a misorientation of 0 and 6° in the direction [111] were used. The use of misoriented substrates leads to a decrease in the degree of ordering. In addition to the misorientation of the substrate, the degree of ordering can also be influenced by the group V and III component flow ratio. The growth of the layers was carried out with a V/III group flow ratio equal to 150 and 15. In ternary solid solutions of GaInP₂, a decrease in the V/III flow ratio leads to a decrease in the degree of ordering at the growth temperature of 690 °C. Together with the effect of using misoriented substrates, the degree of ordering can vary from 0.56 (ratio V/III = 150, 0° disorientation) to 0.05 (ratio V/III = 15, 6° disorientation) [4].

Table 1. Layer parameters AlGaInP₂

Sample	#150–0	#150–6	#15–0	#15–6
$d, \mu\text{m}$	1.58	1.66	1.74	1.82
$x_{\text{In}}, \%$	50.3	49.4	48.7	48.2
$y_{\text{Al}}, \%$	35.6 (0.9)	35.8 (1.7)	34.8 (2.4)	36.5 (1.3)
$\Delta E_g(\text{PL})@4\text{ K}, \text{ meV}$	131.4 (3.9)	72.3 (6.5)	61.3 (10.2)	27.6 (5.8)
η_4	0.64 (0.01)	0.47 (0.02)	0.44 (0.04)	0.29 (0.03)
$\Delta E_g(\text{PL})@300\text{ K}, \text{ meV}$	68.7 (3.9)	23.6 (6.5)	61.3 (10.2)	27.6 (5.8)
η_{300}	0.46 (0.01)	0.27 (0.04)	0.29 (0.05)	0.16 (0.06)

Note. The standard deviations of the measurements are indicated in parentheses.

2.2. Measurement methods

An integrated approach using energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) methods was applied to evaluate the composition of the solid solution. The composition, morphology of the layers and their thickness were studied using a SUPRA 25 Carl Zeiss scanning electron microscope equipped with Ultim Oxford Instruments energy dispersive X-ray spectroscopy unit. The lattice parameter of the layers was estimated using rocking curves obtained by a DRON-8 X-ray diffractometer with CuK α (0.154 nm) radiation.

The presence of ordering and structure of solid solutions were assessed using transmission electron microscopy (TEM) by the presence of superstructural reflections at positions $1/2\{111\}$ corresponding to the CuPt_B type, and by images obtained using reflexes of $1/2\{111\}$ type.

Photoluminescence spectra were measured at a microphotoluminescence research facility (μ -PL) at temperatures from 5 to 300 K. The Kelvin probe microscopy (KPM) method was used to measure the surface potential distribution and determine the magnitude of the built-in electric field of ordered layers. Surface potential maps were measured before and after elastic mechanical action on the samples (cleaving) along the growth plane, as well as along the cleaved surface to determine the difference between the potential of the layer and the substrate. The intensity of the built-in field was estimated based on the potential difference and layer thickness.

3. Results

3.1. Determining the degree of ordering

Table 1 presents the results of studies of the AlGaInP₂ layers to determine the degree of ordering. 4 samples were studied, grown with a ratio of flows V/III of 150 and 15 on substrates with a misorientation of Θ equal to 0 and 6° (reflected in the designation of the samples). Due to the fact that the accuracy of determining the composition by the EDX method is low: the standard deviation reaches several percent, an integrated approach was used to increase the accuracy. The In content was estimated based on the X-ray diffraction rocking curves, assuming that the lattice-matched composition is 0.49 for GaInP₂ and 0.48 for

AlInP₂ and varies linearly for intermediate compositions. Based on the obtained values of x_{In} , the values of Al and Ga concentrations obtained by the EDX method were correlated.

The degree of ordering was determined by the formula

$$\eta = \sqrt{\Delta E_g / \Delta_1},$$

where $\Delta_1 = -0.32\text{ eV}$ is the calculated value of the band gap narrowing for an ideally ($\eta = 1$) ordered solid solution of GaInP₂ [6]. No such calculations have been performed for quadruple AlGaInP₂ solid solutions, therefore, the value of the degree of ordering obtained in this way is an estimate and can be used to compare the parameters of layers with similar composition values. The magnitude of the band gap narrowing was estimated using a quadratic formula with the corresponding bowing parameters [7].

It follows from the table that the use of misoriented substrates leads to a decrease in the degree of ordering, however, unlike triple solid solutions [4], the effect of reducing the V/III flows ratio is less noticeable. Measurements at room temperature demonstrate the maximum degree of ordering $\eta = 0.46$ for sample #150–0, its decrease to 0.27–0.29 for samples #150–6 and #15–0 (i.e., the effect due to the use of a misoriented substrate and a decrease in the ratio of flows V/III, the groups are approximately the same) and the minimum value of the degree of ordering $\eta = 0.16$ for the sample #15–6.

When the measurement temperature is reduced to 5 K, the results look somewhat different. With a V/III flow

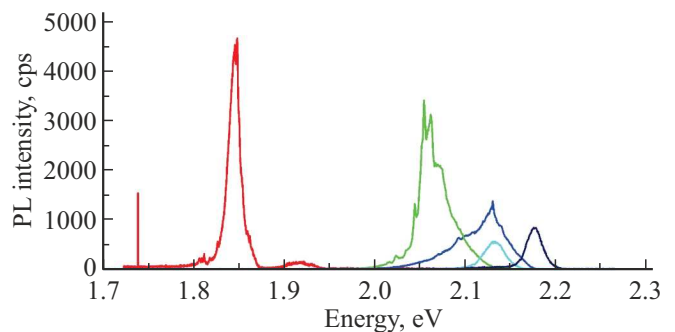
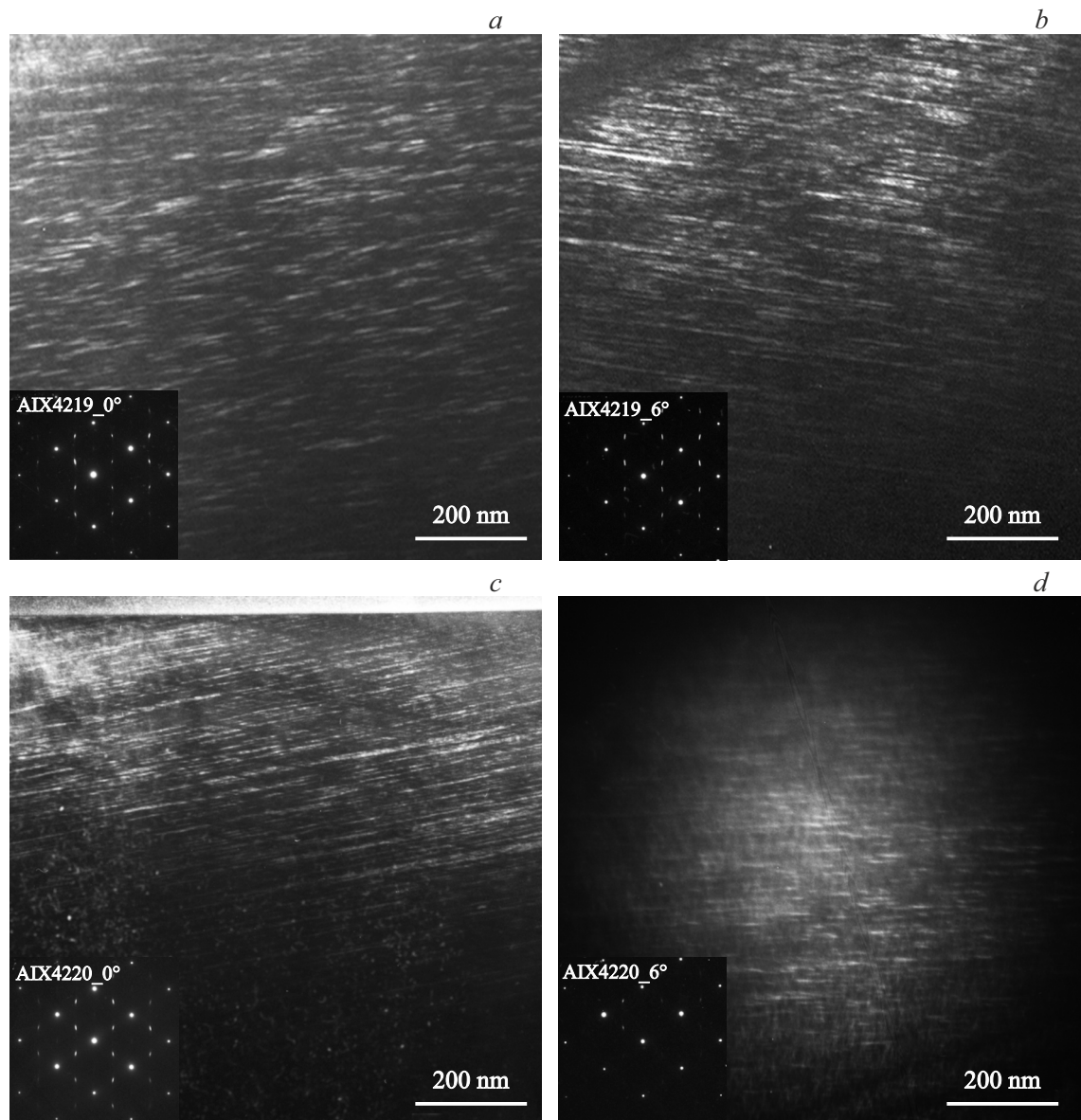


Figure 1. μ PL spectra of ordered GaInP₂ ($\eta = 0.56$) and AlGaInP₂ layers with varying degrees of ordering ($\eta = 0.46$ – 0.16).

Table 2. Results of KPM measurements of layers AlGaInP₂

Sample		#150–0	#150–6	#15–0	#15–6
η		0.46	0.27	0.29	0.16
U^{001} , mV	Initial state	670	480	1130	1200
	After cleavage	940	420	980	1320
	Change	+270	–60	–150	+120

**Figure 2.** Dark-field TEM images of the film cross-section for superstructural reflection of type $1/2\{111\}$ and the corresponding diffraction patterns. Samples: *a* — #150 –0, *b* — #150 –6, *c* — #15 –0 and *d* — #15 –6.

ratio of 150, the degree of ordering is 0.6 and 0.44 for a misorientation of 0 and 6°, and with a V/III ratio of 15, –0.49 and 0.29, respectively.

Figure 1 shows the PL spectra measured at $T = 5$ K. It can be seen from the spectra that in samples grown

at a V/III flow ratio = 150, individual bands associated with localized states, which are traditionally associated with antiphase boundaries between ordered domains [8,9], are clearly visible, and their absence in samples of #15th indicates the difference in the microstructure of the layers.

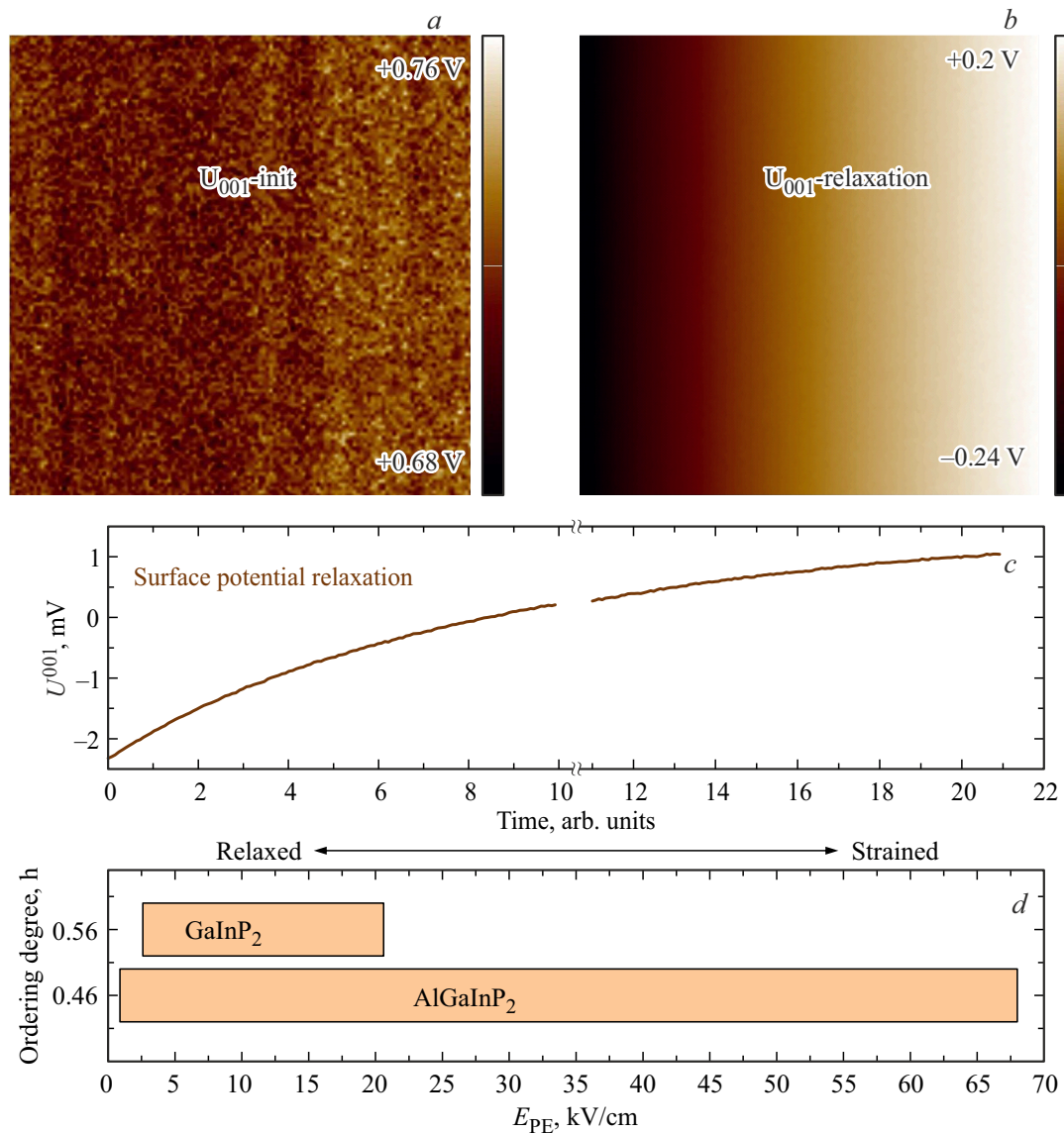


Figure 3. Map of the surface potential of the sample #150–0.05 before (a) and after (b) cleavage, c — time dependence of the change surface potential after cleavage, d — range of variation of the piezoelectric field caused by the martensitic transition in the $AlGaInP_2$ - and $GaInP_2$ -layers.

For comparison, the spectrum of an ordered ternary solid solution of $GaInP_2$ is shown, in which radiation from localized states is also observed, but the radiation bandwidth is significantly lower, which indicates a large magnitude of composition fluctuations in the presence of Al. Due to the fact that studies of the surface potential are carried out at room temperature, the degree of ordering, also obtained from measurements at room temperature, seems to be a more representative value, since it is less susceptible to distortions associated with carrier localization.

Figure 2 shows dark-field TEM images obtained from superstructural reflections of the $1/2\{111\}$ type and their corresponding diffraction patterns (insets in the lower left corner). Transmission electron microscopy data shows that $CuPt_B$ ordering is observed in all samples. It can be noted that, on the one hand, the boundaries between the domains

of the sample #15–0 are clearer compared to the sample #150–0, however, the size of the observed domains is noticeably smaller. At the same time, the signal intensity of the superstructural $1/2\{111\}$ reflections of the sample #15–6 is noticeably lower and, accordingly, the presence of antiphase boundaries is less clearly traced. Indirectly, this may indicate a decrease in the degree of ordering, as well as a decrease in the average size of ordered domains.

3.2. Results of KPM studies of the piezoelectric effect

The results of KPM studies of the average surface potential of layers in the initial state and after elastic action (cleavage) are summarized in Table 2. The surface potential values of all samples are different in the initial state. Given

the fact that the measurements were carried out in darkened conditions (the laser feedback beam was directed to an area far from the probe tip), such discrepancies cannot be explained by a small change in the doping level. According to admittance spectroscopy studies, the concentration level of free carriers in the studied layers varies in the range from $n = 2 \cdot 10^{17} \text{ cm}^{-3}$ to $p = 1 \cdot 10^{16} \text{ cm}^{-3}$. In semiconductor materials, due to the presence of Fermi level pinning, the effect of doping on the surface potential measured by the KPM method is minimal and can reach several tens of millivolts under additional illumination [10,11]. The difference in the KPM potential values of the AlGaInP₂ layers reaches several hundred millivolts. In a sample with the maximum degree of ordering, an average surface potential of +670 mV is observed, which differs from the substrate potential by only 120 mV. A decrease in the degree of ordering leads to a change in the value of the surface potential both downward (up to 480 mV in the sample #150–6) and upward to 1200 mV in the layer with the minimum degree of ordering. Cleavage of samples leads, at first glance, to insignificant effects: the change in the potential ranges from several tens to 270 mV, while the changes may have a multidirectional character, both decreasing and increasing the potential. Thus, based on the measurement data, it is possible to judge the existence of a relationship between the magnitude of the surface potential and the degree of ordering and the existence of an built-in electric field caused by the effects of ordering. More noticeable systematic changes are found when examining layers of lower thickness.

Figure 3 shows maps of the surface potential of a sample similar to #150–0 with a thickness of 500 nm (#150-0.05) in the initial state and after cleavage. It is clearly visible that the potential map is uniform in the initial state (Figure 3, *a*), the deviations are on average ± 10 mV (hardware noise). After cleavage (Figure 3, *b*), a potential jump is observed to the value -2.2 as a result of the martensitic transition of the crystal to the stressed state [3], while a gradual potential recovery occurs during the measurement (Figure 3, *b–c*). Unlike the ternary compounds GaInP₂, the presence of Al leads to faster effects. While it may take days for the GaInP₂ layers to restore their initial state at room temperature, the AlGaInP₂ layer demonstrates a return to its initial state within a few tens of minutes. Figure 3, *d* shows a comparison of the range of variation in the magnitude of the built-in electric field in GaInP₂- and AlGaInP₂-layers with a thickness of ~ 500 nm and the degree of ordering 0.56 and 0.46, respectively. It can be seen that the magnitude of the piezoelectric effect in the Al-containing layer is significantly higher and the built-in electric field can reach values of 68 kV/cm with a layer thickness of 500 nm (versus 20.5 kV/cm in GaInP₂).

4. Conclusion

The surface potential of the AlGaInP₂ layers arranged in the CuPt_B structure has been studied by Kelvin probe

microscopy. It is found that the magnitude of the surface potential in the stationary state depends on the degree of ordering. A comparative analysis of AlGaInP₂ layers with ordered GaInP₂ layers showed that the addition of Al to a solid solution layer leads to an increase in the potential jump and the associated electric field as a result of the martensitic transition from a relaxed state to a stressed one. In addition, the quadruple solid solutions showed noticeably shorter recovery times before the crystal is returned to its initial (relaxed) state.

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Conflict of interest

The authors declare that they have no conflict of interest.

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