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# Effect of Al concentration on the pyroelectric properties of $AlGaInP_2$ alloys

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**Abstract.** $CuPt_B$ ordered $AlGaInP_2$ alloys grown on GaAs by MOVCD epitaxy were studied by structural (X-ray diffraction, electron microscopy), optical (photoluminescence) and Kelvin probe microscopy methods. A strong dependence of the layer surface potential on the alloy composition was found. The effect of martensitic transition in the ordered $AlGaInP_2$ layers was found to be in connection with the alloy composition: higher Al concentrations lead to an increase of the piezoelectric field changes and shorter recovery time (relaxation) of the layers after mechanical effect (cleavage).

**Keywords:** AlGaInP, martensitic transition, pyroelectric properties

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# Влияние концентрации Al на пироэлектрические свойства твердых растворов $AlGaInP_2$

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**Аннотация.** Методами кельвин-зонд, а также структурного и оптического анализов были изучены $CuPt_B$ спонтанно-упорядоченные твердые растворы $AlGaInP_2$, выращенные на подложках из GaAs методом МОС-гидридной эпитаксии. Была найдена сильная зависимость значения поверхностного потенциала и эффекта мартенситного перехода от состава образцов: повышение концентрации Al ведет к увеличению напряженности встроенного поля и сокращению времени восстановления (релаксации) после механического воздействия (скола).

**Ключевые слова:** AlGaInP, мартенситный переход, пироэлектрические свойства

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## Introduction

Ternary $GaInP_2$ and quaternary $AlGaInP_2$ alloys lattice matched to GaAs substrates are used in many modern optoelectronic devices: LEDs, lasers, photovoltaic converters. $GaInP_2$ grown on [001] GaAs reveals $CuPt_B$-type spontaneous ordering, which corresponds to a rhombohedral monolayer superlattice $GaP_1$/ $InP_1$ oriented along $[111]_B$ diagonals [1]. Mixing of Al to the Ga sublattice allows to vary the bandgap in the range of 1.9–2.3 eV preserving the lattice parameter. These quaternary alloys also reveal a tendency to $CuPt_B$ ordering. This type of ordering is followed by changes in the electronic structure (narrowing of the bandgap and splitting of the valence band), and by the uprising of a built-in electric field, i.e., the material shows pyroelectric properties [2, 3]. Here we demonstrate the effect of aluminum concentration on the pyroelectric properties of $AlGaInP_2$ epi-layers.

## Materials and Methods

Samples with different Al compositions, referred to as $GaInP_2$, $AlInP_2$ and $AlGaInP_2$, were grown by metalorganic vapor phase epitaxy (MOVPE) on an Aixtron AIX-200/4 unit at the growth temperature of 690°C and V/III fluxes ratio of 150. Exactly oriented (100) GaAs substrates were used to ensure the high ordering degree. The samples were not intentionally doped and possessed $n<10^{17}$ cm$^{-3}$ conductivity.

The alloy composition was obtained on a Carl Zeiss SUPRA 25 scanning electron microscope equipped with energy dispersive X-ray spectroscopy unit (EDX). X-ray diffraction (XRD) was measured on a DRON-8 diffractometer. Since the EDX method accuracy is poor and reveals high deviations up to several per cents, XRD data was used for In composition estimation and further correction of the EDX data by linear extrapolation having in mind that GaAs lattice matched compositions are $Ga_{0.51}In_{0.49}P$ and $Al_{0.52}In_{0.48}P$. Also EDX data was corrected assuming stoichiometry of the alloy (i.e. 50% of the Phosphorous composition).

Photoluminescence spectra were measured on a micro photoluminescence research unit (μ-PL) (50x objective) at temperatures from 5 to 300°K. The value of the ordering induced bandgap narrowing was estimated by a quadratic formula [1], disordered alloy band gap was estimated using the obtained composition and the corresponding bowing parameters [4]. All samples revealed high ordering degree ($\eta$ > 0.45). Ordering degree of $AlInP_2$ was not estimated due to its indirect bandgap, but assumed to be high, since the growth conditions did not change.

Kelvin probe microscopy (KPM) technique was used to measure surface potential distribution and to determine magnitude of built-in electric field of the ordered layers. NT-MDT Integra Aura atomic force microscope was used. The value of the built-in electric field caused by pyroelectric effect was estimated from the layer thickness and potential difference between ordered and disordered samples.

## Results and Discussion

Fig.1, *a*–*c* shows the initial state growth plane surface potential map $U^{001}$ of $Al_xGa_{1-x}InP_2$ samples with $d$ = 0.5 μm and different compositions. All samples exhibit uniform distribution of the surface potential with average deviations of +/–20mV. It should be noted that average surface potential values strongly depend on the alloy composition. Sample with $x$ = 18% reveals

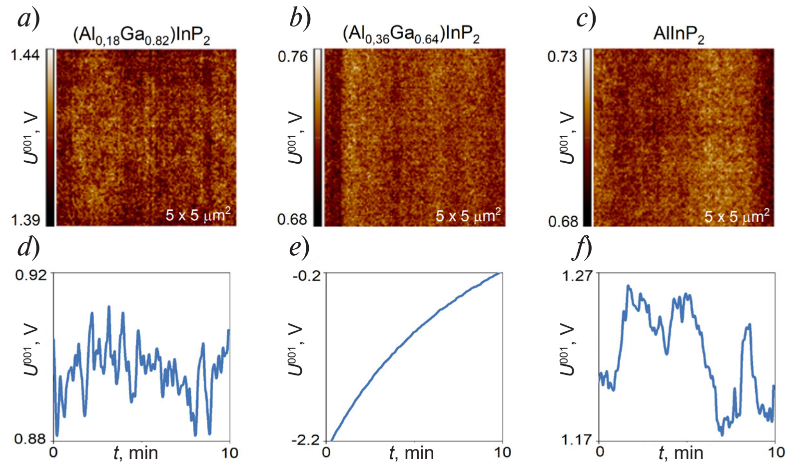


Fig. 1. Examples of growth plane surface potentials before (*a*, *b*, *c*) and changes of $U^{001}$ over the time after the cleavage (*d*, *e*, *f*) of samples at different *x*

$U^{001}$ = 1.42 V, which is quite close to the ternary $GaInP_2$ alloy [5], while samples with higher Al concentrations (x = 0.36, 1.0) possess much lower surface potential $U^{001}$ = 0.7–0.72 V. Also $AlGaInP_2$ samples behaved as *n*-type, while $AlInP_2$ samples behaved as *p*-type. In KPM measurements the conductivity type is determined by the sign of the built-in electric field of the surface space charge region: positive changes in surface potential are characteristic for *n*-type semiconductor, when illumination is applied, negative are characteristic for *p*-type. In case of a pyroelectric material or material with charged states (e.g. non-stoichiometric dielectrics) KPM signal also reacts to the surface charge indicating on the built-in electric field.

After the cleavage procedure, surface potential is measured at one point and we can see the changes occurring during a certain period of time (Fig.1, *d*–*f*). These changes take place due to the martensitic transition of the crystal lattice from relaxed to stressed state [5]. The stress between the substrate and the layer is local and occurs due to the $CuPt_B$-type atomic ordering in the $AlGaInP_2$ alloy. Ordered alloy structure has a trigonal $C^{3v}$ lattice symmetry with rhombohedral elementary unit, which is distorted in the [111] direction due to the substrate-to-layer interaction.

The behavior of the surface potential differs greatly depending on the Al composition. $Al_{0.36}Ga_{0.64}InP_2$ sample reveals the highest drop in the $U^{001}$ value, changing from 0.72 to almost -2.2 V. However, the new state is unstable, and we can observe fast relaxation that takes place during the measurement. Samples with $x = 0.18$ reveal smaller changes of the surface potential and it seem to be quasi-stable with $U^{001}$ = 0.9V and average noise of 20 mV. Same behavior was observed in ternary $GaInP_2$ samples [5]. Surface potential of $AlInP_2$ sample on the contrary increases to ~1.2 V.

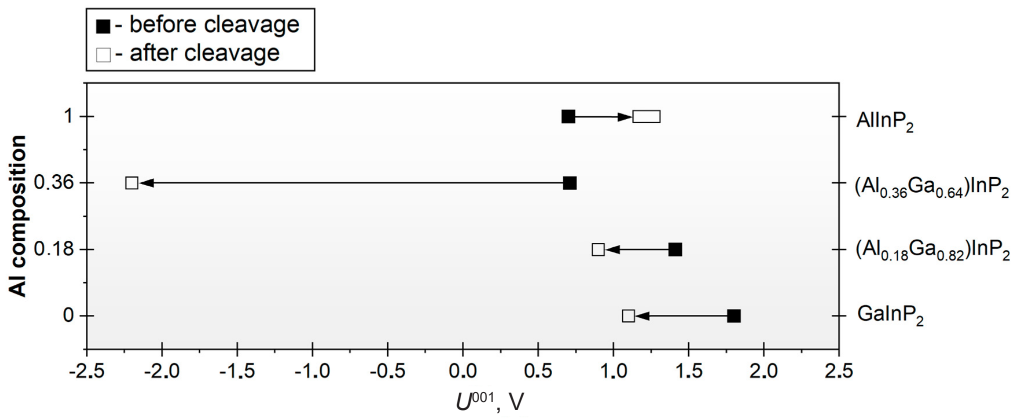


Fig. 2. Surface potential changes induced by martensitic transition in $GaInP_2$ [5] and $AlGaInP_2$ layers with different Al compositions

Instead of relaxation (as $Al_{0.36}Ga_{0.64}InP_2$) or quasi-stable state ($GaInP_2$) this sample reveal rapid switching between some quasi-stable states. Also, it can be noticed that after the cleavage the dark-to-illuminated surface potential change its sign indicating n-type conductivity. Change in conductivity type behavior is a strong indication that they originate from the pyroelectric effect.

Fig. 2 summarizes the observed changes of the pyroelectric effect caused by the martensitic transition.

## Conclusion

It has been shown that the pyroelectric properties of the $CuPt_B$ ordered $AlGaInP_2$ alloy depend on the Al composition. Among all studied samples, $Al_{0.36}Ga_{0.64}InP_2$ epi-layers seem to have a fast relaxing state with the highest changes of surface potential. At the same time $AlInP_2$ and $Al_{0.18}Ga_{0.82}InP_2$ reveal smaller surface potential changes. Layer with Al concentration of $x = 0.18$ reveals quasi-stable behavior similar to the previously observed ternary $GaInP_2$. $AlInP_2$ reveals rapid switching between some quasi-stable states and changed its Kelvin-probe detected conductivity from p-type to n-type after the cleavage.

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