

## Твердотельная электроника

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### Pyroelectric Response of Strain Limited III-V Semiconductor

*Under the anisotropy of boundary conditions, a high-gap III-V semiconductor indicates a behavior of pyroelectric crystal (in spite of it is a piezoelectric only). Partial limitation of strain in the [111]-plate of this crystal provides its substantial electric response to time-variation of temperature  $dT(t)$  or pressure  $dp(t)$ . Herewith the voltage sensitivity of semi-insulating GaAlAs or GaN sensor is close to one of the PZT ceramics. However, PZT cell-transducer used as sensor device needs a hybrid integration with semiconductor amplifier. Unlike of this, if sensor device is based on the III-V crystal, transducer and amplifier are various parts of one crystal chip. References 4, figures 5.*

**Keywords:** *pyroelectric sensor, piezoelectric sensor, III-V semiconductors.*

#### Introduction

The most of sensor devices are fabricated with the use of microelectronics. By this it is meant that the sensor should be integrated with the semiconductor chip to amplify and to convert information. Integration of this sort occurs naturally for semiconductor sensors but sometimes their possibilities and sensitivity are limited. Typical semiconductor sensors of temperature  $T$  or pressure  $p$  are based on the conductivity variation:  $\sigma(T)$  and  $\sigma(p)$ . However, the Johnson noise that accompanies conductivity limits the sensitivity of semiconductor-based sensors. That is why, for example, far infrared (IR) sensor using a low-gap semiconductor needs cooling.

For this reason, dielectric sensor might have a generous advantage. The point is that very high resistive dielectric sensor has much lower noise coefficient, and it usually uses the change of spontaneous polarization  $P_S$  in the crystal of pyroelectric symmetry:  $P_S(dT)$  or  $P_S(dp)$ . However, a cardinal objection of microelectronic sensors based on dielectrics consists in its hybrid structure of various materials: sensor-dielectric must be combined with the semiconductor-amplifier and read-out chip, Kohler et al [1]. It is well known that processing of constituent hybrid structures might cause problems

because their components have quite different chemical and physical properties.

In the case of III-V semiconductor crystals, the joint sensor-amplifier device and read-out functions can be realized in a single chip. Being a piezoelectric, III-V polar crystal is not belongs to the pyroelectric symmetry; nevertheless, it would be very promising as a sensor material if its pyroelectric potentiality would be unveiled. For this reason, our early efforts were devoted to convert piezoelectric type of response into a pyroelectric one. This idea was realized by the constructional control of crystal boundary conditions, Poplavko et al [2].

It is significant that many of III-V semiconductors are very close to dielectrics in their conductivity. Semi-insulating (*s/i*) GaAs that was one of basic material in our experimental study is characterized by the  $\sigma \approx 10^{-7}$  Ohm/m. Later the AlGaAs alloy that was used in our test sensor device has  $\sigma < 10^{-12}$  Ohm/m. But the most promising sensor material might be GaP or GaN which technology now is in progress.

#### State of Art

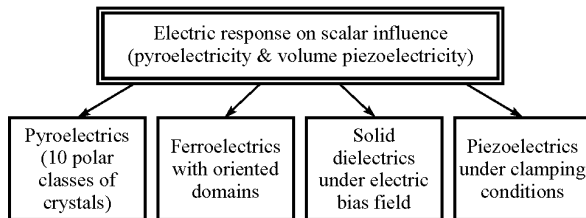
Dielectric properties of III-V semiconductors, partly their piezoelectric activity, usually were out of consideration because of carriers screening effect. However, this effect becomes negligible in the *s/i*-GaAs above the frequency 1 kHz while AlGaAs is possible to be used as "dielectric" sensor even at the frequency 20 Hz. That is why, in this work, a charge generation process in the discussed III-V crystals might be ignored, while a "charge separation" (that is the change of electric polarization) should be regarded as the main process.

Correspondingly, the lattice of III-V semiconductor is considered here as a dielectric, so the only electric polarization is taken into account. This assumption is rather close to reality in *s/i*-GaAs and all the more in its solid solutions with AlAs or in the case of GaN. Previously piezoelectric properties of III-V crystals practically have not been used in devices. Nevertheless, any crystal of the III-V type has a polar structure that is used in this work to convert effect of external pressure or temperature

into electric signal (in the same manner as pyroelectric works).

Polar responses in dielectrics, including a new one, are classified in Table 1. Among the 32 classes of crystal point symmetry, 20 classes represent piezoelectric crystals, but the only 10 classes of them are simultaneously pyroelectric ones. Most of “classic” pyroelectric crystals such as tourmaline have comparatively small sensitivity. Much more sensitive are ferroelectrics, that is why they are used in pyrosensors. Most of ferroelectrics usually have a random orientation of its domains. To be used as a sensor, ferroelectric crystal should be “polarized” by the external electric field that arranges a preferential “single domain” structure.

Note that any solid dielectric acquires polar properties under the external electric field (bias field) that induces as piezoelectricity and pyroelectricity.



**Fig. 1. Solid dielectrics that polar properties can be used in the sensors of temperature and pressure**

Electrically induced pyroelectricity in solid dielectrics is proportional to the [dielectric constant]<sup>2</sup> =  $\varepsilon^2$ . That is why IR image arrays use paraelectric ceramics or diffuse phase transition ferroelectric ceramics with  $\varepsilon > 10^4$ . The advantages of ceramics are low cost and a homogeneous structure, but based on these ceramics IR image hybrid structure has some disadvantages. First of all, internal polarization of high- $\varepsilon$  ceramics should be supported by the electric bias field. This is a cause of electrically stimulated aging so it might be electrochemical breakdown of ceramic element pitches. The second problem is the difficulty in the wet etching of ceramics that have a polycrystalline (grain) structure. The speed of etching is quite different in the grains and in the interfacial layers between them; as a result, the wet etching can destroy ceramics.

The etching of III–V semiconductor causes no problems. Above all, instead of strong electric bias field, piezoelectric crystal needs a sort of “mechanical bias” to decrease the symmetry of its electric response. Nevertheless, being a sensor

device, the piezoelectric cell is not stressed continually: the special boundary conditions are used only to limit one type of deformations (usually to limit a plane strain). Due to this limitation, the only measured influence produces in the element some stress even though very small. Therefore, on contrary to sensor elements made from ceramics, no drastic external influence is required for piezoelectric based sensor. That is why this work proposes to use artificially arranged polar response in piezoelectric, namely, in the semi-insulating high-gap III-V semiconductor that is practically dielectric.

### Artificial Pyroelectric Effect in III-V Crystals

As a rule, to evaluate temperature change ( $dT$ ) or pressure alteration ( $dp$ ), dielectric sensors use correspondent change in its spontaneous polarization  $P_S$ . In polar crystals, the  $P_S$  variation provides pyroelectric effect ( $dP_i = \gamma_i dT$ ) as well as volumetric piezoelectric effect ( $dP_i = \xi_i dp$ ). At this point, the  $dP_i$  is the change of vectorial value. Thus, pyroelectric coefficient  $\gamma_i$  and volumetric piezoelectric coefficient  $\xi_i$  is a material-type vector. That is why pyroelectric transferees scalar values ( $dT$  or  $dp$ ) into the vectorial responses, which are electric field or electric current.

It is considered that vectorial characteristics  $\xi_i$  and  $\gamma_i$  are possible only in the crystals the symmetry of which belongs to one of 10 “pyroelectric classes”, because any pyroelectric has the “intrinsic vector”  $P_S$ .

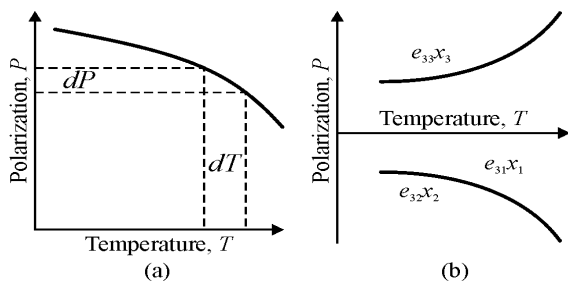
The novelty of proposed effect needs the more detailed explanation based on classic pyroelectric response. Conventional pyroelectric effect is the variation of the spontaneous polarization  $dP_i$  in polar crystal during uniform change of its temperature  $dT$ , Fig. 2(a). Pyroelectric coefficient in a free-stress crystal is  $\gamma_i = dP_i/dT$ . Pyroelectric effect is divided into a primary part  $\gamma_i^{(1)}$  and a secondary part  $\gamma_i^{(2)}$  being represented by the sum:  $\gamma_i = \gamma_i^{(1)} + \gamma_i^{(2)}$ . Primary effect is pyroelectricity of a clamped (free-strain) crystal in the condition when any component of strain is absent:  $x_n = 0$ . Secondary pyroelectric coefficient can be measured as a difference between the effects of free and clamped crystals, and this coefficient can be calculated from the equation of piezoelectric response:  $P_i = e_{in}x_n$ , where  $e_{in}$  is the component of piezoelectric module, and  $x_n$  is the component of strain. Under a thermal influence, piezoelectric effect is excited by the thermal deformation of crystal:  $x_n = \alpha_n dT$  where  $\alpha_n$  is the compo-

ment of thermal expansion coefficient. As a result:

$$\gamma_i^{(2)} = e_{in}\alpha_n. \quad (1)$$

Figure 2(a) explains pyroelectricity and Fig. 2(b) illustrates secondary pyroelectric effect as a polarization produced by thermal strain  $x_n(T)$  that is transformed to the electric response through the piezoelectric effect. One part of polarization ( $P_3 = e_{33}x_3$ ) is induced by the longitudinal piezoelectric effect, while the other part ( $P_3 = e_{31}x_1 + e_{32}x_2$ ) is induced by the transverse piezoelectric effect.

It was usually assumed that the sum  $e_{in}\alpha_n$  is nonzero only in pyroelectric that has spontaneous (intrinsic) polarization  $P_s$ . On the contrary, in the “proper piezoelectric”, such as III-V semiconductor (which is not pyroelectric), the sum in the Eq. (1) is suggested to be zero.



**Fig. 2. Non-central symmetric crystals polarization temperature dependence: (a) spontaneous polarization in the ferroelectric; (b) thermo-mechanically induced polarization in the piezoelectric crystal**

However, as it was established [2], any “proper piezoelectric” can demonstrate a “secondary-type” pyroelectric effect at the conditions of partial clamping. As a consequence, it is possible to make the sum  $e_{in}\alpha_n \neq 0$ . It is this effect that is proposed here to utilize in the sensor devices. In the Table 1 it is referred as “Piezoelectric under non-isotropic clamping”.

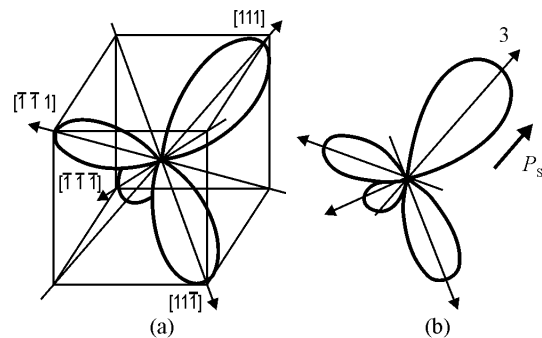
Being a crystal of  $43m$  class of point symmetry, cubic crystal of GaAs type has a maximum of its piezoelectric activity in the direction of  $[111]$ -type axes. However, standard crystallographic representation of these crystals is based on the  $[100]$ -type axes. In this case, the correspondent matrix of piezoelectric module has the only share-type components of the piezoelectric module:

$$e_{im} = \begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{36} \end{pmatrix} \quad (2)$$

This matrix represents a third rank tensor of piezoelectric coefficients. In this instance, for the  $(100)$ ,  $(010)$ , and  $(001)$  crystal plates all longitudinal ( $e_{11}$ ,  $e_{22}$ ,  $e_{33}$ ) as well as all transverse ( $e_{12}$ ,  $e_{13}$ ,  $e_{21}$ ,  $e_{23}$ ,  $e_{31}$ ,  $e_{23}$ ) modules are zero. Therefore, usually used in the industry and in the most of experiments  $[100]$ -oriented plates of III-V semiconductors are not sensitive to any strain except the shear one (the last corresponds to the share modules  $e_{14} = e_{25} = e_{36}$ ). It is obvious from the Eq. (2) that no response is possible if the external influence on crystal is of scalar type.

In other words, being applied to the standard  $(100)$ -plates of III-V crystals, partial clamping cannot invoke its polar response. Meanwhile, the crystal plates of  $(100)$  orientation are conceptually the sole chips using for GaAs type devices. It is not improbable that this is the main reason for mentioned polar effects previously were unknown.

Polar properties of some cubic crystals have strong anisotropy, Mason [3]. As it is clear from Fig. 2(a) to obtain the maximum of piezoelectric response in the GaAs type crystal one must use a polar  $[111]$ -direction of the crystal.



**Fig. 3. Spatial distribution of the III-V crystal piezoelectric responsibility shows the appearance of dipole component that is equivalent to the spontaneous polarization  $P_s$ : (a) free-stress crystal, in which four 3-fold axes internal polarity is compensated totally; (b) partially clamped crystal with a dipole-type responsibility in the  $[111]$ -direction**

That is why the installation of a crystal should be changed. In the new (nonstandard) crystallographic orientation, new axis “3” is directed to the  $[111]$  while another new axis “1” should be oriented perpendicularly to the plane passing

through the “3” axis of a cube. As for the last new axis “2”, its direction is predetermined by the rectangular coordinate system. In other words, crystal plate should be cut perpendicularly to the [111] direction.

Correspondent matrix of piezoelectric module for a new crystal orientation is given by:

$$e_{im} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & e_{16} \\ e_{21} & e_{22} & 0 & e_{24} & 0 & 0 \\ e_{31} & e_{32} & e_{33} & 0 & 0 & 0 \end{pmatrix} \quad (3)$$

where  $e_{21} = -e_{22}$  and  $e_{31} = e_{32} = -0.5 e_{33}$ . It is seen that polar (111)-cut of GaAs type crystal shows longitudinal piezoelectric effect:  $P_3 = e_{33}x_3$  and a transverse one:  $P_3 = e_{31}x_1 + e_{32}x_2$ .

Before proceeding further, let us show that homogeneous influence (uniform change of temperature or hydrodynamic contraction) can not induce any electric response even in the piezoelectric (111)-plate of the GaAs specimen. First of all, share stress or strain in the (111)-plate cannot be excited, because share components of piezoelectric module are absent in the third line of the Eq. (3), and that the external influence is of a scalar type. Therefore, the only longitudinal and transverse electrical responses have to be taken into account.

However, in free-stress crystal sample of any form, the longitudinal piezoelectric effect ( $e_{33}$ ) and two transverse effects ( $e_{31}$  and  $e_{32}$ ) compensate each other:  $e_{31} + e_{32} = -e_{33}$ . It was illustrated in the Fig. 1 (b) which describes the thermal treatment of GaAs (111)-plate: one part of piezoelectric polarization ( $e_{33}x_3$ , induced by thermal deformation  $x_3$ ) equals to other parts ( $e_{31}x_1 + e_{32}x_2$ ) but with the opposite sign (in this case, index “3” corresponds to the [111]-axis). Strain components in free-stress cubic crystal are equal:  $x_1 = x_2 = x_3$  because the excitation is homogeneous. That is why, in the non-pyroelectric crystal the sum of piezoelectric coefficients of transverse and longitudinal piezoelectric coefficients is zero:

$$e_{31} + e_{32} + e_{33} = 0 \quad (e_{31} = e_{32} = -\frac{1}{2} e_{33}).$$

As a result, piezoelectric effect produced by the longitudinal strain component  $x_3 = \alpha dT$  should be compensated by the effect of two transverse strain components  $x_1 = x_2 = \alpha dT$ , therefore no polar response is possible. Consequently, free-stress polar (111)-plate of GaAs type crystals is not sensible to the homogeneous excitations.

Fundamental idea of this work is that the artificial limitation of any one of mentioned strain components ( $x_3$  or  $x_1 + x_2$ ) should transform the

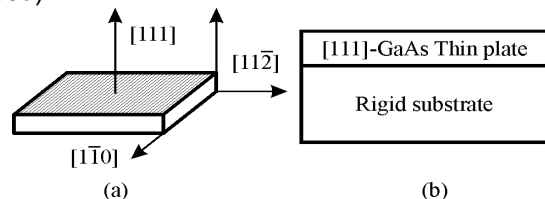
piezoelectric (111)-plate of GaAs type crystal into the artificially created “pyroelectric”.

In practice, it is easier to limit the plane strain ( $x_1 + x_2$ ) by a special mechanical design. In this case, the only thickness strain  $x_3$  can be excited, and just in the direction of polar axis “3” ([111]-direction) which is transferred into a “peculiar” polar axis.

New effects are impossible as in the free-stress so in the free-strain crystals: both artificial effects are the result of non-isotropic partial clamping. Therefore, piezoelectric crystal, being partially clamped, manifests artificial pyroelectricity. By the same manner, with a rigid substrate, the volumetric piezoelectric effect is also possible to obtain.

### Experimental study

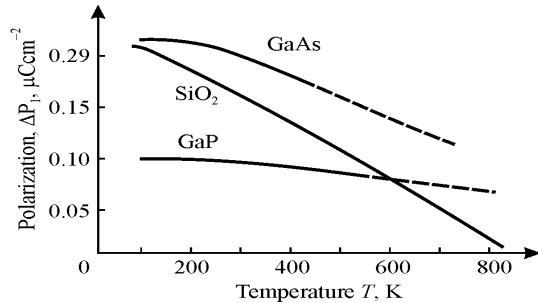
At a quasi-static condition, one simple way to provide experimentally strain limitation is demonstrated in Fig. 4. Any plane strain of (111)-cut crystal plate is fixed by the “ideally hard” substrate. In the case of volumetric piezoelectric effect investigation, the hard steel would be used as a rigid substrate. This makes impossible any plane component of strain ( $x_1 = x_2 = 0$ ) so the only thickness electric response  $P_3 = e_{33}x_3$  can be realized. It is obvious that the volumetric piezoelectric effect is created artificially in such composite structure. By a similar fashion, the *s/i*-GaAs crystal (111)-plate could be activated for pyroelectric response, if the rigid substrate shown in Fig. 4(b) would have its thermal expansion coefficient  $\alpha \sim 0$  (in our experiments, a fused silica was used).



**Fig. 4. Partial (plane) clamping realization: (a) experimentally used orientation of *s/i*-GaAs [111]-cut; (b) thin plate soldered to rigid substrate**

Under this condition, any plane thermal strain is forbidden, so the [111]-polarization component imitates “pyroelectricity”:  $P_{111} = P_3 = e_{33}\alpha dT = \gamma_3 dT$ . In the *s/i*-GaAs (111)-plate  $\gamma_3 \sim 2 \mu\text{C}/\text{m}^2\text{K}$  was obtained with correspondent voltage sensitivity  $S_V \sim 0.02 \text{ m}^2\text{C}^{-1}$ . Parameter  $S_V$  of *s/i*-GaAs is close to one of commonly used PZT-type pyroelectric ceramics because GaAs dielectric constant is at least 50 times less than PZT dielectric constant. It is important to note that some of III-V

semiconductors (capable to form solid solution and epitaxial layer with GaAs) have parameters  $\gamma$  and  $S_V$  many times better than the GaAs ones. Above all, these III-V crystals are much closer to the dielectrics than semi-insulating GaAs.



**Fig. 5. Dipole component  $\Delta P_{111}$  temperature dependencies in the GaAs and GaP crystals, in comparison to the  $\Delta P_{100}$  of  $\text{SiO}_2$  ( $\alpha$ -quartz) crystal**

Dynamic investigations of artificial pyroelectric effect were provided by Pereverzeva et al [4]. In this case, no substrate need to use to stuck a sample. Partial clamping conditions were realized by the use of mechanical inertia of a sample itself that is above its first (at the lowest frequency) piezoelectric resonance. The sample under study should have a quite non-isometric form, such as a very thin piezoelectric disk. Dynamic effect occurs between sample acoustic resonances:  $\omega_L \leq \omega \leq \omega_T$ , where  $\omega_L$  is low frequency radial mode of disk while  $\omega_T$  is much more high frequency of thickness vibration mode. In other experiments with artificial pyroelectric response, a thin but very long piezoelectric bar of *s/i*-GaAs was used to provide an inertial type clamping at the frequencies above first longitudinal electromechanical resonance of the bar. In this case, the difference between low frequency piezoelectric resonance ( $\omega_L$ ) after which the sample becomes partially clamped, and high frequency thickness resonance ( $\omega_T$ ) was very large.

Experimental arrangement consisted of IR laser with the optical shutter used to modulate the radiation at the frequency range of  $10^3$ - $10^6$  Hz while the pyroelectric response was measured by the selective voltmeter. The investigated samples were freely suspended and irradiated by a modulated laser beam. High precision of orientation and processing of samples was ensured by the optical standards. Thin electrodes were deposited on the flat surfaces of disks and on the sides of bars. Artificial pyroelectric response did not occur at low laser modulation frequency until the first acoustic resonance at frequency  $\omega_L$ . A maximum of response was observed near  $\omega_L$  accompanied by

the series of other resonance peaks ( $2\omega_L$ ,  $3\omega_L$ , etc.) up to highest frequency  $\omega_T$  correspondent to thickness resonance. Temperature dependence of artificial pyroelectric response of partially clamped in (111)-plane GaAs and GaP crystals are shown in Fig. 5.

Thermal-mechanically induced pyroelectricity was demonstrated in other piezoelectric crystals as well. For the comparison, in the Fig. 5 correspondent characteristic of piezoelectric crystal  $\alpha$ -quartz is shown. Nowadays silicon and quartz are the most common crystals in microelectronic sensors because the first one is a good semiconductor, and the other is one of the best piezoelectrics. GaAs type crystals combine the advantages of both silicon and quartz crystals. That is why, the *s/i*-GaAs with the other III-V crystals have a large unexploded potential. Strong etching anisotropy as well as the possibility to use AlGaAs layer as the etch-stopper is very favorable in sensor array processing. As for the feasibility to use in the far infrared sensors, GaAs type crystals have some important advantages such as high thermal expansion coefficient and low thermal conductivity. The first one is very important to increase the response while the second essentially limits the thermal diffusion.

Being fabricated by the microelectronics, one-crystal GaAs based sensors would have a low cost as for single-element sensor, so in the case of several sensor-cells joint in a matrix. Finned structure can be realized by micromachining, and it is need to note that sensitivity of thermal image processor increases as square root of cell number. The identity of each cell of such array is feasible using microelectronics.

## Conclusions

Charge separation phenomena in dielectrics have always been associated with the change of spontaneous polarization under the scalar (thermal or mechanical) influence. It was supposed previously that these properties are related to the crystals of 10 pyroelectric classes only. This work shows that scalar thermal influence may induce pyroelectricity in the other 10 "true piezoelectric" classes of polar crystals, and the most important application of this effect is expected in the III-V semiconductor-piezoelectric.

Artificial pyroelectric effect is defined as stress-induced polarization of partially clamped piezoelectric subjected to uniform heating. Partial clamping is created by the non-uniform boundary conditions, which limit the thermal deformation of piezoelectric crystal providing a uniform but non-

isotropic stress. Artificial pyroelectricity of partially clamped piezoelectric has a maximum in the direction of one of the polar axes of piezoelectric crystal. Artificial volumetric piezoelectric effect is quite analogues.

Limitation of plane strain in the (111)-plates or membranes of III-V type semi-insulating crystal opens up the possibilities of a new type of micro-electronic sensor. This would have advantages over semiconductor photon array that need cooling and over pyroelectric one produced by the hybrid processing.

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## Пироотклик в полупроводниках группы $A^{III}B^V$ в условиях ограничения их деформации

*Показано, что скалярные тепловое воздействие может вызвать пироэлектричество в пьезоэлектрических классах полярных кристаллов, и самое важное применение этого эффекта ожидается полупроводниках-пьезоэлектриках группы  $A^{III}B^V$ . Искусственный пироэлектрический эффект определяется как механически индуцированная поляризация в частично зажатом пьезоэлектрике, подвергнутому равномерному нагреву. Частичное зажатие создается неоднородными граничными условиями, которые ограничивают тепловую деформацию пьезоэлектрического кристалла, обеспечивая создание в нем равномерного но не изотропного напряженного состояния. Ограничение планарной деформации в плоскости (111) пластины или мембраны из полупроводниковых кристаллов типа  $A^{III}B^V$  открывает возможности разработки нового типа микроэлектронных датчиков. Они могут иметь преимущества по сравнению с гибридными датчиками типа «диэлектрик-полупроводник» и полупроводниковыми датчиками, которым необходимо охлаждение. Библиография. 4, рис. 5.*

**Ключевые слова:** пироэлектрический сенсор, пьезоэлектрический сенсор, полупроводники  $A^{III}B^V$ .

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## **Піровідгук у напівпровідниках групи $A^{III}B^V$ в умовах обмеження їх деформації**

*Показано, що скалярний тепловий вплив може викликати піроелектрику в п'єзоелектричних класах полярних кристалів, і найважливіше застосування цього ефекту очікується у напівпровідниках-п'єзоелектриках групи  $A^{III}B^V$ . Штучний піроелектричний ефект визначається як механічно індукована поляризація в частково затиснутому п'єзоелектрику, підданому рівномірному нагріванню. Часткове затискання створюється неоднорідними граничними умовами, які обмежують теплову деформацію п'єзоелектричного кристала, забезпечуючи створення в ньому рівномірно але не ізотропно напруженого стану. Обмеження планарною деформації в площині (111) пластини або мембрани з напівізолюючих кристалів типу  $A^{III}B^V$  відкриває можливості розробки нового типу мікроелектронних датчиків. Вони можуть мати переваги в порівнянні з гібридними «діелектрик-напівпровідник» датчиками і напівпровідниковими датчиками, яким необхідно охолодження. Бібл. 4, рис. 5.*

**Ключові слова:** піроелектричний сенсор, п'єзоелектричний сенсор, напівпровідники  $A^{III}B^V$ .