PYROELECTRIC-LIKE RESPONSE IN SEMI-INSULATING III-V CRYSTAL

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

I. INTRODUCTION

The most of future sensor devices will be fabricated with the use of microelectronics. By this it is meant that sensor must be integrated in a 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 $\sigma(p)$. Notwithstanding, a 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 dielectric sensor has lower noise coefficient because 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 a dielectric 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 causes 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 piezoelectric, III-V polar crystal is not belongs to 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 the piezoelectric type of response into a pyroelectric one. The idea was realized by the constructional control of crystal boundary conditions, Poplavko et al [2].

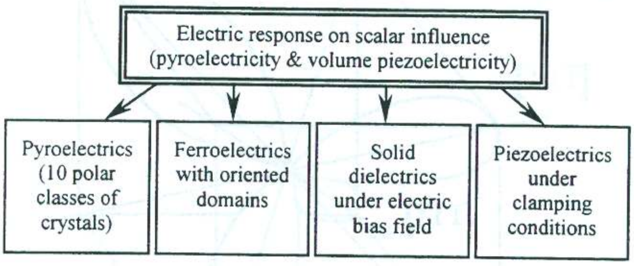
It is significant that the most of III-V semiconductors are very close to dielectrics in their conductivity. Semi-insulating (*s/i*) GaAs that is one of basic material of our experimental study is characterized by the $\sigma \approx 10^{-7}$ Ohm/m. Moreover the AlGaAs alloy used in our test sensor device has $\sigma < 10^{-12}$ Ohm/m.

Dielectric properties of III-V semiconductors, partly their piezoelectric activity, usually were out of consideration because of carries 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) is regarded as the main process. Correspondingly, the lattice of III-V semiconductor is considered here as a dielectric, so only the 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 AlP. Previously piezoelectric properties of III-V crystals practically have not been used in devices. Nevertheless, any crystal of the GaAs 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. It is obviously that "classic" pyroelectric usually has too small sensitivity to be used as a sensor. Being much more sensitive and using in sensors, ferroelectric also belongs to 10 polar (pyroelectric) classes. However, the most of ferroelectrics usually have a random orientation of its domains. To be used as sensor, ferroelectric crystal needs to be "polarized" by an 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, Table 1. Pyroelectric sensitivity of dielectrics is as mush as its [dielectric constant] $^2 = \varepsilon^2$. That is why IR image arrays use the paraelectric ceramics or diffuse phase transition ferroelectric ceramics with $\varepsilon > 10^4$. As in the ferroelectrics, internal polarization of high-ε ceramics should be induced or supported by the electric bias field.

TABLE 1:
SOLID DIELECTRICS, WHICH POLAR PROPERTIES CAN BE USED IN THE SENSORS OF TEMPERATURE AND PRESSURE.



The advantages of ceramics are low cost and a homogeneous structure. However, based on ceramics IR image hybrid structure has some disadvantages. First of all, to induce pyroelectric properties in the non-polar ceramics, a strong external electric bias field must be applied to the element pitch. As a result, there is a cause of electrically stimulated aging and even 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 sensor device, the piezoelectric cell is not stressed continually: boundary conditions are used only to limit one type of deformations (usually 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.

II. ARTIFICIAL PYROELECTRIC EFFECT IN III-V CRYSTALS

As a rule, to evaluate the 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, dP_i is the change of vectorial value. Thus, pyroelectric coefficient γ_i and volumetric piezoelectric coefficient ξ_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 ξ_i and γ_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 studied effect needs a more detailed explanation based on classic pyroelectric response. Conventional pyroelectric effect is the variation of spontaneous polarization dP_i in polar crystal during uniform change of its temperature dT, Fig. 1(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 which any component of strain is absent: $x_n = 0$. Secondary pyroelectric coefficient can be measured as a difference between 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 thermal influence, piezoelectric effect is excited by the thermal deformation of crystal: $x_n = \alpha_n dT$ where α_n is the component of thermal expansion coefficient. As a result:

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

Figure 1(b) illustrates secondary pyroelectric effect as a polarization produced by thermal strain $x_n(T)$ that is transformed to electric response through the piezoelectric effect. One part of the 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.

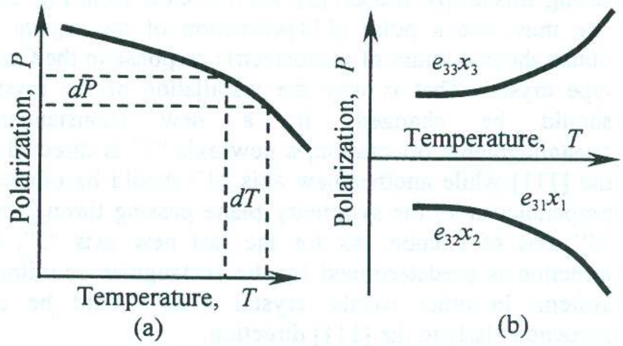


Fig. 1. Non-central symmetry crystals polarization temperature dependence: (a) spontaneous polarization in the ferroelectric; (b) thermo-mechanically induced polarization in the piezoelectric crystal.

It was usually assumed that the sum $e_{in}\alpha_n$ is nonzero only in pyroelectric that has a spontaneous (intrinsic) polarization P_S. On the contrary, in a "true piezoelectric", such as III-V semiconductor (which is not pyroelectric), the sum in the Eq. (1) is suggested to be zero. However, as it was recently established [2], any "true piezoelectric" is liable to a "secondary-type" pyroelectric effect at partial clamping conditions. As a consequence, it is possible to make the sum $e_{im}\alpha_n \neq 0$. It is this effect that is proposed here to utilize in the sensor devices. In 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 representation of these crystals is based on the [100]-type axes. In this case, a correspondent matrix of piezoelectric module has the only share-type components of piezoelectric module:

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

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 twist 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) one must use a polar [111]-direction of the crystal to obtain the maximum of piezoelectric response in the GaAs type crystal. That is why the installation of the crystal should be changed. In a new (nonstandard) crystallographic orientation, a new axis "3" is directed to the [111] while another new axis "1" should be oriented perpendicular to the symmetry 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 new crystal orientation is given by:

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

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 a longitudinal piezoelectric effect: $P_3 = e_{33}x_3$ and a transverse one: $P_3 = e_{31}x_1 + e_{32}x_2$.

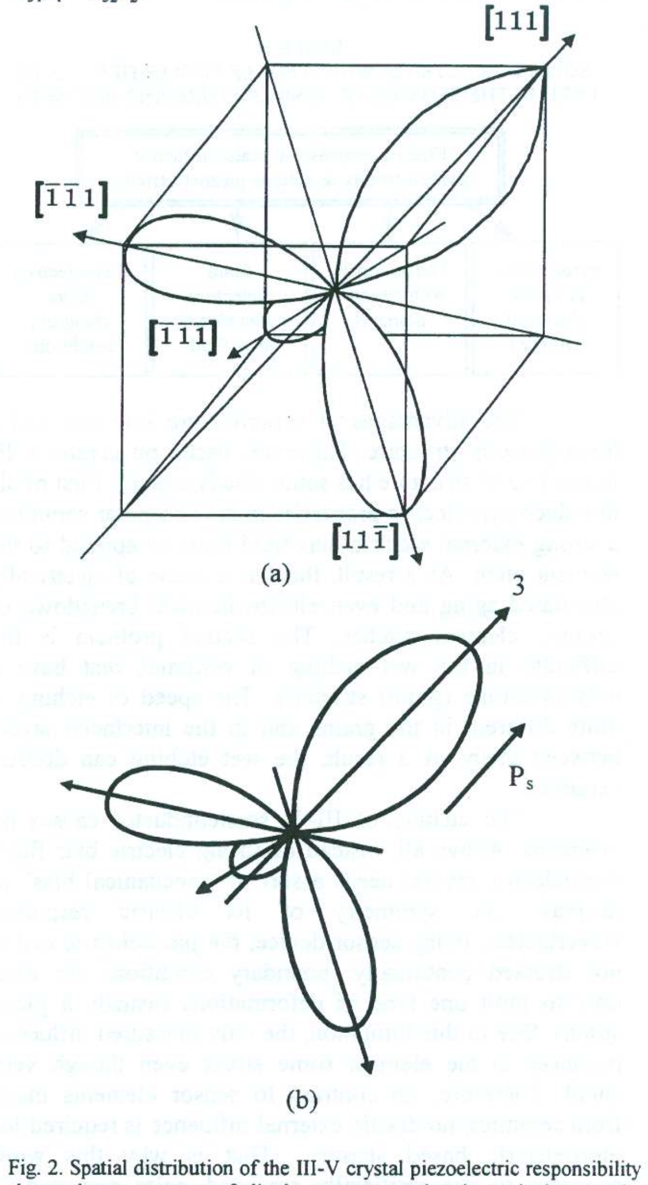


Fig. 2. Spatial distribution of the III-V crystal piezoelectric responsibility shows the appearance of dipole component that is equivalent to the spontaneous polarization P_s: (a) free-stress crystal, in which four 3-fold axes internal polarity is compensated totally; (b) partially clamped crystal with a dipole-type responsibility in the [111]-direction.

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}) will compensate each other: $e_{31} + e_{32} = -e_{33}$. It is 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 must be zero:

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

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" (a [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.

III. EXPERIMENTAL STUDY

At a quasi-static condition, one simple way to provide experimentally strain limitation is demonstrated in Fig. 3(b). 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. In similar fashion, the *s/i*-GaAs crystal (111)-plate could be activated for pyroelectric response, if the rigid substrate shown in Fig. 3(b) would have its thermal expansion coefficient $\alpha \sim 0$ (in our experiments, a fused silica was used). Under this condition, any plane thermal strain is forbidden, so [111]-polarization component imitates "pyroelectricity": $P_{111} = P_3 = e_{33}\alpha dT = \gamma_3 dT$. In the *s/i*-GaAs (111)-plate $\gamma_3 \sim 2$ $\mu C/m^2K$ was obtained with correspondent voltage sensitivity $S_V \sim 0.02$ m^2C^{-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 γ and S_V 10 times better than the GaAs ones. Above all, these III-V crystals are much closer to the dielectrics than semi-insulating GaAs.

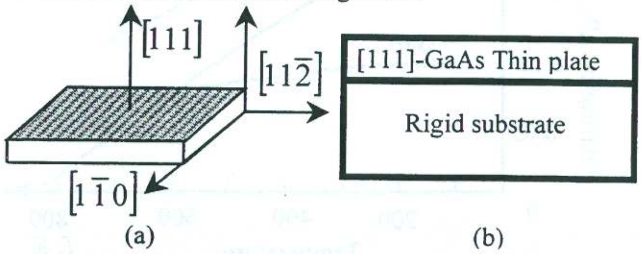


Fig. 3. Partial (plane) clamping realization: (a) experimentally used orientation of *s/i*-GaAs [111]-cut; (b) thin plate soldered to rigid substrate.

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: $\omega_L \le \omega \le \omega_T$, where ω_L is low frequency radial mode of disk while ω_T is much more high frequency of thickness vibration mode. In other experiments with artificial pyroelectric response, a thin but very long piezoelectric bars of *s/i*-GaAs were 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 (ω_L) after which the sample becomes partially clamped, and high frequency thickness resonance (ω_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 ω_L. A maximum of response was observed near ω_L accompanied by the series of other resonance peaks ($2\omega_L$, $3\omega_L$, etc.) up to highest frequency ω_T correspondent to thickness resonance. Temperature dependence of artificial pyroelectric response of partially clamped in the (111)-plane GaAs and GaP crystals are shown in Fig. 4. Thermal-mechanically induced pyroelectricity was demonstrated in other piezoelectric crystals as well. For the comparison, in the Fig. 4 correspondent characteristic of piezoelectric crystal α-quartz is shown.

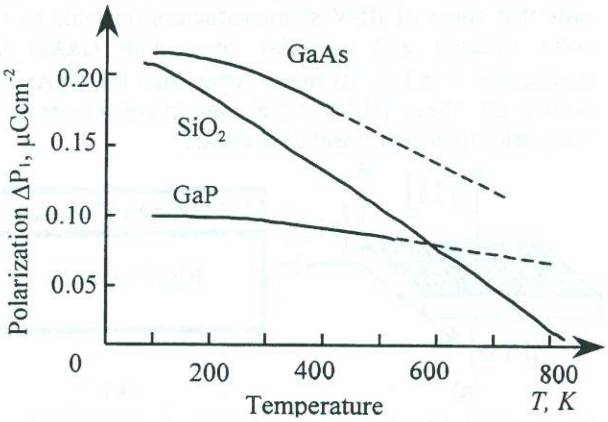
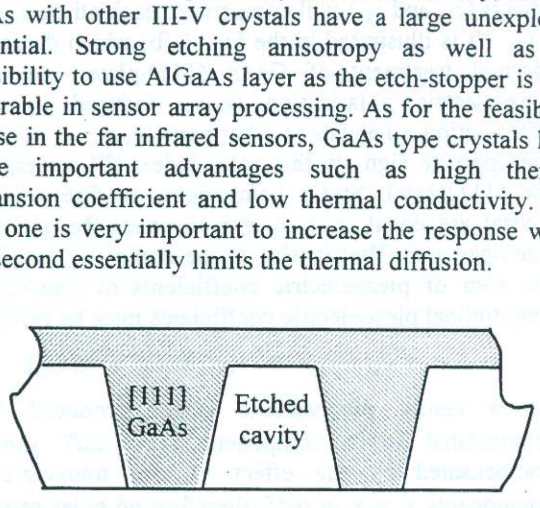


Fig. 4. Dipole component ΔP_{111} temperature dependencies in the GaAs and GaP crystals, in comparison to the ΔP_{100} of SiO_2 (α-quartz) crystal.

IV. ONE CRYSTAL SENSOR

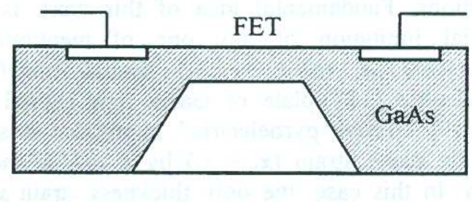
In the case of application in a sensor device, the other way of plane strain limitation should be used, as shown in Fig. 5. Pyroelectric or piezoelectric response can be obtained in the finned design of *s/i*-GaAs substrate. Using mask and etching technique, the cavities could be created in the basis plate forming the membranes, which plane strain is limited by the thick edges. Thin and "soft" membranes separated by thick and "hard" edges provide a way to obtain the artificial pyroelectric effect as well as the volumetric piezoelectric effect. Through the edges, the substrate provides appropriate planar strain limitation of membrane based cell. Experiments show that a membrane type structure provides the electric response in 2-4 times more than thin plate soldered on a rigid substrate, shown in Fig. 3(a). This amplification is due to the "moonie" effect, Onitsuka et al [5], when transverse piezoelectric modulus d_{31} and d_{32} add to the longitudinal module d_{33}.

Being heated by the IR illumination (or being compressed by the change of external pressure) the membrane generates electric potential that controls field effect transistor. Thus, the membrane is used in a FET instead of the gate, Fig. 5(b). A new device is named "pyroelectric transistor", and it consists of the membrane-transducer integrated with the FET amplifier in the one-crystal structure. "Pyrotransistor" need the cavity covered from inside by the infrared absorbent layer, while in the case of "piezotransistor" the etched cavity should be closed. 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 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.



(a)

Fig. 5. Plane strain limitation by the use of finned structure: (a) etched



(b)

cavities in the (111)-plate of GaAs; (b) FET integrated onto membrane that works as a "pyroelectric gate".

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 clear 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.

A possible design of one-crystal matrix sensor is shown in Fig. 6. Very high resistive (nearly a dielectric) AlGaAs layer should be deposited previously on the [111] GaAs wafer by the liquid phase epitaxial process. After the etching, this layer will form the piezoelectric membranes. Thin epitaxial GaAs film (which is the basis of a FET type amplifier) is located onto the membrane, which works as a "piezoelectric gate". Pyroelectric sensor can be realized in practice only if the heat flux is varied (modulated) in time. Otherwise, there would be enough time for the charge carriers to neutralize the thermally induced polarization. The modulation frequency of IR-radiation in the III-V crystal "pyroelectric" detector depends on the equilibrium concentration of charge carries. In the *s/i*-GaAs, the screening of pyroelectric field is overlooked at the modulation frequency higher than 1 kHz. In crystalline solid solutions AlGaAs, GaAsP as well as in some other

III-V crystals-dielectrics, the frequency of heat modulation could be reduced to 20 Hz that is commonly accepted in other pyroelectric device. However, integrated with the membrane high frequency FET is capable of very rapid operation (up to 10^{-10} s). The inertia-less is one of the advantages of feasible device, and such a sensor could be applied to the very fast IR or microwave pulse measurements.

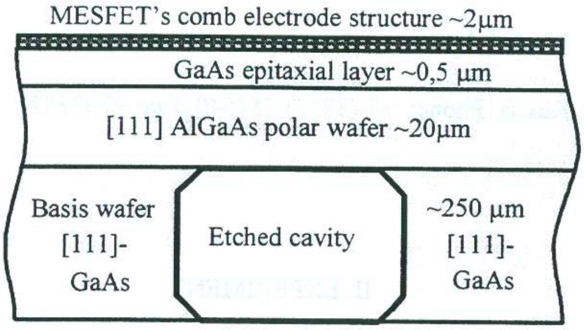


Fig. 6. Design of one-crystal pyroelectric sensor that is a part of array.

V. 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 microelectronic 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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