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Pyroelectric coefficient estimations for aluminum and gallium compounds

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Analytical expression for pyroelectric coefficient p for the compounds with wurtzit structure is given. Obtained values of p for AlN and GaN are in satisfactory agreement with the first-principles calculations. Pyroelectric effect in the uniform epitaxial films and heterostructures is discussed.

Keywords: pyroelectric coefficient, wurtzite structure, monocrystal, thin film, heterostructure.

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1. Pyroelectric effect known as early as from ancient time [1] still attracts the interest of researchers [2–4]. This effect is defined by the dependence of the spontaneous polarization P_s on the temperature T and characterized by total pyroelectric coefficient $p(T) = (dP_s/dT)_\sigma$, where σ is the mechanical stress, and it is supposed that vector $\mathbf{P}_s$ has only one component along axis $\hat{z}$. The fundamentals of the modern pyroelectricity theory were laid by Born [5] and Szigeti [6], the current status of the theory is reflected in [7–9]. In accordance with [5–9], we have

$$p(T) = p_1(T) + p_2(T) = \left(\frac{\partial P_s}{\partial T}\right)_\varepsilon + \sum_i \left(\frac{\partial P_s}{\partial \varepsilon_i}\right)_T \left(\frac{\partial \varepsilon_i}{\partial T}\right)_\sigma, \qquad (1)$$

where ε is elastic strain with components ε_i. Summand $p_1(T)$ is known as a primary pyroelectric coefficient (PC) at constant external strain when the sample volume and shape remain unchanged („clamped-lattice“ pyroelectricity). The second summand in (1) known as a secondary PC is compliant with the constant stress and can be calculated as $p_2(T) = \sum d_{ijk} c_{jklm} \alpha_{lm}$, where $\mathbf{d}, \mathbf{c}$ and $\boldsymbol{\alpha}$ are tensors of piezoelectric stresses, elastic constants and thermal expansion coefficients [4]. If we assume that tensors $\mathbf{d}, \mathbf{c}$ and $\boldsymbol{\alpha}$ are known, then the problem of PC definition is limited to the calculation of $p_1(T)$ which may be written as a sum of $p_1^{(1)}(T)$ and $p_1^{(2)}(T)$, where the first term meets the hard point ion model and the second term describes the electron charge redistribution caused by lattice vibrations [8,9]. Further we will address only $\mathrm{A}_N\mathrm{B}_{8-N}$ type compounds with wurtzite structure. When $p_1^{(2)}(T)$ is neglected according to [8], we obtain

$$p_1(T) = \frac{4eZ^* u_T}{\sqrt{3}\, a^2}. \qquad (2)$$

Here e is the elementary charge, Z^* is the the Born effective transverse charge, $u_T = du/dT$, u is the internal strain. It is also assumed that in the ideal wurtzite structure $u = 3/8$ and lattice cell volume containing 4 atoms is equal to $\Omega = \sqrt{3}\, a^2 c/2$, where a and c are the lattice constants, axis c coincides with axis $\hat{z}$. Using the findings from [8], after a set of transformations, we obtain

$$u_T = \frac{4\gamma_{\mathrm{TO}} C_V(T)}{3c^2 M \omega_{\mathrm{TO}}^2},$$

$$C_V(T) = k_{\mathrm{B}} \sum_{q_j} (\hbar\omega_{q_j}/k_{\mathrm{B}}T)^2 \exp(\hbar\omega_{q_j}/k_{\mathrm{B}}T) n_{q_j}^2, \qquad (3)$$

where $\gamma_{\mathrm{TO}} = -d\ln\omega_{\mathrm{TO}}/d\ln u$ is the Gruneisen constant for transverse optical mode $\omega_{\mathrm{TO}} \equiv \omega_{\mathrm{TO}}(0)$ at wave vector $\mathbf{q} = 0$, $C_V(T)$ is the heat capacity of lattice at constant volume, $n_{q_j} = [\exp(\hbar\omega_{q_j}/k_{\mathrm{B}}T) - 1]^{-1}$ is the Bose–Einstein, M is the reduced weight, k_{B} is the Boltzmann's constant, index j enumerates the phonon spectrum branches. Thus, $p_1^{(1)}(T) \propto u_T(T) \propto C_V(T)$, as reported in [8–10].

2. Consider AlN and GaN single crystals and assess the parameters included in equations (2) and (3). Since $Z^* \propto \sqrt{\varepsilon_0 M\left(\omega_{\mathrm{LO}}^2(0) - \omega_{\mathrm{TO}}^2(0)\right)}$ [11], where ε_0 is the static dielectric constant, then using the findings from [12] ($\omega_{\mathrm{TO}}(0) = 611\,\mathrm{cm}^{-1}$ for AlN and $532\,\mathrm{cm}^{-1}$ for GaN) and [13] ($\varepsilon_0 = 8.5$ for AlN and 8.9 for GaN) and assuming that for GaN the ab initio calculated Born charge $Z^* = 2.2$ [8], for AlN we obtain $Z^* = 2.4$ (in [14] for cubic AlN 2.36 is given). Geometrical parameters of lattice cells are specified in [15–17]. To assess γ_{TO}, use the Gruneisen constants $\gamma_{\mathrm{TO}} = 0.92$ and 0.87 for AlN and GaN [18]. Function $C_V(T)$ for GaN shown in Fig. 1 in [10] is almost coincident with the lattice heat capacity approximation at constant pressure $C_P(T) = (35.6 + 9.32 \cdot 10^{-3}T)10^{-5}\,\mathrm{eV/K}$ at $298 < T(K) < 1773$ [13]. For AlN $C_P(T) = (47.8 + 3.48 \cdot 10^{-3}T)10^{-5}\,\mathrm{eV/K}$ at $300 < T(K) < 1800$ [13] (for semi-quantitative assessments, neglect the difference between C_V and C_P). Using the

calculated parameter values, we obtain at room temperature $u_T = 1.8 \cdot 10^{-6}\,\mathrm{K}^{-1}$ for AlN and $1.4 \cdot 10^{-6}\,\mathrm{K}^{-1}$ for GaN. Thus, $u_T(\mathrm{GaN})/u_T(\mathrm{AlN}) \approx C_P(\mathrm{GaN})/C_P(\mathrm{AlN}) \approx 0.8$. It should be noted that $M\omega^2_{\mathrm{TO}}$ values are determined by force constants that are virtually the same for AlN and GaN as a result of proximity of lattice constants a and c.

By substituting u_T values in equation (2), we obtain $p_1^{(1)} = 1.4\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$ for AlN and $1.2\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$ for GaN. Considering the approximations made, the obtained results are satisfactorily in line with the ab initio calculations: $-p_1^{(1)} = 0.9$ and $\sim 1.4\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$ at $T = 300\,\mathrm{K}$ and $1000\,\mathrm{K}$ for AlN [10]; $-p_1^{(1)} \cong 1.8\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$ at $T = (300{-}1000)\,\mathrm{K}$ for GaN [8] (symbol $\sim$ means that PC values are read from curves). (Negative values assigned traditionally to coefficients $p_1^{(1,2)}$, p_2 and p are not derived directly from equations (1)−(4), but only show that spontaneous polarization P_s is assumed as negative. The matter is that the dipole moment of interatomic bond extended along axis c is directed from anion to cation, i.e. opposite to axis c.) On the other hand, it is a bit surprising that there is a significant quantitative discrepancy of findings in [8] and [10]. It should be also noted that the calculations in [9] have shown that for high temperatures the contribution of $|p_1^{(2)}|$ to $|p_1|$ is twice as large as the contribution of $|p_1^{(1)}|$ (the result caused the calculation authors surprise).

As already mentioned above, PC $p_2 = \sum d_{ijk} c_{jklm} \alpha_{lm}$, whence we have for the wurtzite structure [10]:

$$p_2 = 2e_{31}\alpha_1 + e_{33}\alpha_3, \tag{4}$$

where e_{ij} are piezoelectric constants [19], α_i are anisotropic thermal expansion coefficients [18]. Dependences $p_2(T) \propto T$ are shown in [8,9] and [10] for GaN and AlN, respectively.

In [15–17], spontaneous polarization of ternary compounds formed by AlN, GaN and InN binary compounds was investigated. For AlN and GaN, the following values were obtained $P_s = -8.70 \cdot 10^{-2}\,\mathrm{C/m^2}$ and $P_s = -3.73 \cdot 10^{-2}\,\mathrm{C/m^2}$ [15], so for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$—$P_s(x)| \propto x$. The obtained results suggest that PC $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ are also linear composition functions.

3. To this point, we have discussed single crystals,but now we are going to focus on pyroelectric properties of more complex structures, for which we will certainly have to use additional simplifications. Begin from thin films formed on bulk solid-state substrates for which the phenomenological theory of pyroelectric effect was developed in [20]. According to this theory, thin film PC

$$\bar{p} = p_1 + \bar{p}_2, \qquad \bar{p}_2 = p_2 + 2\bar{e}_{31}(\alpha_{\mathrm{sub}} - \bar{\alpha}), \tag{5}$$

where α_{sub} and $\bar{\alpha}$ are thermal expansion coefficients of substrate and thin film, $\bar{e}_{31}$ is the piezoelectric constant of thin film. In [21,22], where AlN films on silicon substrate were addressed, PC values were obtained which were equal to, respectively, $\bar{p} = 4.8$ and $6{-}8\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$. In [23], for $\mathrm{Al}_{1-x}\mathrm{Sc}_x\mathrm{N}$ the following was found (in $\mu\mathrm{C/m^2} \cdot \mathrm{K}$): $\bar{p} = 5.46 + 15x$ for $x < 0.35$, and $\bar{p}$ is independent of the temperature within 20−80°C. Thus, PC is positive for thin films, since for wurtzite structures $e_{31} < 0$ [14,20], $\alpha_{\mathrm{Si}} < \alpha_{\mathrm{AlN}}$ [18,24,25] and $\bar{p} = p_1 + \bar{p}_2$, $\bar{p}_2 = p_2 + 2\bar{e}_{31}(\alpha_{\mathrm{sub}} - \bar{\alpha}) > |p|$.

Let's discuss the findings of [26], which is focused on dielectric and pyroelectric properties of AlN- and GaN-based compounds grown by chloride-hybrid epitaxy on SiC/(111)Si substrate and where high PC values were obtained within $(9{-}18)\,\mu\mathrm{C/m^2} \cdot \mathrm{K}$, and the maximum value is observed for $\mathrm{AlN/Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ structure with Al/N equal to 50.9/49.1.

We believe that in this case we shall imply effective PC p_{eff}, since the stoichiometric composition regions of $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{N}$ represent thin interlayers located inside $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ layers. (In this case an analogy with electrical conductance suggests itself, when instead of conductivity characterizing a homogeneous sample we have to imply conductance of a specific structure.) In [26], such structure is addressed as a composite material containing heterojunctions between the regions with different aluminum and gallium concentrations. It should be noted that similar, but chemically homogeneous banded structures (superlattices) have been detected before in epitaxial films of silicon carbide [27,28].

The problem of PC of a composite material for ferroelectrics was addressed in [29]. The effective PC of a composite was expressed as a PC function and dielectric constants of the compounds included in the composite and effective dielectric constant of the composite. According to this scheme, $p_{\mathrm{eff}}(x) = x\bar{p}_{\mathrm{AlN}} + (1-x)\bar{p}_{\mathrm{GaN}}$, where, as above, the overline is related to an epitaxial layer characteristic. However, this expression does not explain the presence of $p_{\mathrm{eff}}^{\max} = 18\,\mu\mathrm{C/m^2}$. Moreover, high PC values can't be described only by the substrate effect using expression (5). Therefore, following the authors of [26], it should be assumed that heterojunctions are the main factors that determine the PC magnitude. The role of spontaneous polarization P_s of hexagonal NH−SiC polytypes in formation of the energy-level diagram of 3C−SiC/NH−SiC/3C−SiC heterojunctions, where cubic 3C−SiC polytype has no spontaneous polarization, was addressed in [30]. To describe the energy band diagram of a composite consisting of hexagonal gallium and aluminum nitrides that have spontaneous polarization, P_s in the model [30] shall be substituted with $P_s(\mathrm{AlN}) - P_s(\mathrm{GaN})$. And T variation causes the change in the energy band diagram, quantum well depths on heterojunctions and occupancy of their quasi levels. The problem, thus, becomes rather challenging and self-consistent. For the problem to be set up and solved properly, additional experimental investigations are required first of all.

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Conflict of interest

The author declares that he has no conflict of interest.

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