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# Influence of spontaneous and piezoelectric polarizations on the phonon frequencies in strained GaN/AlN superlattices

J. Gleize, J. Frandon, and M. A. Renucci
*Laboratoire de Physique des Solides, UMR 5477 CNRS, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex 4, France*

F. Bechstedt
*Institut für Festkörpertheorie und Theoretische Optik, Friedrich-Schiller-Universität, D-07743 Jena, Germany*

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The influence of spontaneous and piezoelectric polarizations on the lattice dynamics of a strained GaN/AlN superlattice is investigated within a macroscopic framework. It is found that both effects alter the effective strain in the growth direction of the heterostructure in a significant way. This change in the strain state can also be connected to the internal strain in the GaN and AlN layers. The effects result in a change of the phonon frequencies of GaN and AlN of about 1 and 2 $\mathrm{cm}^{-1}$, respectively.

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The group-III nitrides such as wurtzite GaN and AlN display important piezoelectric polarization fields in a strained condition, as well as important spontaneous polarization even in the absence of strains.[1,2] Although recent publications discuss these effects in strained GaN/AlN heterostructures such as quantum wells and superlattices (SL's),[3–5] no work has been yet devoted to the influence of these polarization fields on the lattice dynamics of strained GaN/AlN layered structures. Indeed, some experimental and theoretical reports deal with the phonon deformation potentials of GaN and AlN as a mean to obtain the zone center phonon frequencies for these materials under given biaxial strain.[6–8] However, in these studies, the piezoelectric and spontaneous polarizations have always been neglected. Another important issue closely connected to the piezoelectric as well as pyroelectric effect is how the internal strain, corresponding to the change of the $u$ parameter of the wurtzite structure, affects the phonon frequencies in wurtzite GaN and AlN. The aim of this paper is thus to evaluate the influence of spontaneous and piezoelectric polarization fields, as well as of internal strain, on the phonon frequencies in strained GaN/AlN layered structures.

As a model system, we consider an infinite wurtzite GaN/AlN SL grown along the [0001] direction ($c$ axis, taken along the $z$ direction) on a substrate. The SL layers are labeled with an index $j$ in the following discussion ($j=1$ for GaN and $j=2$ for AlN). Due to the lattice mismatch between GaN and AlN, or to the substrate, the GaN and AlN layers undergo biaxial strains, which induce a change of the polarization fields $P^{(j)}$ in the SL layers. Assuming that the strains do not change the symmetry of the unit cell, we have $P_x^{(j)}=P_y^{(j)}=0$.

In a macroscopic description, the change in the polarization field in the layers $j$ is related to the strains by the piezoelectric constants $e_{31}^{(j)}$ and $e_{33}^{(j)}$:

$$\Delta P_z^{(j)}=2e_{31}^{(j)}\varepsilon_{xx}^{(j)}+e_{33}^{(j)}\varepsilon_{zz}^{(j)}, \tag{1}$$

where $\varepsilon_{xx}^{(j)}$ and $\varepsilon_{zz}^{(j)}$ are the strains in the layers $j$, in the layers planes, and along the growth direction, respectively. In order to explicitly show the contribution of the internal strain, i.e., the change in the $u$ parameter of the wurtzite structure, the piezoelectric constants can be expressed as[1]

$$e_{31}^{(j)}=e_{31}^{(0)(j)}+\frac{eZ_B^{(j)}}{V^{(j)}}\frac{\partial u^{(j)}}{\partial\varepsilon_{xx}^{(j)}} \tag{2}$$

and

$$e_{33}^{(j)}=e_{33}^{(0)(j)}+\frac{eZ_B^{(j)}}{V^{(j)}}\frac{\partial u^{(j)}}{\partial\varepsilon_{zz}^{(j)}}, \tag{3}$$

where $e$ is the electronic charge, $Z_B^{(j)}$ is the Born effective charge for material $j$, and $V^{(j)}$ is the bulk cell volume for material $j$. In the above equations, $e_{31}^{(0)(j)}$ and $e_{33}^{(0)(j)}$ are the clamped-ion terms, which describe the effects of strains in the layers planes and along the $c$ axis, respectively, and the second terms describe the effect of internal strain. Thus, for nonvanishing internal strains, the change in polarization due to the piezoelectric effect is

$$\Delta P_z^{(j)}=2e_{31}^{(0)(j)}\varepsilon_{xx}^{(j)}+e_{33}^{(0)(j)}\varepsilon_{zz}^{(j)}+\frac{eZ_B^{(j)}}{V^{(j)}}\Delta u^{(j)}, \tag{4}$$

where

$$\Delta u^{(j)}=2\frac{\partial u^{(j)}}{\partial\varepsilon_{xx}^{(j)}}+\frac{\partial u^{(j)}}{\partial\varepsilon_{zz}^{(j)}}. \tag{5}$$

Equation (5) can be reformulated using Eqs. (2) and (3) as

$$\Delta u^{(j)}=\frac{V^{(j)}}{eZ_B^{(j)}}[2(e_{31}^{(j)}-e_{31}^{(0)(j)})\varepsilon_{xx}^{(j)}+(e_{33}^{(j)}-e_{33}^{(0)(j)})\varepsilon_{zz}^{(j)}]. \tag{6}$$

The piezoelectric polarizations will in turn lead to the presence of electric fields $E^{(j)}$ in the SL layers, with $E_x^{(j)}=E_y^{(j)}=0$, the total polarization fields being

$$P_z^{(j)} = P_{z,sp}^{(j)} + \Delta P_z^{(j)} + \epsilon_0(\epsilon_{zz}^{\infty,(j)} - 1)E_z^{(j)}, \tag{7}$$

where the first term is the contribution of the spontaneous polarization in the layers $j$ and the last term, which is governed by the electronic dielectric constant $\epsilon_{zz}^{\infty,(j)}$ for fields parallel to the $c$ axis, represents the electronic screening polarization. The electric displacement field is then related to the polarization and electric fields by

$$D_z^{(j)} = \epsilon_0 E_z^{(j)} + P_z^{(j)}. \tag{8}$$

We can also express the components of the stress tensor in the layers $j$ as a function of the strains and electric fields:

$$\sigma_{xx}^{(j)} = (C_{11}^{(j)} + C_{12}^{(j)})\varepsilon_{xx}^{(j)} + C_{13}^{(j)}\varepsilon_{zz}^{(j)} - e_{31}^{(j)}E_z^{(j)}; \tag{9}$$

$$\sigma_{zz}^{(j)} = 2C_{13}^{(j)}\varepsilon_{xx}^{(j)} + C_{33}^{(j)}\varepsilon_{zz}^{(j)} - e_{33}^{(j)}E_z^{(j)}, \tag{10}$$

where the $C_{kl}^{(j)}$ are the elastic constants of material $j$. The first two terms in these expressions represent the usual elasticity relationships (Hooke's law), whereas the third term is included to take into account the piezoelectric and pyroelectric effects inside the SL. We note that the electric fields $E_z^{(j)}$ appearing in Eqs. (7)–(10) implicitly depend on the internal strain, since the $e_{kl}^{(j)}$ are used in Eqs. (9) and (10) and not the $e_{kl}^{(0)(j)}$.

For an infinite SL, the electrostatic boundary conditions yield

$$D_z^{(1)} = D_z^{(2)}, \tag{11}$$

and the periodicity of the SL is taken into account by writing[5]

$$E_z^{(1)}d_1 + E_z^{(2)}d_2 = 0, \tag{12}$$

where $d_j$ is the thickness of the layers $j$. If we consider the case of a biaxially strained SL, the mechanical boundary conditions read as

$$\sigma_{zz}^{(j)} = 0. \tag{13}$$

With the boundary conditions (11)–(13), we can express all quantities as functions of only two independent variables, which we choose to be the in-plane strains $\varepsilon_{xx}^{(j)}$. In addition, we assume that the in-plane lattice constant $a$ is the same for all layers in the SL. Thus, the in-plane strains of the layers $j$ will not be independent. This condition can be expressed as

$$\varepsilon_{xx}^{(2)} = (1+f)\varepsilon_{xx}^{(1)} + f, \tag{14}$$

where

$$f = \frac{a_0^{(1)} - a_0^{(2)}}{a_0^{(2)}} \tag{15}$$

is the lattice mismatch between AlN and GaN, and $a_0^{(j)}$ is the strain-free in-plane lattice constant of material $j$. We note that Eq. (14) is valid, whether we consider an infinite free-standing SL, or a pseudomorphically grown SL on a given substrate. The only difference is that in the former case, the SL in-plane lattice constant is derived from the minimization of the free energy of the whole SL, whereas in the latter case it is given by the substrate. Thus, using Eq. (14), we can express all quantities as functions of $\varepsilon_{xx}^{(1)}$.

Using Eqs. (13) and (9) and (10) we obtain a relationship between stress and strain including the piezoelectric and pyroelectric effects:

$$\sigma_{xx}^{(j)} = \left[C_{11}^{(j)} + C_{12}^{(j)} - 2\frac{e_{31}^{(j)}}{e_{33}^{(j)}}C_{13}^{(j)}\right]\varepsilon_{xx}^{(j)} + \left[C_{13}^{(j)} - \frac{e_{31}^{(j)}}{e_{33}^{(j)}}C_{33}^{(j)}\right]\varepsilon_{zz}^{(j)}. \tag{16}$$

The strain along the growth direction can also be expressed as a function of the in-plane strains for layers $j$, using Eqs. (11) and (12):

$$\varepsilon_{zz}^{(j)} = -2\frac{C_{13}^{(j)}}{C_{33}^{(j)}}\varepsilon_{xx}^{(j)} - (-1)^j\frac{e_{33}^{(j)}}{d_j C_{33}^{(j)}\Delta} \times [(P_{z,sp}^{(2)} - P_{z,sp}^{(1)}) - 2\Delta_1\varepsilon_{xx}^{(1)} + 2\Delta_2\varepsilon_{xx}^{(2)}], \tag{17}$$

with

$$\Delta = \sum_{j=1}^{2}\frac{1}{d_j}\left[\epsilon_0\epsilon_{zz}^{\infty,(j)} + \frac{e_{33}^{(j)2}}{C_{33}^{(j)}}\right] \tag{18}$$

and

$$\Delta_j = e_{31}^{(j)} - e_{33}^{(j)}\frac{C_{13}^{(j)}}{C_{33}^{(j)}}. \tag{19}$$

The first term in Eq. (17) is the usual elasticity relationship between in-plane strain and strain parallel to the growth axis in the case of biaxial strains. The other term contains a pyroelectric and a piezoelectric part. The pyroelectric contribution is governed by the difference of the spontaneous polarizations of both materials, and the piezoelectric term is influenced by the in-plane strains of both materials. These features are essentially caused by the presence of GaN/AlN interfaces in the heterostructure.

In this paper, we first turn our attention to the influence of the internal strain and pyroelectric effect on the strains in the SL layers. For the sake of simplicity, the GaN and AlN layers are supposed to have equal thicknesses, since the $d_j$ parameters do not appear in Eq. (17) in this case. Our calculations were performed using the elastic constants given by Wagner and Bechstedt[8] $C_{11}^{(1)} + C_{12}^{(1)} = 515$ GPa, $C_{13}^{(1)} = 104$ GPa, $C_{33}^{(1)} = 414$ GPa for GaN, and $C_{11}^{(2)} + C_{12}^{(2)} = 538$ GPa, $C_{13}^{(2)} = 113$ GPa, $C_{33}^{(2)} = 370$ GPa for AlN. All other parameters used in our calculations can be found in Ref. 1. In particular, the spontaneous polarizations are $-0.029$ C/m$^2$ for GaN, and $-0.081$ C/m$^2$ for AlN. The difference in the spontaneous polarizations between GaN and AlN is confirmed in a recent calculation using another method.[9] $\varepsilon_{zz}^{(1)}$ and $\varepsilon_{zz}^{(2)}$ are plotted versus $\varepsilon_{xx}^{(1)}$ in Fig. 1, for four different cases. First, we plotted these strains using only the elasticity theory (dotted lines) and using Eq. (17) (solid lines). The full inclusion of the piezoelectric and pyroelectric fields leads to a shift of $\varepsilon_{zz}^{(j)}$, which is about 0.2% for the GaN layers and about 0.4% for the AlN layers. We also note

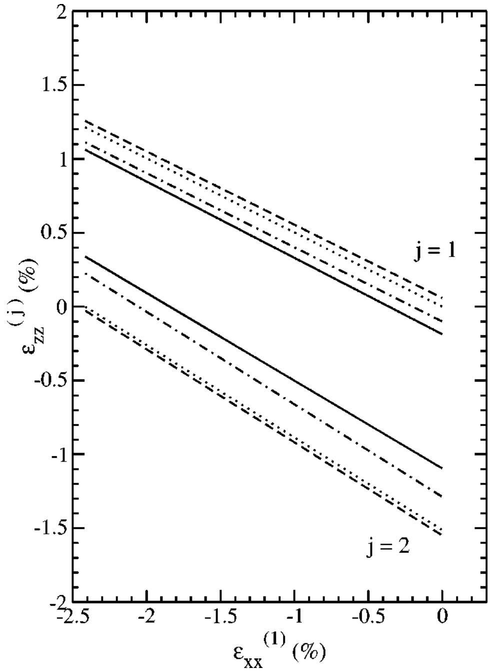

FIG. 1. Strain along the growth direction for GaN ($j=1$) and AlN ($j=2$) layers of an infinite wurtzite GaN/AlN SL for different in-plane strains, where only elasticity theory is used (dotted line), spontaneous and piezoelectric polarizations are fully included (solid line), internal strains are neglected (dashed line), and only spontaneous polarizations are included (dot-dashed line).

that in the case of totally relaxed GaN or AlN layers, as could be the case if a suitable buffer layer was inserted in the heterostructure, the permanent polarizations still induce a nonzero strain in the growth direction. Finally, we see that the global effect of these polarization fields is to reduce the values of the strains which would be expected from purely elastic considerations. We also showed in Fig. 1 the results obtained for vanishing internal strains (dashed lines). This was simply done by setting $u^{(j)}=0$ in Eqs. (2) and (3), i.e., by setting $e_{31}^{(j)}=e_{31}^{(0)(j)}$ and $e_{33}^{(j)}=e_{33}^{(0)(j)}$ in Eq. (17). It should be remembered that the strains so obtained cannot be related to real GaN / AlN SL's, but are used to emphasize the influence of the internal strains on $\varepsilon_{zz}^{(j)}$. We can see that this influence is very strong, as the strains obtained for vanishing $\Delta u^{(j)}$ are negligible, and even opposite to those obtained when the piezoelectric effect is fully taken into account. Finally, the part played by the spontaneous polarizations is investigated by plotting $\varepsilon_{zz}^{(j)}$ when the piezoelectric terms in Eq. (17) are set to zero (dashed-dotted lines). It is clear that spontaneous polarizations influence strongly the strains, as the change in strain due solely to this effect is, on the average, half the shift obtained when both spontaneous and piezoelectric polarizations are included. We also note that the shift is larger for the AlN layers, which is related to the larger piezoelectric moduli of AlN with respect to GaN.[1]

These changes in the $z$ component of the strain tensor also influence the zone center phonon frequencies of both materials, since the shift in frequency for a given phonon $\lambda$ ($\lambda=A_1$LO or TO, $E_1$LO or TO, $E_2$ high or low) can be expressed as

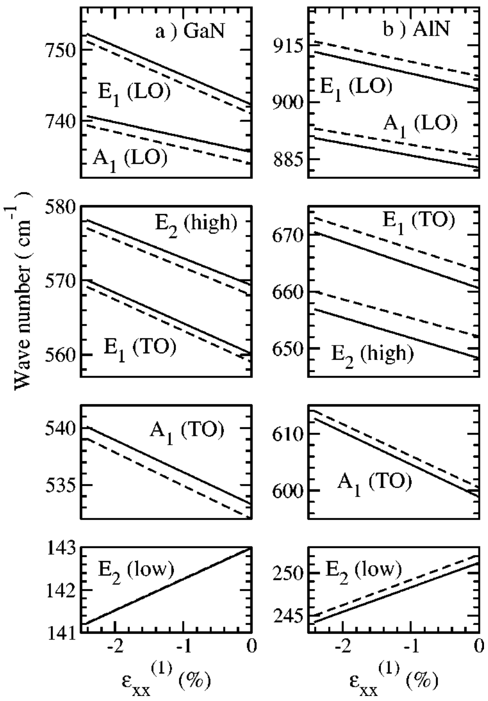

FIG. 2. Influence of the permanent polarization on the strain-induced shifts of the zone center phonon frequencies in a wurtzite GaN/AlN SL. The phonon frequencies are plotted for different in-plane strain values, for elasticity theory (dashed line), and for a theory including spontaneous and piezoelectric polarizations (solid line).

$$\Delta\omega_{\lambda}^{(j)}=2a_{\lambda}^{(j)}\varepsilon_{xx}^{(j)}+b_{\lambda}^{(j)}\varepsilon_{zz}^{(j)}, \tag{20}$$

where $a_{\lambda}^{(j)}$ and $b_{\lambda}^{(j)}$ are the corresponding phonon deformation potentials. Using the deformation potentials calculated by Wagner and Bechstedt,[8] we obtained the shifts for all GaN and AlN optical phonons for different strain values, as shown in Fig. 2. We have plotted the results obtained within the conventional elasticity theory, along with the ones we got by including the polarization effects. The global tendency we observe is a blueshift of the GaN phonon frequencies of about 1 cm$^{-1}$ and a redshift of the AlN phonon frequencies of about 2 cm$^{-1}$. This effect, although weak with respect to the strain-induced shifts observed by Raman scattering in a GaN/AlN SL,[10] seems likely to induce errors in the determination of strains in such a structure, using Raman-scattering measurements and neglecting the contribution of spontaneous and piezoelectric polarizations.

In summary, we have calculated the influence of the spontaneous and piezoelectric polarizations on the strains and phonon frequencies of a wurtzite GaN/AlN SL using a macroscopic theory. Our calculations predict a significant change in the strain tensor components along the growth direction, which is directly connected to the internal strain. The shift for the phonon frequencies of GaN and AlN, though weak, show that spontaneous polarization effects should not be neglected in Raman measurements used as a way of probing the strains inside a wurtzite GaN/AlN layered structure.

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