Non-linear macroscopic polarization in III-V nitride alloys

Fabio Bernardini and Vincenzo Fiorentini

Istituto Nazionale per la Fisica della Materia and Dipartimento di Fisica, Università di Cagliari, Cagliari, Italy

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We study the dependence of macroscopic polarization on composition and strain in wurtzite III-V nitride ternary alloys using ab initio density-functional techniques. The spontaneous polarization is characterized by a large bowing, strongly dependent on the alloy microscopic structure. The bowing is due to the different response of the bulk binaries to hydrostatic pressure, and to internal strain effects (bond alternation). Disorder effects are instead minor. Deviations from parabolicity (simple bowing) are of order 10% in the most extreme case of AlInN alloy, much less at all other compositions. Piezoelectric polarization is also strongly non-linear. At variance with the spontaneous component, this behavior is independent of microscopic alloy structure or disorder effects, and due entirely to the non-linear strain dependence of the bulk piezoelectric response. It is thus possible to predict the piezoelectric polarization for any alloy composition using the piezoelectricity of the parent binaries.

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I. INTRODUCTION

III-V nitrides and their alloys have recently emerged as a strategic materials system for the design and manufacture of high-frequency light emitting devices and high-power transistors. Recent theoretical investigations have suggested that the macroscopic polarization of wurtzite nitrides has a major influence on the design criteria of low-dimensional nanostructures aimed to address the technological goals mentioned above. Indeed, III-V nitrides in their wurtzite structure possess a large spontaneous polarization and larger-than-usual piezoelectric constants. As a consequence, fixed and approximately two-dimensional charges resulting from polarization discontinuities occur at nitride heterointerfaces, causing built-in electrostatic fields and/or free-charge accumulation, completely unusual in conventional III-V’s. By and large, these findings have been confirmed experimentally through the observation of optical shifts in quantum wells, and of high-density two-dimensional electron gases in field-effect transistor structures, and have been used as a guideline in the design and optimization of non-conventional high-frequency, high-breakdown voltage heterostructure field-effect transistors.

In nanostructure modeling or experiment interpretation, it was assumed so far that polarization in nitride alloys would interpolate linearly between the limiting values determined by the parent binary compounds i.e. follow a Vegard-like behavior. The structural properties generally follow Vegard’s law in many semiconductor alloys. On the other hand, electronic properties such as the optical band gap often depart from linear behavior: it is thus a plausible expectation that macroscopic polarization may also exhibit non-linearity. In this paper, we investigate the dependence of the macroscopic polarization on the composition and microscopic structure in AlGaN, InGaN and AlInN alloys, by means of ab initio density-functional techniques. Whereas the structural properties do follow Vegard’s law closely, we find a strong non-linear dependence of the polarization on alloy composition. The non-linearity of the spontaneous polarization depends appreciably on the microscopic structure of the alloy. By contrast, the non-linearity of the piezoelectric polarization is a pure bulk effect: Vegard’s law holds closely if the non-linear strain dependence of bulk piezoelectricity is accounted for.

II. ALLOY STRUCTURE

The calculation of the macroscopic polarization of an alloy requires the knowledge of its equilibrium structure. Nitride alloys are commonly thought to be characterized by a random distribution of the group-III elements on the wurtzite cation sites, while anion sites are always occupied by nitrogen. Recent experimental work (with support from theoretical investigations) has suggested that ordering takes place in some nitride alloys under suitable growth conditions. The ordering in question was reported to consist of 1 × 1 super-lattice structures oriented along the (0001) direction, with Al (or In) atomic planes alternating with Ga planes. Given these suggestions, a theoretical investigation of the alloy phase diagram would require the study of surface thermodynamics and kinetics as a function of the growth conditions. This is outside the scope of the present work. Here we accept as plausible that both random and ordered structures may be obtained depending on the growth conditions, and consider a sample of both structures in our polarization calculation. The ordered structure just mentioned bears evident similarities with the CuPt-like structure found in epitaxially ordered alloys of zincblende materials where the super-lattices are formed in the (111) direction; we therefore label this structure as CP. On the other hand, the microscopic structure of a random alloy can also be represented efficiently in periodic conditions using the
special quasi-random structure (SQS) method. Given its successes in the prediction of band gap non-linearity in zincblende-structure alloys, the SQS method is the natural choice to study polarization non-linearity in III-V nitride alloys. We enforce the periodic boundary conditions needed to compute the macroscopic polarization in the Berry phase approach by using repeated supercells, as done previously in Ref. 11 to study Born charges and IR spectra in amorphous SiO$_2$. As a compromise between computational workload and the accurate description of random structures, a 32-atom $2 \times 2 \times 2$ wurtzite supercell is adopted. In analogy to zincblende-based alloys, it is possible to reproduce the statistical properties (pair correlation functions, etc.) of a random wurtzite alloy for a molar fraction $x=0.5$ by suitably placing the cations on the 16 sites available in the cell, i.e. by a so-called SQS-16 structure. Even smaller structures such as SQS-8 were previously found to be adequate to mimic random zincblende-based alloys, so we are confident that our SQS-16 is a good model of the present random alloys. Since other molar fractions cannot be described as easily, and also because non-linear effects are expected to be largest for this concentration, our investigation on random alloys is restricted to the case $x=0.5$.

As a further ingredient, we consider ordered structures other than the CuPt mentioned earlier for each of the ternaries (AlGaN, InGaN, AlInN). The chalcopyrite-like structure (henceforth labeled CH) is defined by each anion site being surrounded by two cations of one species and two of the other, with the constraint of fitting periodically into our $(2 \times 2 \times 2)$ wurtzite supercell. This structure is highly symmetric, as there are only two kinds of inequivalent anion sites, differing in the orientation of the neighbors, and not in their chemical identity. Among the possible ordered structure, CH is in a sense the most homogeneous for the given composition. A further useful ordered structure we consider is luzonite-like structure, resembling the luzonite structure (henceforth labeled LZ), each nitrogen atoms is surrounded by three cations of one species, and one of the other: in a sense, this is the analog to the CH structure for molar fractions $x=0.25$ and 0.75.

The comparison between chalcopyrite-like and SQS “random” structures will give us insights on the effect of randomness versus ordering without the biases due to specific super-lattice ordering as in the CuPt structure. Luzonite-like structure will provide values of the polarization at intermediate molar fractions.

III. METHOD

As for the technical ingredients of the calculations, we work within the density-functional-theory pseudopotential plane-wave framework as implemented in the VASP code provided with VASP are used for all the elements involved; Ga and In $d$ semicore states are included in the valence. Since we are interested in the effects on polarization due to (among other) internal strains related to size mismatch of the two alloyed materials, it is imperative that our calculation reproduce relative mismatches with the highest possible accuracy. Comparing DFT calculations using both the LDA and GGA (in its PW91 variant) exchange-correlation functional, we found that GGA does a better job of reproducing the relative mismatch between the binary constituents, besides getting closer to the experimental structure. We therefore used the GGA for all the present calculations. We reported recently in some detail the properties of binary nitrides, including polarization, as calculated in the GGA vs LDA in Refs. 12 and 13.

Another precaution adopted throughout this work was to use the same 32-sites supercell for both binaries and alloys, the same k-points for reciprocal space integration (a $4 \times 4 \times 4$ Monkhorst-Pack mesh) and for the Berry phase calculations, and the same safe plane-wave cutoff of 325 eV, regardless of composition. Although more costly, this route reduces the systematic convergence errors. All forces and stress components have been converged to zero within 0.005 eV/Å and 0.01 Kbar, respectively, for free-standing alloys. For GaN-epitaxial alloys (Sec. V), only the $zz$ stress component has been zeroed. The polarization of the binary compounds as obtained in the supercell calculations is always within less than 0.001 C/m$^2$ of the value obtained in a bulk calculation using a $12 \times 12 \times 12$ k-points mesh.

IV. SPONTANEOUS POLARIZATION

We start our analysis comparing the values of the lattice constants and spontaneous polarization computed for the free standing alloys, with the predictions of Vegard’s law. The latter relates the lattice constants $a$ and $c$, and the spontaneous polarization $P_{sp}$ of an alloy $A_xB_{1-x}N$, to their values for the binary constituent AN and BN (A and B indicate two generic cations among In, Al, and Ga) by

$$a(A_xB_{1-x}N) = x a(AN) + (1 - x) a(BN), \quad (1)$$

$$c(A_xB_{1-x}N) = x c(AN) + (1 - x) c(BN), \quad (2)$$

and

$$P_{sp}(A_xB_{1-x}N) = x P_{sp}(AN) + (1 - x) P_{sp}(BN). \quad (3)$$

The existence of compositional non-linearities (i.e. non-Vegard behavior) in a generic measurable quantity in an alloy can be described in a first approximation by a parabolic model involving a so-called bowing parameter. In particular, we expect to be able to describe the possible non-linear dependence of the spontaneous polarization on the composition as
\[ P(A_xB_{1-x}N) = x P(AN) + (1 - x) P(BN) - b_{AB} x (1 - x), \]  
(4)

where the bowing parameter is by definition as

\[ b_{AB} = 2P(AN) + 2P(BN) - 4P(A_{0.50}B_{0.50}N) \]  
(5)

involving only the knowledge of the polarization for ternary alloys with molar fraction \( x = 0.5 \). Given the bowing parameter, the spontaneous polarization can be obtained at any composition.

### A. Polarization non-linearity

In Fig. 1, we compare with Vegard-law predictions our calculated equilibrium lattice parameters \( a \) and \( c \) for all the alloy structures and compositions studied. Both \( a \) and \( c \) follow quite closely Vegard’s law in all cases. The dependence of the polarization on composition is then the same as that on the lattice parameter(s), modulo a multiplicative factor. Therefore, in Figs. 2 and 3 we can compare with Vegard-law predictions the calculated data, respectively, for the random and Cu-Pt-ordered (Fig. 2), and chalcopyrite- or luzonite-like ordered (Fig. 3) alloys, displayed in the \( (P, a) \) plane. The ordinates of the filled symbols are the calculated spontaneous polarization, the abscissas are the calculated lattice constants; the open symbols and dashed lines are the Vegard-law predictions; the solid lines are fits of Eq. 4 to the calculated values.

We identify two main points. First, there is a large non-linear dependence of the spontaneous polarization on the lattice parameter, hence on alloy composition. Alloys with large lattice mismatch between the constituents (e.g., AlInN and InGaN) show the largest bowing, while in AlGaN the non-linearity is modest, although sizable. Regardless of the alloy structure and composition, the spontaneous polarization shows always an upward bowing. Second, CP-ordered (Fig. 2) and CH-ordered (Fig. 3) alloys have very different bowing. This is at variance to the case of the band gap: ordering is known to cause an increase of the band gap bowing, but more homogeneous across different ordered structures, and never as dramatic as that of polarization in the CP ordered alloy.

![Fig. 1. Basal (a) and axial (c) lattice constants of wurtzite-based nitride alloys. Directly calculated values for various alloy structures are denoted by open circles (random), squares (CH and LZ), triangles (CP). The dashed lines are Vegard’s law.](image1.png)

![Fig. 2. Spontaneous polarization versus equilibrium lattice constant in free-standing random and CuPt-ordered nitride alloys (filled symbols). Solid lines are interpolations according to Eq. 4. Dashed lines and open symbols are Vegard predictions.](image2.png)
(Eq. 19), the non-parabolicity causes relatively modest additional deviations (of order 10 %) for AlInN. A legitimate conclusion is then that the bowing relation should predict polarization in AlInN with about 10 % accuracy, and much better for InGaN and AlGaN.

It is clear that these result have a considerable technological relevance for nanostructure devices. Polarization differences across interfaces in, say, multi-quantum-wells, generate localized interface charges which in turn cause electrostatic fields and/or charge accumulation at the interfaces. The non-linearity just reported modifies considerably the polarization-induced interface charge densities, and must be accounted for in any attempt at quantitative comparisons with, or predictions on experiments. We will be considering this aspect in detail in forthcoming work. In the following Sec. IV B we attempt instead to gain insight on the nature of the non-linear behavior of the polarization in III-V nitrides.

B. Microscopic origin of polarization non-linearity

It is known from earlier theoretical work on III-V zincblende-based alloys that band gap non-linearities can be attributed to essentially three sources: i) chemical effects due to the different cation electronegativity of the components; ii) internal strain effects, due to varying cation-anion bond lengths (the so-called bond alternation); iii) disorder effects due to the random distribution of the chemical elements on the cation sites. Chemical effects and internal strain are dominant, whereas disorder gives only a modest contribution. On the basis of these indications, one expects a large bowing in random alloys whose constituents have a large lattice mismatch. Such a behavior for the fundamental gap bowing was indeed found for zincblende III-V nitrides alloys. Also, the bowing in ordered structures should be similar to, but larger than in random structures.

For the polarization, we only find a qualitative behavior similar to the band gap bowing in the case of random alloys, while the ordered phases CH and CP do not seem to show identifiable trends. It is especially surprising that i) the random and CP phases of AlGaN have nearly the same bowing; ii) the InGaN CH ordered alloy shows a smaller bowing than its random phase. The reason for this anomalous behavior must be found in the peculiar nature of the polarization bowing. While the band gap is a scalar, the polarization is a vector of fixed direction, namely, for wurtzites, the (0001) direction. Thus, bond alternation will affect the polarization bowing only if it changes the projection of the bond length in the (0001) direction. This idea is supported by the fact that in pure binaries the polarization is strongly influenced by the relative displacement of the cation and anion sub-lattices in the (0001) direction.

Indeed, we find that a clear correlation exists between the so-called $u$ parameter of the wurtzite structure, i.e. the bond length along the singular polar (or pyroelectric) axis, and the value of the polarization. In Fig. 4 we show the calculated spontaneous polarization of free-standing binaries and $x=0.5$-alloys in the various structures, vs. the average internal parameter $u$. The latter is defined as the average value of the projection of the connecting vector of a nitrogen atom with its first neighbor in the (0001) direction along this same direction. This definition can be used also for random phase alloys in spite of the displacements off the ideal sites. We see in Fig. 4 that for a given alloy composition, the spontaneous polarization of free-standing alloys of different microscopic structure depends linearly on the average $u$ parameter of the alloy structure. This indicates that spontaneous polarization differences between alloys of the same composition are due essentially to structural and bond alternation effects; disorder appears to have a negligible influence. It appear instead that the chemical identity of the constituents plays a role of some importance (beyond the obvious fact that it implicitly determines the structure).

The points mentioned above are now easily explained. The random and CP phases in AlGaN have almost the same average $u$, hence almost the same polarization. In InGaN, the random alloy has a larger $u$ than the CH phase, while the opposite holds for AlInN and AlGaN; therefore the CH-vs-random bowing behavior in InGaN is opposite with respect to the others. Also, the huge bowing of CP-ordered AlInN and InGaN matches the very large deviation of the average $u$ in those phases from the random and CH-like structures. If structure were the only source of polarization bowing, all of the points in Fig. 4 would fall on the same straight line.
To check this role, we set up a model based on the polarization of binaries and alloys in a constrained ideal wurtzite structure. In this structure, only the $a$ parameter is independent, whereas $c$ and $u$ are fixed at the values determined by maximal sphere packing, namely $u=0.375$ and $c/u=\sqrt{8}/3$. Each nitrogen atom is then surrounded by four equidistant cations – that is, all bonds have the same length for a given lattice parameter $a$. By construction, then, bond alternation do not play any role, and the effects of chemical identity of the constituents can be easily disentangled.

We assume that Vegard’s law holds for the lattice constant $a$, as was found to be the case for the alloys in the preceding Subsection. This establishes a (linear) relation between composition and lattice constant. We then calculate the polarization in each of the binary nitrides in their ideal structure as function of the lattice constant $a(x)$. Finally, we express the alloy polarization as a composition-weighted Vegard-like average of the polarizations of the binaries as

$$P_{sp}(A_xB_{1-x}N) = xP_{sp}^0(AN) + (1-x)P_{sp}^0(BN).$$

In this model, any non-linearity must come from the different response of polarization to changes in $a(x)$, hence to hydrostatic compression, in the ideal binary compounds.

We report in Fig. 4 three sets of quantities: the polarizations computed in the ideal wurtzite structure for the three ternary alloys at their calculated equilibrium volume (filled circles); the polarization of the binaries in the ideal structure as a function of the lattice parameter $a$ (open symbols); the Vegard interpolation Eq. 5 of the latter polarizations (the bowed shaded triangle) for the alloys. We see that the computed values for the alloys and the Vegard prediction essentially coincide. Therefore, the origin of the “chemical” non-linearity, and its large values in In-containing alloys, becomes clear: in AlN and GaN, the polarization decreases with hydrostatic pressure, while it increases in InN. Also to be noted, polarizations in the ideal structure are between 35 to 50 % of their value in free standing alloys, and despite the absence of bond alternation, the bowing is still very large.

The above model provides an expression of the bowing parameter of ideal wurtzite structure alloys as function of the polarization response to hydrostatic pressure:

$$b_{AB}^{\text{model}} = (a_{BN} - a_{AN}) \left( \frac{\partial P_{BN}}{\partial a} - \frac{\partial P_{AN}}{\partial a} \right) |_{a=a(1/2)} + \frac{1}{4}(a_{BN} - a_{AN})^2 \left( \frac{\partial^2 P_{AN}}{\partial a^2} + \frac{\partial^2 P_{BN}}{\partial a^2} \right) |_{a=a(1/2)}.$$  

The agreement of the latter expression with the $b$ resulting from a fit to the calculated values is very good (e.g. for the extreme case of AlInN, $b_{model}=-0.0225$ C/m$^2$, while from direct calculation we get $-0.0208$ C/m$^2$). On the basis of the model, it is now understandable that the AlGaN bowing is pretty moderate since the region of interest is small (3.1 Å to 3.2 Å) and the responses to hydrostatic pressure of AlN and GaN are similar. On the contrary, in the large range 3.1–3.6 Å, AlN and InN have opposite behaviors, whence the huge bowing found in AlInN alloys. The same goes, although to a lesser extent, for InGaN alloys.

V. PIEZOELECTRIC POLARIZATION

The knowledge of the spontaneous polarization in alloys is not sufficient to predict the values of interface
charge accumulations or electrostatic fields in wurtzite-nitride–based nanostructures, because the latter are usually grown pseudomorphically and under strain on the (0001) or (0001) faces of a substrate (typically sapphire or SiC, with or without AlN or GaN buffer layers). The ensuing symmetry-conserving strain causes a change in polarization that amounts to a piezoelectric polarization. In general, the polarization in the active layers of a nanostructure is a combination of spontaneous and piezoelectric polarization. In this context, the aim of this Section is threefold. First, we demonstrate that piezoelectricity in nitride alloys is non-linear; second, we show that this non-linearity is due to a pure bulk effect, i.e. the non-linear behavior of bulk binary piezoelectric constants vs symmetry-conserving strain; third, we suggest how to use this understanding in practice to predict piezoelectricity in any nitride alloy.

We consider for definiteness (but with no loss of generality as to the scheme to predict piezoelectricity in arbitrary alloys) the technologically relevant case of an alloy pseudomorphically grown on an unstrained GaN substrate. Using the same technical ingredients as previously, we repeat the polarization calculations with the constraint that \( a_{\text{alloy}} = a_{\text{GaN}} \), fully reoptimizing all structures. We compute the piezoelectric polarization as the difference between the total polarization obtained in this calculation and the spontaneous part calculated previously for the free-standing alloy.

In Fig. 6 we show the piezoelectric polarization as a function of the alloy composition. Symbols are the calculated polarizations in the various alloy structures and compositions; it is clear that, contrary to spontaneous part, the piezoelectric polarization component hardly depends on the microscopic structure of the alloy. We now ask whether the piezoelectric polarization of the alloy can be reproduced by a Vegard-like model containing only the knowledge of the properties of the binaries, i.e.

\[
P_{\text{pz}}^{\text{ABN}}(x) = x P_{\text{pz}}^{\text{AN}} + (1 - x) P_{\text{pz}}^{\text{BN}}.
\]

In a first approximation, one may calculate the piezoelectric polarization of the binary compounds for symmetry-conserving in-plane and axial strains as

\[
P_{\text{pz}}^{\text{AN}} = e_{33} \epsilon_3 + 2 e_{33} \epsilon_1,
\]

where the piezoelectric constants \( e \) are calculated in the equilibrium structure of the binary \( \text{AN} \), and by definition do not depend on strain. The dashed lines in Fig. 6 represent the piezoelectric term as computed from the above relations using the piezoelectric constants computed for the binaries. Clearly, when combined with Eq. 8, Vegard’s law (Eq. 8) fails to reproduce the calculated polarization, and misses the strong non-linearity of the piezoelectric term evident in Fig. 6.

This is due to a genuine non-linearity of the bulk piezoelectricity of the binary constituents, of non-structural origin; hence, the bowing due to the microscopic structure of the alloys is negligible. The proof of this statement is in two steps. First, we directly calculate the piezoelectric polarization as a function of basal strain for \( \text{AlN} \), \( \text{GaN} \), and \( \text{InN} \), optimizing all structural parameters. The results, collected in Fig. 7, clearly show that the piezoelectric polarization of the binaries is an appreciably non-linear function of \( a \), i.e. of basal strain. Since all lattice parameters closely follow Vegard’s law, the non-linearity cannot be related to deviations from linearity in the structure.
Second, we plug the non-linear piezoelectric polarization just computed for the binaries into the Vegard interpolation Eq. 6. We obtain thereby the solid lines in Fig. 6, we see that the predictions of this scheme are in excellent agreement with the polarization calculated directly for the alloys. Therefore, we can conclude that a) the non-linearity in bulk piezoelectricity dominates over any effects related to disorder, structure, bond alternation, etc., and that b) Vegard’s law holds for the piezoelectric polarization of III-V nitrides alloys, provided that the non-linearity of the bulk piezoelectric of the constituents is accounted for.

The latter conclusion suggests a straightforward scheme for predicting the piezoelectric polarization of any nitride alloy at any strain: pick a value for \( x \), calculate the basal strain \( \varepsilon(x) \) from Vegard’s law, calculate \( P_{pa} \) from Eq. 8 using the non-linear piezoelectric polarization of the binaries (Fig. 1). This scheme is of obvious interest in the modeling of nanostructures, especially for high In contents and AlInN alloys.

VI. SUMMARY AND ACKNOWLEDGEMENTS

In this paper, we studied the non-linear dependence of the polarization on composition and strain in ternary III-V nitride wurtzite-based alloys. The spontaneous polarization is characterized by a large bowing, strongly dependent on the alloy microscopic structure. The bowing is due to the different response of the bulk binaries to hydrostatic pressure, and to internal strain effects due to bond alternation. Disorder effects are minor. Deviations from parabolicity (simple bowing) are of order 10 % in the most extreme case (the AlInN alloy), much less for all other compositions.

Piezoelectric polarization is also strongly non-linear. This behavior is independent of microscopic structure or disorder effects (the structural parameters for all alloys closely follow Vegard’s law and linear elasticity), and is due entirely to the non-linear strain dependence of the bulk piezoelectric response. Based on our understanding of this behavior, we suggested that it is possible to predict the (non-linear) piezoelectric polarization for any alloy composition using the knowledge of the binary compound piezoelectricity.

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19. We adopt for the wurtzite structure the convention according to which each anion sits at (0,0,u) from the cations, i.e. all the vertical bonds between, say, Ga and N point along (0001).