Piezoelectric coefficients and spontaneous polarization of ScAlN

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We present a computational study of spontaneous polarization and piezoelectricity in Sc$_x$Al$_{1-x}$N alloys in the compositional range from $x = 0$ to $x = 0.5$, obtained in the context of density functional theory and the Berry-phase theory of electric polarization using large periodic supercells. We report composition-dependent values of piezoelectric coefficients $e_{ij}$, piezoelectric moduli $d_{ij}$ and elastic constants $C_{ij}$. The theoretical findings are complemented with experimental measurement of $e_{33}$ for a series of sputtered ScAlN films carried out with a piezoelectric resonator. The rapid increase with Sc content of the piezoelectric response reported in previous studies is confirmed for the available data. A detailed description of the full methodology required to calculate the piezoelectric properties of ScAlN, with application to other complex alloys, is presented. In particular, we find that the large amount of internal strain present in ScAlN and its intricate relation with electric polarization make configurational sampling and the use of large supercells at different compositions necessary in order to accurately derive the piezoelectric response of the material.

I. INTRODUCTION

ScAlN is an emerging semiconductor material with potential applications in optics and electronics due to its unique properties. It can be integrated with conventional group-III nitrides, which are extremely important materials in the context of the lighting industry and other emerging applications,1,2 in order to improve device performance.3,4 In addition, AlN is CMOS-compatible and elements based on ScAlN could potentially be used in integrated circuits. The rapid enhancement of the piezoelectric (PZ) response of ScAlN compared to bulk AlN as the Sc fraction increases, together with its high Curie temperature, makes it interesting for use in PZ devices.5 Since the first experimental evidence of this enhanced PZ behavior by Akiyama et al. in 2009,5 a number of experimental6–8 and theoretical7,9 studies have confirmed this result, and the research in ScAlN for PZ applications has gathered pace.

Reliable material parameters are critical in device modeling and characterization. However, the accurate experimental determination of PZ constants of ScAlN is hindered by several factors, in particular the ability to grow high-quality single-phase films using sputtering techniques.10 Also, a full set of PZ coefficients $e_{ij}$ and PZ moduli $d_{ij}$ for ScAlN is somewhat lacking from the literature. In the case of spontaneous polarization, experimental measurement is simply too challenging.

In the present paper we present a consistent set of composition-dependent PZ parameters for Sc$_x$Al$_{1-x}$N in the range from $x = 0$ to $x = 0.5$ derived from density functional theory11,12 (DFT) calculations using large periodic supercells and the Berry-phase theory of polarization.13,14 We report PZ coefficients $e_{15}(x)$, $e_{31}(x)$ and $e_{33}(x)$, PZ moduli $d_{15}(x)$, $d_{31}(x)$ and $d_{33}(x)$, and spontaneous polarization $P_{SP}(x)$. We compare these values to experimental and theoretical data available from the literature and add an own set of experimental values of $e_{33}$ obtained with a bulk acoustic wave (BAW) resonator setup and sputtered ScAlN films. In addition, we provide a full set of composition-dependent elastic constants $C_{11}(x)$, $C_{12}(x)$, $C_{13}(x)$, $C_{33}(x)$ and $C_{44}(x)$ fully consistent with our methodology for PZ coefficients. We thoroughly discuss the complete theoretical methodology employed, its shortcomings and challenges. This detailed description can now guide the calculation of PZ properties of other complex piezoelectric alloys.

The paper is structured as follows. Sec. II describes the whole simulation procedure: Sec. II A deals with the choice of supercell, and is complemented by the Appendix; Sec. II B introduces the calculation details, including some practicalities related to the Berry-phase formalism; Sec. II C relates the procedure needed to retrieve the hexagonal PZ tensor from the triclinic supercell calculations; Sec. II D gives the spontaneous polarization results and details the strategy needed to compute it; Sec. II E contains the main results of the paper, the composition-dependent expressions for the PZ coefficients of ScAlN; Sec. II F deals with the transformation between PZ coefficients $e_{ij}$ and PZ moduli $d_{ij}$ and gives composition-dependent expressions for $d_{ij}$ and the elastic constants $C_{ij}$. In Sec. III we explain the experimental procedure carried out to determine the values of $e_{33}$ for a series of ScAlN films. Finally, in Sec. IV we discuss our
results and present our conclusions.

II. SIMULATION

There are several practical complications associated with the calculation of PZ constants and spontaneous polarization of crystalline solids. The formal theoretical framework to carry out this kind of calculation, in particular (but not limited to) in the context of ab initio methods, is known as the modern—or Berry-phase—theory of polarization, and was not developed until the early 1990s. A good account of this technique is available in the seminal papers by Vanderbilt and King-Smith,13,14 the early review by Resta15 and, more pedagogically, in a recent book chapter by Resta and Vanderbilt.16 The Berry-phase approach has been successfully employed to calculate polarization values in technologically important materials, notably “traditional” nitrides (GaN, InN and AlN).17 More recently, also studies of ScAlN have relied on this technique to calculate the $e_{33}$ PZ coefficient.9 The scope of the present work poses, however, additional difficulties owing to the huge internal strain present in ScAlN, which makes its structure largely deviate from a true wurtzite crystal. Calculation of spontaneous polarization and all of the PZ constants of ScAlN through the whole compositional regime requires a very careful study of configurational (alloy) effects on the results. In this section we describe this process in detail. Section II A deals with the finite supercell representation of the macroscopic alloy. In Sec. II B we provide the numerical details of the DFT and Berry-phase calculations. We discuss the implications of using triclinic supercells and how to deal with them in Sec. II C. Finally, Secs. II D, II E and II F present the computational results and discussion of spontaneous polarization, PZ coefficients and PZ moduli, respectively.

A. Supercell choice: random and quasirandom structures

In this study, the representation of realistic ScAlN alloys is carried out using periodic supercells containing 128 atoms, 64 cations (Sc or Al) and 64 N atoms, in a construction of $4 \times 4 \times 2$ wurtzite primitive unit cells (each containing 4 atoms). The different compositional regimes are achieved by replacing the corresponding number of Al atoms by Sc atoms in the cation sublattice. Although the supercells used are considerably large, the effect of configurational disorder is observed to affect the results, as will be shown later on. We therefore study different ways to obtain the macroscopically-averaged values of spontaneous polarization and piezoelectric tensor through the use of random and quasirandom supercells. To ensure that finite-size effects related to periodicity are minimized, randomly populated supercells are observed to be required. We also explore the degree of applicability of the special quasirandom structure (SQS) approach, which consists in placing the different atoms in optimal lattice sites such that the pair-correlation function (or other properties) of the periodic system resembles that of a random alloy as closely as possible.18 Different optimizations methods for SQS cells have been studied, using two series of SQSs: those used by Zhang et al.19 in previous work, that we refer to by “SQS#1”, and a new series “SQS#2” at 12.5%, 25%, 37.5% and 50% Sc content, which were further optimized to yield zero pair-correlation coefficients up to bigger pair distances for the supercell size employed (128 atoms). We observe that SQSs are not as well suited for the representation of average piezoelectric properties of ScAlN alloys as they are for other properties, for instance elasticity. This trend suggests a strong fluctuation of the local piezoelectric properties of ScAlN at the microscopic scale, in line with (but stronger than) the local effects predicted for the related nitride alloy InGaN.20 A more detailed analysis, presented in the Appendix, reveals that there appears to be no obvious correlation between supercell “randomness” (in the sense of calculated pair-correlation coefficients) and closeness of the supercell’s piezoelectric coefficients to the configurational average.

B. Calculation details

Structural properties (lattice vectors and atomic positions) and self-consistent wave functions for the chosen ScAlN supercells are obtained within the framework of density functional theory (DFT)11,12 as implemented in the VASP package21–23 in the context of the projector augmented wave (PAW) method.24 Together with the three outermost valence electrons of Sc (4s23d), the semicore 3s and 3p electronic states were also explicitly included as valence states. For the exchange-correlation part of the total energy, the gradient-corrected functional of Perdew, Burke and Ernzerhof (PBE)25 was used. The k-point sampling in the first Brillouin zone is done using a $2 \times 2 \times 2$ Monkhorst-Pack grid centered at $\Gamma$. The plane wave cutoff was set to 600 eV. Such a high cutoff is needed in order to correctly describe internal strain in wurtzite nitrides,26–28 which has a large impact on piezoelectric and spontaneous polarization.20 The calculation of the electric polarization was carried out following the directives of the modern (or Berry-phase) theory of polarization,13–15 using Martijn Marsman’s implementation of this method as available in VASP.

To calculate the electric polarization a reference state of well-defined polarization is needed.16 In the case of wurtzite materials, a straight-forward reference is the closely-related centrosymmetric (unstrained) zinc blende (ZB) lattice. In the case of the in-plane components of the polarization vector the unstrained WZ configuration can also be used: the polarization components vanish by symmetry along the c plane in unstrained wurtzite. Fig. 1 depicts the workflow that leads to the calculation
of the PZ tensor through the different steps involved: i) the ZB structure allows to establish a zero-polarization reference; ii) the ideal WZ structure serves in order to obtain the offset corrections to electronic and ionic polarizations (see next paragraph); iii) the evolution of the polarization from ideal WZ to the WZ-like relaxed structures gives the value of the spontaneous polarization; iv) the variation of the polarization upon small deformations of the relaxed structures enables the calculation of the piezoelectric tensor. In practice (the present case with hexagonal supercells, for instance), the ideal WZ supercell might sometimes lead to straight-forward polarization offsets and the first step (ZB calculation) may be skipped under those circumstances. Note that although ScAlN alloys are macroscopically hexagonal, a finite-size supercell will in general be triclinic, with lattice vectors similar, but not equal, to those of the hexagonal supercell, as shown in Fig. 1.

A complication associated to the Berry-phase approach stems from the choice of origin and the existence of the quantum of polarization when computing the electronic contribution to the electric polarization. The issue with the choice of origin is also present when computing the ionic part of the polarization. These lead to offsets in the polarization values calculated directly, that must be subtracted before the physically-meaningful result can be obtained. However, if the origin to compute the polarization vector is chosen carefully, one can obtain simple expressions for the polarization offset as fractional multiples of the lattice vectors. Given the lattice vectors of the ideal WZ supercells employed in this work:

\[
\begin{align*}
\mathbf{a} &= (a_0, 0, 0), \\
\mathbf{b} &= 4 \left( -\frac{a_0}{2}, \frac{\sqrt{3} a_0}{2}, 0 \right), \\
\mathbf{c} &= (0, 0, c_0),
\end{align*}
\]

when the origin for computing the supercell’s dipole moment is taken at \((0, 0, 0)\), in the specific case of a pure Al\(_{64}\)N\(_{64}\) supercell, the calculation leads to the following offsets for the electronic and ionic parts of the dipole moment vector:

\[
\begin{align*}
P^\mathrm{ele}_0 &= \frac{2e}{3}a - \frac{2e}{3}b + ec, \\
P^\mathrm{ion}_0 &= \frac{640e}{3}a + \frac{704e}{3}b + 252ec,
\end{align*}
\]

where \(e\) is the elementary charge. The strain dependence of the lattice vectors is inherited by the dipole moment and it must be taken into account when correcting the polarization results. Different (although similar) offsets are obtained for the ScAlN supercells because of having considered 11 valence electrons for Sc (including 8 semicore electrons). Otherwise, having considered only 3 valence electrons for Sc, the offsets would be identical.

C. Symmetry considerations

The use of supercells in theoretical calculations of alloyed compounds imposes a number of drawbacks. The most immediate consequence is that macroscopic properties of a material which lacks full periodicity (e.g. any disordered alloy) cannot be reproduced exactly with finite-size periodic structures. To minimize this problem one must rely, on the one hand, on supercells which are as large as computationally affordable and, on the other hand, configurational sampling of different supercells with the same composition. This combined strategy allows to both better represent the different microscopic configurations found in the macroscopic alloy and to remove the effect of spurious periodicity effects introduced by the supercell’s geometry. In the case of ScAlN alloys, the large amount of internal strain does indeed lead to important deviations from hexagonal symmetry for relaxed supercells. This is even true for supercells containing as many as 128 atoms, as is presently the case.

Therefore, one is left dealing with supercells that have in general triclinic symmetry, i.e. no symmetry at all, and correspondingly complicated triclinic material tensors. In the case of the piezoelectric tensor, this means dealing with 18 independent piezoelectric coefficients \(e_{ij}\) rather than the three independent WZ coefficients \(e_{15}\), \(e_{31}\) and \(e_{33}\). The implications might be better understood when these tensors are written down side by side...
in matrix representation. The supercell’s PZ tensor has the form:

\[
e^{\text{tric}} = \begin{pmatrix}
e_{11} & e_{12} & e_{13} & e_{14} & e_{15} & e_{16} \\
e_{21} & e_{22} & e_{23} & e_{24} & e_{25} & e_{26} \\
e_{31} & e_{32} & e_{33} & e_{34} & e_{35} & e_{36}
\end{pmatrix},
\]

(3)

while the macroscopic alloy’s PZ tensor has the form: \(e^{\text{hex}}\):

\[
e^{\text{hex}} = \begin{pmatrix}0 & 0 & 0 & 0 & e_{15} & 0 \\
0 & 0 & 0 & e_{15} & 0 & 0 \\
e_{31} & e_{31} & e_{33} & 0 & 0 & 0
\end{pmatrix}.
\]

(4)

Similarly, the corresponding supercell’s SP polarization will not be directed exactly parallel to the hexagonal [0001] direction (or \(c\) axis). Instead, it will point along some direction close to the triclinic [001], since the triclinic cell was obtained as a modification of an input hexagonal one (Fig. 1).

In order to retrieve the macroscopic material tensor from the supercell results, one can resort to the method proposed by Moakher and Norris,\(^{32}\) whereby auxiliary projectors \(P_{\text{sym}}\) are used to “project” low symmetry tensors (triclinic in the present case) onto a higher symmetry tensor (hexagonal here) such that the Euclidean distance between the two tensors is minimized. In this context, one can obtain the “closest” hexagonal tensor to the original triclinic one. Moakher and Norris presented their method for analysis of elastic tensors (rank 4), which has already been used by Zhang \emph{et al.},\(^{33}\) to study elastic constants of ScAlN. It can however also be used to study lower (or higher) rank tensors, such as the PZ tensor (which has rank 3), provided that the appropriate projector is available. We have obtained this projector following Moakher and Norris’s recipe.\(^{32}\) One starts by expressing the PZ tensor as an 18-dimensional vector, with corresponding normalizing coefficients to preserve the Euclidean norm:

\[
e^{\text{tric}} \equiv (e_{11}, e_{12}, e_{13}, \sqrt{2}e_{14}, \sqrt{2}e_{15}, \sqrt{2}e_{16}, e_{21}, e_{22}, e_{23}, \sqrt{2}e_{24}, \sqrt{2}e_{25}, \sqrt{2}e_{26}, e_{31}, e_{32}, e_{33}, \sqrt{2}e_{34}, \sqrt{2}e_{35}, \sqrt{2}e_{36}).
\]

(5)

The hexagonal version of Eq. (5) would then be

\[
e^{\text{hex}} \equiv (0, 0, 0, 0, \sqrt{2}e_{15}, 0, 0, 0, 0, \sqrt{2}e_{15}, 0, 0, e_{31}, e_{31}, e_{33}, 0, 0, 0),
\]

(6)

which can be expanded in the basis \(\{\psi_i^{\text{hex}}\}\), that has the following three components:

\[
\psi_1^{\text{hex}} = \frac{1}{\sqrt{2}} (0, 0, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0),
\]

\[
\psi_2^{\text{hex}} = \frac{1}{\sqrt{2}} (0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 0, 0, 0, 0),
\]

\[
\psi_3^{\text{hex}} = (0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 0, 0, 0).
\]

(7)

Following Moakher and Norris,\(^{32}\) \(P^{\text{hex}}\) for the PZ tensor is then:

\[
P^{\text{hex}} = \sum_{i,j} (D^{-1})_{ij} \psi_i^{\text{hex}} \times \psi_j^{\text{hex}},
\]

(8)

with \((D)_{ij} = \langle \psi_i^{\text{hex}}, \psi_j^{\text{hex}} \rangle\) being the elements of matrix \(D\), and where \(\langle \cdot, \cdot \rangle\) denotes the Euclidean inner product and \(\times\) the outer product. \(N\) is the size of the basis, \(N = 3\) in this case. The result is a sparse matrix of dimension 18 × 18:

\[
P^{\text{hex}} = \begin{pmatrix}
0_{18 \times 4} & \cdots & 0_{18 \times 4} & 0_{8 \times 10} \\
\vdots & \ddots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
0_{10 \times 8} & \cdots & 0_{3 \times 3}
\end{pmatrix}
\]

(9)

The hexagonal projection of \(e^{\text{tric}}\) is then

\[
P^{\text{hex}} e^{\text{tric}} = \left(0, 0, 0, 0, \frac{e_{15} + e_{24}}{\sqrt{2}}, 0, 0, 0, 0, \frac{e_{15} + e_{24}}{\sqrt{2}}, 0, 0, \frac{e_{31} + e_{32}}{2}, \frac{e_{31} + e_{32}}{2}, e_{33}, 0, 0, 0\right).
\]

(10)

Note that in general, due to the arbitrariness of choosing a specific set of Cartesian axes as reference frame for the triclinic cell, the rotational degrees of freedom also need to be taken into account when optimizing the projection. This means that a general rotation of the triclinic PZ tensor around the coordinate Cartesian axes (denoted by \(R(\theta_x, \theta_y, \theta_z)\)) needs to be performed before minimizing the Euclidean distance between \(e^{\text{tric}}\) and its hexagonal projection. The numerical optimization problem is then

\[
\frac{\partial}{\partial \theta_i} \| R(\theta_x, \theta_y, \theta_z) e^{\text{tric}} - P^{\text{hex}} R(\theta_x, \theta_y, \theta_z) e^{\text{tric}} \|^2 = 0.
\]

(11)

The reader is referred to Ref. 34 for further details.

In the case of the spontaneous polarization, it is straightforward to see that the optimized hexagonal projection of the SP polarization vector after rotating the triclinic value is simply minus its norm.\(^{35}\)

**D. Results: spontaneous polarization**

The calculation of the spontaneous (SP) polarization is done, as outlined in Sec. II B, by studying the evolution
of the polarization vector as the structure is transformed from ideal WZ (internal parameter set to \(u = \frac{2}{3}\)) to the WZ-like ScAlN equilibrium structure. The ionic part of the polarization can be calculated in a straightforward manner, once the offsets are known and subtracted (e.g. Eq. (2)), as the difference between the ionic polarization of the relaxed structure and the reference ideal WZ (which is zero):

\[
P_{i,SB}^{\text{ion}} = P_{i,\text{tric}}^{\text{ion}} - P_{i,\text{idWZ}}^{\text{ion}},
\]

where tric and idWZ denote the triclinic and ideal WZ supercell values, respectively, and \(i\) runs over each Cartesian component. For simplicity, we refrain from explicitly including the offset corrections in the equations for the ionic polarization, since they maintain their functional dependence on the lattice vectors throughout the transformation. This is true as long as the periodic replicas chosen to calculate the polarization are always the same. While the ionic polarization offset for a given structure is fully determined by the choice of origin, in the case of the electronic polarization this offset is also influenced by the quantum of polarization.\(^{15,16}\) Since the Berry phase is an angular variable, well-defined only modulo 2\(\pi\), large changes in its value corresponding to large changes in the sample’s dipole moment may lead to ambiguous results. The total dipole moment of the supercell scales linearly with the number of primitive unit cells \(N_{\text{cells}}\) considered, whereas the length of the lattice vectors scales only as \(N_{\text{cells}}^{1/3}\). Since the quantum of polarization ambiguity is related to lattice translations, this means that the “jumps” in the electronic polarization components are more likely to be observed as the supercell size grows larger. For our 128-atom supercells we observe this issue to be severe because the amount of internal strain is so large for ScAlN alloys that the separate ionic and electronic contributions change quickly (although the total polarization behaves more smoothly).

Therefore, for large changes in polarization, such as that expected from ideal WZ to WZ-like ScAlN, the evolution of the electronic polarization must be carefully monitored for jumps. In Fig. 2 we show the evolution of the three Cartesian components of the SP polarization vector for a \(\text{Sc}_{12}\text{Al}_{52}\text{N}_{64}\) supercell, where the transformation from clamped-ion to fully relaxed structure has been characterized in 10 steps: for fixed lattice vectors, the internal atomic positions are linearly scaled from the clamped-ion configuration to the fully relaxed structure. The first observation for this particular structure are the jumps in the electronic polarization for \(P_x\) and \(P_y\). If we had naively computed only the end points, as we did for the ionic part in Eq. (12), the results of SP polarization would be wrong (even the wrong sign) for \(P_x\) and \(P_y\) and only correct for \(P_z\), which presents no jumps in the electronic polarization part. Instead, by monitoring the full transition from ideal WZ to triclinic we can reconstruct the true evolution of the electronic polarization, as shown in the bottom panel of Fig. 2 for the \(P_z\) component.

In this context, in order to find a fitting curve one needs to construct a generalization of a straight line that takes jumps into account. In our implementation, this curve is the following:

\[
f(\lambda) = (m \lambda + f_0) \text{step(left}(\lambda, \lambda_i) + (m \lambda + f_{N_{\text{jumps}}}) \text{step(right}(\lambda, \lambda_{N_{\text{jumps}}}))_{\sum_{i=1}^{N_{\text{jumps}}-1}} (m \lambda + f_i) \text{pulse}(\lambda, \lambda_i, \lambda_{i+1}),
\]

where \(\lambda\) is a parameter that characterizes the transformation, in Fig. 2 it would be the step out of 10. \(f_i\) are constant vertical shifts and \(m\) is the slope of the curve. The different \(\lambda_i\) are the positions of the jumps, ideally chosen to lie in between data points, and \(N_{\text{jumps}}\) is the total number of jumps: one for \(P_x\), none for \(P_y\), and 4 for \(P_z\) in Fig. 2. step(left)(\(\lambda, \lambda_i\)) is a step function, equal to 1 to the left of \(\lambda_i\) and 0 elsewhere. Similarly,
The results obtained for the different samples and compositions studied are shown in Fig. 3. A small scatter of data can be observed, in particular as the amount of Sc, and therefore the lattice distortion, increases. In the case of SP polarization, the use of SQS instead of configurational sampling of random structures might be justified. Indeed, the SQS values are remarkably close to the averages of random configurations for all compositions. A quadratic fit to the random supercell data yields the following interpolation formula for the SP polarization of Sc$_x$Al$_{1-x}$N:

$$P_{SP}(x) = -0.089 (1-x) - 0.874 x + 0.741 x (1-x) \text{ C/m}^2.$$  \hspace{1cm} (16)

For consistency with the PZ tensor results from the next section, the SQS results have been left out of the fitting. The expression above has been given in the fashion usually employed for ternary compounds, where it is easy to identify the end values of the binaries and the bowing parameter $b$,\textsuperscript{36} which gives the quadratic correction. In the case of ScAlN a large non-linearity with composition of the SP polarization can be observed, with $b = 0.741 \text{ C/m}^2$ in this case. Note, for comparison, that the SP polarization bowing parameter of the traditional nitride ternaries AlGaN, AlInN and InGaN is one order of magnitude smaller.\textsuperscript{37,38} Equation (16) also allows to identify the SP polarization of pure AlN ($-0.089 \text{ C/m}^2$) and the (very large) extrapolated value of a hypothetical pure wurtzite ScN ($-0.874 \text{ C/m}^2$). The latter is only an artifact of the interpolation procedure and does not bear connection to any real material, since WZ ScN is not stable and high Sc-content ScAlN adopts a hexagonal-layered configuration.\textsuperscript{9}

It is worth mentioning that the jumps in the spontaneous polarization introduce a discontinuity in the evolution of the polarization vector that affects the calculation of the PZ tensor through a shift in the reference polarization of the unstrained system. The calculated uncorrected polarization at a (small) finite strain $P'(\epsilon)$ will belong to the same polarization branch as for $\epsilon = 0$, i.e. the branch at $\lambda = 10$ in the example of Fig. 2. If there have been polarization jumps between the polarization of the ideal structure and that of the unstrained structure, this means that the reconstruction needed for the spontaneous polarization also needs to be carried out for the strained structure. The corrected dipole moment of the unit cell $p(\epsilon)$ can be related to the uncorrected value $P'(\epsilon)$ in the following way:

$$p(\epsilon) = P'(\epsilon) + (\mathbb{I} + \epsilon)(p_{SP} - p(0)).$$  \hspace{1cm} (17)
where $\mathbb{I} + \epsilon$ represents a strain transformation applied to the dipole moment vectors. The correct polarization at $\epsilon$ is then obtained by dividing Eq. (17) by the unit cell volume at strain $\epsilon$. Note that if there have been no jumps, $\mathbf{P}_{\text{SP}} - \mathbf{P}'[0]$ vanishes and the correction above becomes trivial. One can choose to calculate the uncorrected PZ tensor components $e'_{ij}$ for the given polarization branch and carry out the corrections afterwards, which is arguably a more straightforward route. The corrections are as follows:

$$
e_{ij} = \begin{cases} 
e'_{ij} & \text{if } i = j \text{ or } j = i + 3 \\ e'_{ij} - P_{i, \text{SP}} + P'_{i}[0] & \text{if } i \neq j, j = 1, 2, 3 \\ e'_{ij} + \frac{1}{2} (P_{k, \text{SP}} + P'_{k}[0]) & \text{if } j > 3, j \neq i + 3 \end{cases}$$

where $k = 9 - i - j$. Incidentally, these corrections carry a resemblance to the transformation from improper to proper PZ coefficients\textsuperscript{39} that will be discussed in more detail in Sec. IV.

**E. Results: piezoelectric tensor**

In order to calculate the components of the triclinic PZ tensor of the different supercells, we monitor the evolution of the three Cartesian components of the polarization vector $P_i$ as small strains $\epsilon_j = \pm 0.2\%$ are applied.\textsuperscript{40} A finite difference calculation then leads to the 18 independent $e_{ij}$. Next, the tensor directly obtained in this way is rotated so as to maximize its hexagonal projection using Eq. (11) and the procedure described in Ref. 34. This allows an optimum hexagonal “alignment” of the tensor. The results for the different configurations and Sc contents are shown in Fig. 4. For clarity of interpretation, the panels in the figure are arranged in the same fashion as the PZ tensor when represented in matrix form, Eq. (3). The vertical scale has been kept fixed for all the PZ coefficients except for $e_{33}$ to enable a direct simultaneous comparison of the magnitude of variation for all the PZ constants. The most immediate observation that can be made is with regards to the large data scattering for different configurations with the same nominal composition. The largest scatter occurs for the hexagonal PZ coefficients $e_{15}$, $e_{31}$ and $e_{33}$, but also for $e_{16}$, $e_{21}$ and $e_{22}$. Although the latter might seem like an unexpected result, we have previously shown that these components in a wurtzite crystal only vanish as an averaging macroscopic effect, cf. Eq. (14) of Ref. 20. This scatter of results is directly related to the large amount of internal strain that distorts the lattice locally in very different ways for different configurations.

The hexagonal projection of the triclinic PZ tensors in Fig. 4 using Eq. (11) leads to the hexagonal PZ constants of internal strain that distorts the lattice locally in very different ways for different configurations.

The PBE functional, similar to other local and semilocal DFT functionals, has a number of shortcomings. Using a more expensive approach, for instance a hybrid-functional, better accuracy can be achieved. Running hybrid-functional calculations for the 128-atom supercells is impractical in the present case due to the increased computational cost. A possible approach is to correct the end points for the AlN binary and then follow the same evolution with composition for the alloy as predicted with PBE. Correcting the AlN end values to the HSE hybrid-functional results from Ref. 20, gives significant changes only for $e_{31}$:

$$e_{15}^{\text{hex}}(x) = -0.367 (1 - x) - 0.435 x + 0.417 x (1 - x),$$

$$e_{31}^{\text{hex}}(x) = -0.424 (1 - x) - 0.286 x - 0.615 x (1 - x),$$

$$e_{33}^{\text{hex}}(x) = 1.449 (1 - x) + 8.182 x - 5.912 x (1 - x).$$

(19)

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$$\tilde{e}_{15}^{\text{hex}}(x) = -0.39 (1 - x) - 0.458 x + 0.417 x (1 - x),$$

$$\tilde{e}_{31}^{\text{hex}}(x) = -0.63 (1 - x) - 0.492 x - 0.615 x (1 - x),$$

$$\tilde{e}_{33}^{\text{hex}}(x) = 1.46 (1 - x) + 8.193 x - 5.912 x (1 - x).$$

(20)

We will denote HSE-corrected (cHSE) results with a tilde.

**F. Elastic constants and piezoelectric moduli**

So far we have discussed the values of the piezoelectric coefficients $e_{ij}$ which relate electric polarization and strain $\epsilon_j$:

$$P_i = \sum_{j=1}^{6} e_{ij} \epsilon_j.$$

(21)

However, it is not uncommon to describe the piezoelectric response of a material in terms of its piezoelectric moduli $d_{ij}$, which give the evolution of the electric polarization...
vector as a function of stress $\sigma_j$:

$$ P_i = \sum_{j=1}^{6} d_{ij} \sigma_j. $$

(22)

The hexagonal tensor of piezoelectric moduli has the same form as that of the piezoelectric constants given in Eq. (4). For completeness and to be able to compare to experimental data on the piezoelectric constants of ScAlN alloys, which is most often given in the literature in terms of the $d_{ij}$, we compute them too. In order to do so, the elastic constants $C_{ij}$ of ScAlN need to be computed, which can be readily done from the same set of calculations that allow to extract the PZ coefficients. Then, the relation between $e_{ij}$ and $d_{ij}$ can be obtained straightforwardly from the strain-stress relation,

$$ \sigma_i = \sum_{j=1}^{6} C_{ij} e_j, $$

(23)

in such a way that the relation between the different PZ coefficients is simply:

$$ e_{ij} = \sum_{k=1}^{6} d_{ik} C_{kj}, \quad d_{ij} = \sum_{k=1}^{6} e_{ik} (C^{-1})_{kj}. $$

(24)

Given the symmetry of the hexagonal stiffness tensor, the independent non-vanishing hexagonal PZ coefficients and PZ moduli can be expressed as follows:

$$ e_{15} = d_{15} C_{44}, \quad e_{31} = d_{31} (C_{11} + C_{12}) + d_{33} C_{13}, $$

$$ e_{33} = 2d_{31} C_{13} + d_{33} C_{33}, $$

(25)

for the $e_{ij}$, and

$$ d_{15} = \frac{e_{15}}{C_{44}}, \quad d_{31} = \frac{e_{31} C_{33} - e_{33} C_{13}}{(C_{11} + C_{12}) C_{33} - 2 C_{13} C_{33}}, $$

$$ d_{33} = \frac{e_{33} (C_{11} + C_{12}) - 2 e_{31} C_{13}}{(C_{11} + C_{12}) C_{33} - 2 C_{13} C_{33}}, $$

(26)

for the $d_{ij}$. The evolution with composition of the $C_{ij}$ for ScAlN from our simulations is depicted in Fig. 6, where less scatter of data can be observed as compared to the PZ coefficient results. Incidentally, the SQS supercells are also observed to be more suitable for calculating elastic properties of ScAlN than PZ coefficients: the average values for random supercells are very close to the SQS values. The $C_{ij}$ have been obtained following the same procedure outlined in Sec. II C with an optimized rotation of the stiffness tensor followed by a hexagonal projection.32,34 The projector for the hexagonal stiffness tensor has been previously obtained by Tasnádi et al.41
The fitted quadratic expressions for the composition-dependent hexagonal elastic constants of Sc$_x$Al$_{1-x}$N are:

\begin{align*}
C_{11}^{\text{hex}}(x) &= 378.8 (1 - x) + 263.9 x - 210.3 x (1 - x), \\
C_{12}^{\text{hex}}(x) &= 128.9 (1 - x) + 185.1 x - 61.9 x (1 - x), \\
C_{13}^{\text{hex}}(x) &= 96.1 (1 - x) + 121.5 x + 78.9 x (1 - x), \\
C_{33}^{\text{hex}}(x) &= 357.5 (1 - x) - 51.3 x - 101.4 x (1 - x), \\
C_{44}^{\text{hex}}(x) &= 112.4 (1 - x) + 159.0 x - 137.3 x (1 - x),
\end{align*}

(27)

given in GPa. Underbinding (too long lattice constants) and the correspondingly low elastic constants are well-known shortcomings of generalized-gradient approximations to DFT, including the PBE functional. For this reason, the correction of the $C_{ij}$ to give the right numbers for AlN becomes more critical than in the case of the PZ coefficients. The HSE values for AlN\cite{28} give much better agreement with experiment\cite{42} than the PBE values. The corrected constants (in GPa) are:

\begin{align*}
\tilde{C}_{11}^{\text{hex}}(x) &= 410.2 (1 - x) + 295.3 x - 210.3 x (1 - x), \\
\tilde{C}_{12}^{\text{hex}}(x) &= 142.4 (1 - x) + 198.6 x - 61.9 x (1 - x), \\
\tilde{C}_{13}^{\text{hex}}(x) &= 110.1 (1 - x) + 135.5 x + 78.9 x (1 - x), \\
\tilde{C}_{33}^{\text{hex}}(x) &= 385.0 (1 - x) - 23.8 x - 101.4 x (1 - x), \\
\tilde{C}_{44}^{\text{hex}}(x) &= 122.9 (1 - x) + 169.5 x - 137.3 x (1 - x).
\end{align*}

(28)

Combining Eq. (27) with the expressions in Eq. (19), and Eq. (28) with Eq. (20), for the PBE and HSE-corrected values, respectively, following the relation given by Eq. (26), leads to the following composition-dependent expressions for $d_{ij}^{\text{hex}}(x)$ (given in pC/N):

\begin{align*}
d_{15}^{\text{hex}}(x) &= -3.27 + 0.454 x + 0.869 x^2 - 0.847 x^3, \\
\bar{d}_{31}^{\text{hex}}(x) &= -1.784 - 23.0 x + 149.9 x^2 - 381 x^3, \\
\bar{d}_{33}^{\text{hex}}(x) &= 5.01 + 67.3 x - 458 x^2 + 1176 x^3,
\end{align*}

(29)

for the direct PBE results and

\begin{align*}
\tilde{d}_{15}^{\text{hex}}(x) &= -3.17 + 0.487 x + 0.660 x^2 - 0.746 x^3, \\
\tilde{d}_{31}^{\text{hex}}(x) &= -2.14 - 15.09 x + 78.8 x^2 - 229 x^3, \\
\tilde{d}_{33}^{\text{hex}}(x) &= 5.02 + 42.3 x - 238 x^2 + 704 x^3,
\end{align*}

(30)

for the HSE-corrected values. The expressions have been obtained as the best third-order fit to the full expressions.

FIG. 5. (Color online) Hexagonal projected components of the triclinic PZ tensor of ScAlN, obtained as explained in detail throughout the text.

FIG. 6. (Color online) Composition-dependent hexagonal projected components of the stiffness tensor of ScAlN.
calculated from Eq. (26) (taking Eqs. (19) and (27), and Eqs. (20) and (28) as input) with the constraint that the values for AlN be reproduced exactly. A second-order fit was not enough to correctly describe the evolution with composition of the $d_{ij}$. Comparison of these results with available literature values will be done in Sec. IV.

III. EXPERIMENTAL MEASUREMENT

Given the more complex setup needed to measure $\varepsilon_{33}$ and, particularly $\varepsilon_{15}$, we carried out measurements of $\varepsilon_{33}$ at three different compositions using an acoustic wave resonator, in order to be able to partially compare and validate the results of the simulation.

Magnetron sputtering was utilized to fabricate the wurtzite-like ScAlN thin film bulk acoustic wave (BAW) structures. The films in the study were co-sputtered in a von Ardenne CS730S cluster sputtering tool. The ScAl composite sputtering target used consisted of an Al (99.999%) body equipped with Sc (99.9%) pieces.

The number of Sc pellets on the target determines the chemical composition of the grown films, which was analyzed using time-of-flight elastic recoil detection analysis (ToF-ERDA). The BAW resonator structure used to extract the $\varepsilon_{33}$ piezoelectric coefficient is made up of a ScAlN plate between metal electrodes which was deposited onto an acoustic Bragg reflector consisting of two pairs of SiO$_2$/W layers with a quarter wavelength thickness. A voltage source is connected across the thickness dimension of the piezolayer, which we denote $z$. Wafer level S-parameter measurements were performed with a Hewlett-Packard 8720D vector network analyzer.

The one-dimensional description of the resonator is as follows. The wave equation for the mechanical displacement $u$ along $z$ is

$$\frac{\partial^2 u}{\partial t^2} = v_D^2 \frac{\partial^2 u}{\partial z^2},$$

where $v_D$ is the sound phase velocity under the prevailing conditions. If the effective stiffness of the material is $C_D^0$ and the mass density is $\rho$, the velocity is given by

$$v_D = \sqrt{\frac{C_D^0}{\rho}}.$$  

We search an analytic harmonic solution of the equation

$$\frac{\partial^2 u}{\partial z^2} = -k^2 u,$$

in a multilayer structure in the form

$$u_i = A_i e^{-ik_iz} + B_i e^{ik_iz},$$

where $k_i = \omega/v_i$ is the wave number in layer $i$. The amplitude coefficients $A_i$ and $B_i$ are determined from the boundary conditions establishing that the stress and displacement are continuous across each interface. The electric field in the piezolayer is

$$E = \frac{J_i}{\omega \varepsilon_i} - h_i \frac{\partial u}{\partial z},$$

where $h_i$ is the piezoelectric coefficient, $\varepsilon_i$ the electrical permittivity and $J_i$ the current density through layer $i$ at angular frequency $\omega$. The voltage $U$ of the device is obtained by integrating the field $E$ over the thickness, and the current $I$ by integrating $J$ over the electrode area. Finally, the impedance is calculated as $Z = U/I$.

From the measured impedance the following quantities are calculated: i) the parallel capacitance $C_0$, which is used to calculate the permittivity, ii) the phase

$$\varphi = \arctan \left( \frac{\operatorname{Im}(Z)}{\operatorname{Re}(Z)} \right),$$

and iii) the quality factor

$$Q = \frac{\omega}{2} \left| \frac{d\varphi}{d\omega} \right|.$$  

The resonance frequencies $f_s$ and $f_p$ are then determined as the frequencies of the maximum values of $Q$. The electromechanical coupling coefficient is given by

$$k_{\text{eff}} = \sqrt{1 - \left( \frac{f_s}{f_p} \right)^2}.$$  

Finally, the piezoelectric coefficient $\varepsilon_{33} = \varepsilon^T h$ is chosen so that the measured and calculated $k_{\text{eff}}$ are equal. The values of $\varepsilon_{33}$ together with the different material parameters obtained for the three ScAlN samples studied are given in Table I.

IV. DISCUSSION, SUMMARY AND CONCLUSIONS

Before comparing results from simulation and experiment it is worth making the distinction between proper and improper PZ coefficients. A more detailed discussion is available from the paper by Vanderbilt and references therein. The “improper” coefficients, that we have calculated in Sec. II.E, link the electric polarization vector and strain through Eq. (21), and can be alternatively expressed as

$$e_{ij}^{\text{p}} = \frac{\partial P_i}{\partial \varepsilon_j},$$

The “proper” PZ coefficient, on the other hand, links the adiabatic change in current density $J$ in response to a slow deformation $\varepsilon_j = d\varepsilon_j/dt$.

$$e_{ij}^{\text{p}} = \frac{\partial J_i}{\partial \varepsilon_j}.$$
TABLE I. Parameters involved in the experimental determination of $\varepsilon_{33}$ used in this work. The density values are calculated from the lattice constants measured by Matloub et al.\textsuperscript{43} and the atomic masses of Sc, Al and N. Note: the elastic constant $C_{33}$ is chosen so that the calculated resonance frequency is close to the measured value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured</th>
<th>Calculated</th>
<th>Measured</th>
<th>Calculated</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB177E13</td>
<td></td>
<td></td>
<td>14%</td>
<td></td>
<td>26%</td>
<td></td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>1270</td>
<td>1070</td>
<td>1010</td>
<td></td>
<td>1010</td>
<td></td>
</tr>
<tr>
<td>Relative permittivity $\varepsilon$</td>
<td>9.37</td>
<td>9.37</td>
<td>10.68</td>
<td>10.68</td>
<td>13.06</td>
<td>13.06</td>
</tr>
<tr>
<td>$\varepsilon_{33}$ (C/m$^2$)</td>
<td>1.46</td>
<td>1.81</td>
<td>3.530</td>
<td>3.560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>3.512</td>
<td>3.512</td>
<td>3.512</td>
<td>3.512</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{33}$ (GPa)</td>
<td>379.9</td>
<td>379.9</td>
<td>379.9</td>
<td>379.9</td>
<td>379.9</td>
<td>379.9</td>
</tr>
<tr>
<td>$f_s$ (MHz)</td>
<td>1969.5</td>
<td>1942.2</td>
<td>1886.6</td>
<td>1856.2</td>
<td>1753.2</td>
<td>1700.7</td>
</tr>
<tr>
<td>$f_p$ (MHz)</td>
<td>2023.3</td>
<td>1996.0</td>
<td>1966.4</td>
<td>1934.8</td>
<td>1872.9</td>
<td>1816.8</td>
</tr>
<tr>
<td>$k_{\text{eff}}$</td>
<td>0.229</td>
<td>0.2306</td>
<td>0.282</td>
<td>0.2822</td>
<td>0.352</td>
<td>0.3517</td>
</tr>
<tr>
<td>$C_0$ (pF)</td>
<td>5.302</td>
<td>5.302</td>
<td>1.862</td>
<td>1.86</td>
<td>1.869</td>
<td>1.87</td>
</tr>
</tbody>
</table>

where $J_i$ indicates current density along direction $i$ (in contrast to Eq. (35), where $i$ denotes layer and the current density is assumed to flow along the polar axis). The definitions in Eqs. (39) and (40) lead in general to different PZ coefficients. The transformation between improper and proper PZ coefficients for the three independent wurtzite $e_{ij}$ is as follows:\textsuperscript{49}

$$
e_{15} = e_1 - \frac{1}{2} P_{3,SP},$$
$$e_{31} = e_3 + P_{3,SP},$$
$$e_{33} = \tilde{e}_{33}.$$ (41)

The improper coefficient is the relevant one when calculating polarization charges, for instance interfacial charge accumulation at quantum well interfaces.\textsuperscript{50} The proper coefficient, on the other hand, is the quantity that should be compared to experiments where PZ coefficients are measured in terms of flowing currents.\textsuperscript{39} For systems with small spontaneous polarization the corrections can be negligible, but in view of the fact that the spontaneous polarization of ScAlN becomes of the same order of magnitude as the PZ coefficients for large Sc fraction, the corrections in Eq. (41) become important. Therefore, we report the different proper coefficients here, as obtained from applying the corrections of Eq. (41) to the different expressions of the previous sections. The proper PZ coefficients $e_{ij}$ directly obtained from the PBE results are:

$$e_{15} = -0.323 (1 - x) + 0.002 x + 0.047 x (1 - x),$$
$$e_{31} = -0.513 (1 - x) - 1.160 x + 0.126 x (1 - x),$$
$$e_{33} = \tilde{e}_{33}.$$ (42)

where $\tilde{e}_{33}(x)$ is taken from Eq. (19). For the HSE-corrected values, the proper $e_{ij}$ become:

$$e_{15} = -0.346 (1 - x) - 0.021 x + 0.047 x (1 - x),$$
$$e_{31} = -0.719 (1 - x) - 1.366 x + 0.126 x (1 - x),$$
$$e_{33} = \tilde{e}_{33}(x).$$ (43)

where $\tilde{e}_{33}(x)$ is taken from Eq. (20). The proper PZ modulus from PBE and HSE-corrected calculations are

$$d_{15} = -2.87 + 0.862 x + 5.35 x^2 - 2.89 x^3,$$
$$d_{31} = -1.979 - 24.3 x + 156.9 x^2 - 403 x^3,$$
$$d_{33} = 5.12 + 70.8 x - 485 x^2 + 1243 x^3,$$ (44)

and

$$d_{15} = -2.81 + 0.846 x + 4.63 x^2 - 2.40 x^3,$$
$$d_{31} = -2.32 - 15.90 x + 82.0 x^2 - 243 x^3,$$
$$d_{33} = 5.12 + 44.4 x - 253 x^2 + 745 x^3,$$ (45)

respectively. Note that unlike for the PZ coefficient, the proper PZ modulus $d_{33}$ is not equal to the improper one because $e_{15}$ and $e_{31}$ are involved in its determination [cf. Eq. (26)].

In Fig. 7 we show a comparison of the present results and available experimental and simulation data from the literature. Most of the available data is for the $d_{15}$, rather than the $e_{ij}$. In particular, there is lack of published data regarding the shear PZ coefficient $e_{15}$ and shear PZ modulus $d_{15}$, for which this work seems to be the first one to report values. In addition, although $e_{31}$ could be estimated from available values of PZ moduli and elastic constants, there does not seem to be any explicit reports for this coefficient either. Matloub et al.\textsuperscript{43} have reported values for the “effective transverse” $e_{31,f}$ which, attending to the definition provided by the authors in previous work,\textsuperscript{51} should relate to $e_{31}$ as $e_{31} = e_{31,f} + C_{13} C_{33}$. Therefore we use our calculated values of $C_{13}$, $C_{33}$ and $e_{33}$ to
to disentangle the contributions to electric polarization arising from a) crystal deformation and b) lattice softening when looking at the PZ moduli. This also means that any uncertainty relating to the knowledge of the elastic constants has a strong impact on the derivation of the $d_{ij}$ values. In contrast, the relation between crystal deformation and polarization is more transparent when looking at the PZ coefficients $e_{ij}$, which preserve a smoother behavior throughout the full compositional regime studied.

Overall, the agreement with previous simulations is difficult to establish due to the fact that both available studies, by Tasnádi et al. and Umeda et al., did not consider configurational sampling, which we have shown to affect the results. The agreement is good between our calculations and Tasnádi’s results of $e_{33}$, obtained using 128-atom SQS supercells, for moderate and low Sc content. For higher Sc content the spread of $e_{33}$ values increases, meaning that a single SQS supercell per composition is not enough to capture the effects of configurational disorder. The agreement between the simulation results of Umeda et al. and the present work is not too bad for $d_{31}$ but less good for $d_{33}$. Umeda used small 32-atom supercells for which the spurious effects of periodicity and artificial alloy order (the structures were generated maximizing the inter-Sc distances) might have influenced the results.

With regards to agreement with experiment, the only experimental values for $e_{ij}$ reported so far seem to be the $e_{33}$ values of the present study, which our simulations slightly underestimate. The $e_{31}$ values from Matloub et al. extracted from their $e_{31,ij}$ as outlined previously, show reasonable agreement with our calculations. Reported values for $d_{31}$ and especially $d_{33}$ are more abundant. Our results seem to be in good agreement with $d_{31}$ and in reasonably good agreement for $d_{33}$ over more or less the full compositional range, especially in the case of the HSE-corrected results. Note that the dips of Akiyama’s values at around 37% Sc content and beyond 45% Sc content, as well as Umeda’s values dip beyond 40% Sc content, are likely due to deteriorating crystal quality.5,10 Note that in every case discussed above, it should be the proper (“pr.” on the graph) PZ coefficient to be compared to the experimental value.

The largest sources of error in experimental measurement are i) those intrinsic to the experimental setup and ii) those due to the lack of knowledge of the ScAlN alloy properties, in particular elastic properties (which are usually measured simultaneously with the PZ coefficients) and the amount of incorporated Sc. Due to the discussed lattice softening that takes over rapidly as the Sc content increases, the lack of accurately-determined elastic properties is likely the largest source of error in experimental measurements. A further source of experimental uncertainty is related to the microscopic structure of the alloy, including the possible effect of clustering, and how it affects the PZ properties of the material. In particular, Akiyama et al. showed that the alloy microstructure, which is influenced by Sc content and growth tem-

FIG. 7. (Color online) Comparison of the present results (“pr.” stands for “proper”) and available literature data, taken from: Matloub et al. (data modified for comparison [see text], experiment); Tasnádi et al. (simulation); Umeda et al. (simulation & experiment); Mayrhofer et al. (experiment); Akiyama et al. (experiment); and Akiyama et al. (experiment). See text for a discussion.

be able to compare to their experimental results. Unfortunately, the relation between electric polarization and stress has a much more extreme dependence on composition for ScAlN alloys due to the lattice softening along the c axis as the Sc fraction increases, if compared to the relation between polarization and strain. This translates into the very rapid variation with composition of $d_{31}$ and $d_{33}$ beyond $x \approx 30\%$. It is then more difficult
perature, affects the PZ performance of ScAlN films.\textsuperscript{52} Zukauskaite \textit{et al.} have also shown that formation of Al-rich and Sc-rich domains can occur under unfavorable growth conditions at high temperature and high Sc concentrations but should not happen for films grown at lower temperature and lower Sc contents.\textsuperscript{53} Therefore, clustering might be directly or indirectly linked to deteriorating PZ properties of ScAlN for low crystalline quality samples (see for instance the dip of Akiyama’s results for $d_{33}$ in Fig. 7) but, otherwise, the assumption of a random alloy for the present simulations should be representative of high crystalline quality experimental samples. The effect of clustering on the simulation results could be an interesting topic to be explored in future studies.

From the simulation, errors arise from two main fronts: i) the effect of finite-size supercells and configurational disorder which we have thoroughly shown in Sec. II to have an impact on the results; ii) the inaccuracy introduced by the choice of DFT functional. We argue that, in order to address the first issue, configurational sampling is required, as evidenced by the large spread of data displayed in Fig. 4. Even if the number of configurations used (9 random supercells per composition) is not enough to accurately determine the PZ tensor at a single composition, the combined effect of all the available data points through the whole compositional regime leads to a much improved fitting of interpolation formulas. This is evidenced by the fact that the fitting curves for the non-hexagonal components of the triclinic PZ tensor are close to zero, even for those with larger spread ($e_{16}$, $e_{31}$ and $e_{22}$). We could have attempted to compute more values for each composition, however from a practical point of view such a study becomes computationally too expensive.\textsuperscript{54} The second issue is more difficult to address. A good benchmark for the performance of DFT functionals for semiconductors is the HSE hybrid functional,\textsuperscript{55} as already discussed. While it performs considerably better than LDA and GGA functionals with respect to prediction of elastic and structural properties,\textsuperscript{56} it has been previously shown that with regards to calculation of spontaneous and piezoelectric polarization the main differences with other functionals lie in the description and impact of internal strain on the results.\textsuperscript{20} Given the large internal strain present in ScAlN, this is probably the main source of error in our simulation results. To account for this, given the computational limitations to carrying out hybrid-functional calculations for large systems, we have corrected the expressions for the PZ coefficients so that the AlN end points are described according to the HSE results. The goodness of this approximation relies on how well the trends with composition are described by the PBE functional.

Taking all these concerns into consideration, we recommend the use of Eqs. (16), (20), (28) and (30) for the composition-dependent values of the spontaneous polarization, the piezoelectric coefficients $e_{ij}$, the elastic constants $C_{ij}$ and the piezoelectric moduli $d_{ij}$, respectively, of ScAlN alloys. For the “proper” PZ coefficients $e_{ij}^p$ and moduli $d_{ij}^p$ we recommend Eqs. (43) and (45), respectively.

\section*{ACKNOWLEDGMENTS}

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\section*{Appendix: Relation between randomness and PZ coefficient}

Given the observed result that SQS cells do not reproduce the average piezoelectric constants of ScAlN as well as they do reproduce other properties, we have attempted to study whether there is any correlation between supercell randomness and the calculated piezoelectric coefficients. The results of this study are presented in Fig. 8. The pair-correlation coefficients of an ideally random alloy are minimal in absolute value for all nearest-neighbor shells, and so SQS supercells are generated by placing the different atoms so that these coefficients are minimized.\textsuperscript{18} The lack of any obvious trend between the “randomness”

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{(Color online) Deviation from the interpolation formulas for $e_{ij}$ versus pair-correlation coefficients of the random ScAlN supercells up to the 5th shell.}
\end{figure}
of the random supercells and their ability to yield PZ coefficients close to the average values then explains, at least in part, why SQSs are not able to produce representative results consistently. Note that this is in contrast to the situation for elastic constants, where SQSs yield values in good agreement with average results (Fig. 6).
In general, the hexagonal projection could be plus or minus the norm of the triclinic spontaneous polarization vector. However, for wurtzite materials in the usual representation the spontaneous polarization value along the polar axis has negative sign. Therefore, if the triclinic cell is well “aligned” with the underlying hexagonal lattice, the rotation angles can be taken to be the smallest possible set, and the corresponding hexagonal projection of the spontaneous polarization is negative.


We have verified that this amount of strain is sufficiently small to ensure we are well within the linear regime, but large enough that the numerical noise does not impact the results – a calculation with $\epsilon_j = \pm 0.5\%$ yielded basically the same PZ tensor for a test configuration.


The expression for $\epsilon_{15}$ differs from Vanderbilt’s$^{39}$ by a factor of 2 because Vanderbilt allowed for an antisymmetric part in the strain tensor. Once the symmetry of the strain tensor upon exchange of the Cartesian indices is considered, $\epsilon_{ij} = \epsilon_{ji}$, the expression that arises for $\epsilon_{15} \equiv \epsilon_{113} = \epsilon_{311}$ is the one given by us.


We employed a total of circa 0.5 million CPU hours on the random supercell calculations, approximately equal to a single-core computer running uninterruptedly for 60 years.
