Strained Hexagonal ScN: A Material with Unusual Structural and Optical Properties

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Local-density approximation calculations are performed to predict properties of compressively strained hexagonal ScN. This material is found to exhibit a large electromechanical response, a structural phase transition from a nonpolar to a polar structure, and a variation of the band gap in the entire visible light range when continuously changing the compressive strain. Microscopic effects responsible for these anomalies are revealed and discussed. Suggestions on how to practically grow ScN-based materials having such unusual properties are also provided.

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The optical properties of some semiconductors are of primary importance. For instance, the change in compositions of $(Ga_{1-x-y}In_xAl_y)N$ alloys or the change in the size of GaN quantum dots leads to photoluminescence in the entire visible spectrum [1,2], which is of considerable interest for the light-emitting device applications. A second class of compounds with fascinating properties is formed by *ferroelectrics*. These materials can undergo a structural phase transition between a nonpolar and a polar structure, when one varies the temperature [3]. This phase transition is associated with huge piezoelectric and dielectric responses, which explains why ferroelectrics are the materials of choice for applications—such as ultrasonic and sonar listening devices—based on an efficient conversion between electrical and mechanical signals [3].

Recently, Ref. [4] *suggested* that disordered hexagonal $(Sc_{1-x}Ga_x)N$ or $(Sc_{1-x}In_x)N$ alloys can bridge the semiconductor and the ferroelectric classes (i) by exhibiting a wide range of band gaps and (ii) by having large electromechanical responses, when varying x. This suggestion was based on the structural difference between hexagonal ScN and wurtzite GaN or InN, and has not yet been confirmed by either calculations or experiments.

The aim of this Letter is threefold. First, we want to *demonstrate* that hexagonal ScN-based materials can result in "smart" multifunctional compounds. Second, we wish to prove that varying another experimentally accessible parameter, namely, the strain rather than the composition, can lead to the simultaneous occurrence of features usually associated with semiconductors or ferroelectrics. Finally, our last goal is to provide suggestions on how to practically grow hexagonal ScN-based materials having such bridging properties.

Here, we report first-principles calculations that indeed show that compressively strained hexagonal ScN simultaneously exhibits (1) a large variation of the band gap in the technologically important light spectral region, (2) a phase transition leading to the appearance of a spontaneous electrical polarization, and (3) large electromechanical responses, when continuously varying the compressive strain. Our simulations also reveal the microscopic mechanisms responsible for the useful combination of these properties. These discoveries imply that simultaneously varying the composition *and* the strain in disordered hexagonal $(Sc_{1-x}Ga_x)N$ or $(Sc_{1-x}In_x)N$ alloys is a promising way to generate polar semiconductors with optimized electromechanical and optical properties.

Here, we use the density-functional theory, within the local-density approximation (LDA) [5–7], to investigate properties of hexagonal ScN. Other technical details of these calculations are given in Ref. [4]. We focus on hexagonal ScN whose primitive lattice vectors are $\mathbf{a}_1 = a[\frac{1}{2}\mathbf{x} - (\sqrt{3}/2)\mathbf{y}]$, $\mathbf{a}_2 = a[\frac{1}{2}\mathbf{x} + (\sqrt{3}/2)\mathbf{y}]$, and $\mathbf{a}_3 = c\mathbf{z}$, where a and c are the two lattice parameters, c/a is the axial ratio, and $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ are the unit vectors along the three Cartesian axes. The primitive cell contains two Sc atoms, located at $\mathbf{r}_1 = \mathbf{0}$ and $\mathbf{r}_2 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3$, and two N atoms whose positions are given by $\mathbf{r}_3 = u\mathbf{a}_3$ and $\mathbf{r}_4 = \frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + (\frac{1}{2} + u)\mathbf{a}_3$, where u is the dimensionless internal parameter.

The minimization of the total energy with respect to *all* degrees of freedom yields [4] $a = a_{eq} = 3.66$ Å, $c/a = 1.207$ and $u = 0.5$, and leads to the structure displayed in Fig. 1(a). This hexagonal phase is a layered structure in which each (0001) plane contains the same amount of Sc and N atoms. This structure, which is referred to as the h phase in Refs. [4,8], also exhibits two other important features. First, this phase is paraelectric, as a result of its $P6_3/mmc$ space group. Second, it is nearly fivefold coordinated: a given Sc (N) atom forms short bonds $\simeq 2.11$ Å with *three* N (Sc) atoms belonging to the same basal plane but also forms slightly longer bonds $\simeq 2.21$ Å with *two* other N (Sc) atoms being in the (0001) planes below and above it, respectively.

One goal of this Letter is to go beyond the study of the equilibrium structure displayed in Fig. 1(a), by

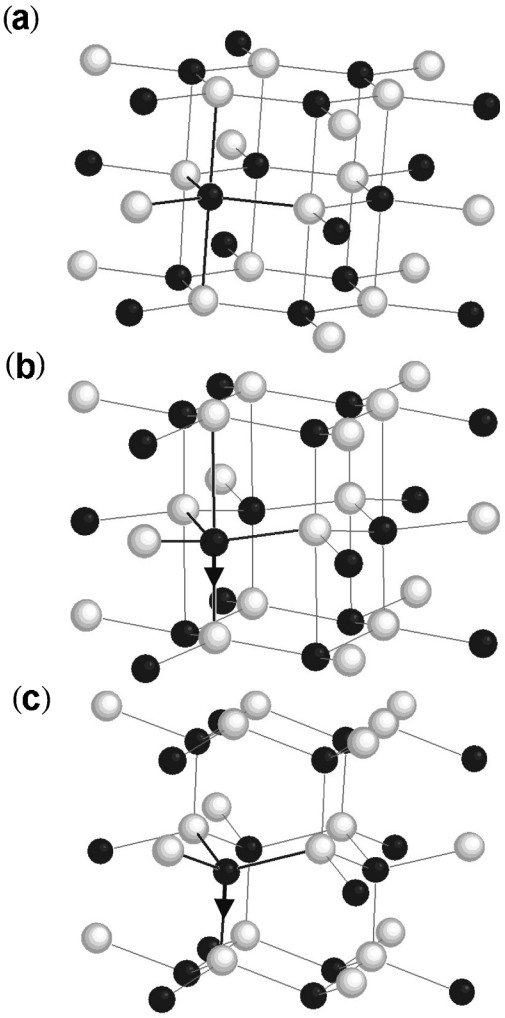

FIG. 1. Schematic representation of hexagonal ScN for three different strains, corresponding to a compression of the in-plane lattice constant with respect to its equilibrium value. The black spheres denote N atoms, while the Sc atoms are represented by white spheres. The bold lines join a given N atom to its nearest Sc neighbors. (a) shows the equilibrium hexagonal ScN ($\eta = 0$), which adopts a nonpolar and nearly fivefold coordinated structure. (b) displays the phase corresponding to a compressive strain of 3.4%, for which a phase transition from a nonpolar to a polar structure is predicted to occur. The arrow indicates that N atoms have all moved down with respect to their internal coordinates associated with (a). (c) represents the phase corresponding to $\eta = 6.4\%$ and for which the number of atomic nearest neighbors becomes nearly 4 rather than 5: the bond between N atoms and Sc atoms located in the (0001) plane above them is broken.

investigating properties of hexagonal ScN as a function of its a in-plane lattice constant. More precisely, we focus on ScN materials that are *compressively* strained in the basal plane. In other words, a is always smaller than a_{eq}, and $\eta = (a_{eq} - a)/a_{eq}$ characterizes the magnitude of this compressive strain. We perform LDA calculations freezing a but relaxing the 2 other degrees of freedom of hexagonal ScN—namely, u and c/a—in order to minimize the total energy and the forces acting on each atom.

Figure 2 displays the resulting behaviors of u and c/a versus η strain and demonstrates the existence of a phase transition, to be denoted by Tr_1, occurring for a compressive strain close to 3.4%. The Tr_1 transition is associated with the deviation of u with respect to its equilibrium value of 0.5. Such deviation results in a change of space group from (nonpolar) $P6_3/mmc$ to (polar) $P6_3/mc$. As shown in Fig. 1(b), this deviation implies that the Sc and N atoms no longer sit in the *same* (0001) plane. As a result, Tr_1 leads to the appearance of a spontaneous electrical polarization, which is analogous to the *temperature*-induced paraelectric-to-ferroelectric transition occurring in some perovskite compounds [3].

Interestingly, there is a second region, to be referred to as R_2, of particular interest in hexagonal ScN. This second region extends from $\eta \sim 5.8\%$ to $\eta \sim 6.4\%$, and is characterized by the rapid decrease of u (or increase of c/a) when increasing η. Furthermore, the (polar) space group remains $P6_3/mc$ before, in, and after R_2. One significant change resulting from R_2 concerns the chemical bonding, or, equivalently, the coordination number. As a matter of fact, the structures corresponding to strain larger than 6.4% look similar to the so-called wurtzite phase—for which $c/a = \sqrt{8/3}$ and $u = 0.375$ in its ideal form—and are thus now roughly fourfold coordinated, as schematized in Fig. 1(c).

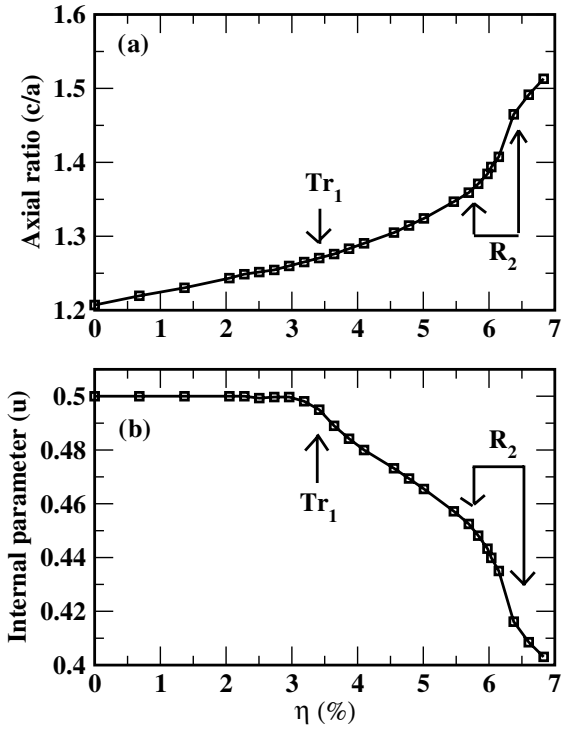

FIG. 2. Structural properties of hexagonal ScN as a function of the compressive strain η. (a) and (b) display the axial ratio c/a and the internal parameter u, respectively. The arrows indicate the regions of particular interest discussed in the text.

To gain further insight into these structural anomalies, we also calculated the phonon dispersions using density-functional perturbation theory [9–11] via the ABINIT code [12,13]. These calculations show that the lowest transverse optical phonon at the Γ point in the $P6_3/mmc$ structure becomes soft, around Tr_1, a phenomenon known to happen in ferroelectric perovskites at the Curie temperature [3]. This softening is responsible for the Tr_1 transition and the development of a spontaneous electrical polarization in the $P6_3/mc$ space group phase [14]. Our *ab initio* simulations also reveal that, unlike Tr_1, there is no off-center or zone-center phonon becoming unstable in R_2. On the other hand, the phonon spectrum as a whole—especially, some optical branches—is affected in R_2. This reflects the change of chemical bonding discussed above. Note that we also found (not shown here) that the magnitude of the Born effective charges decreases when increasing the compressive strain before R_2, while it increases as a function of η just after the (narrow) R_2 region. This nonmonotonic behavior is also consistent with the breaking of the chemical bond that can be seen by comparing Figs. 1(b) and 1(c).

Figure 3(a) sheds some light on the electromechanical properties of hexagonal ScN by displaying the piezoelectric coefficient e_{33}, as predicted within the modern theory of polarization [17,18], as a function of η. One can clearly see that Tr_1 leads to the appearance and to a huge enhancement of piezoelectricity, as consistent with the strain-induced development of a spontaneous polarization. In particular, our calculations yield e_{33} above 12 C/m^2, which is one of the largest piezoelectric coefficients ever predicted using first-principles electronic structure methods [19,20]. Interestingly, e_{33} remains large over a wide range of strain. In particular, it is larger than 4 C/m^2 in the whole region joining Tr_1 to R_2. This is remarkable when realizing that the corresponding parameters of $PbTiO_3$ and $Pb(Mg, Nb, Ti)O_3$ compounds are $\simeq 4$ and 9 C/m^2, respectively [20,21]. In other words, hexagonal ScN exhibits piezoelectricity similar in magnitude to that of ferroelectric perovskites, which are the current materials of choice for piezodevices. Figure 3(a) further indicates that the most noticeable piezoelectric effect occurring in R_2 is the existence of a plateau around 4 C/m^2. Further increasing the compressive strain results in a significant decrease of piezoelectricity.

We now turn our attention to the *optical* properties of hexagonal ScN. Figure 3(b) shows some estimated energetic differences between unoccupied and occupied electronic levels. We find that hexagonal ScN is an indirect band-gap semiconductor, with a valence-band maximum located at the Γ point and a conduction band minimum indexed by the K point, for compressive strains smaller than the one associated with the R_2 region. This band gap is $\simeq 1.5$ eV and nearly independent of the strain for η ranging between 0% and 3.4%, that is before the nonpolar-to-polar Tr_1 transition. One striking feature displayed by Fig. 3(b) is the drastic increase of this

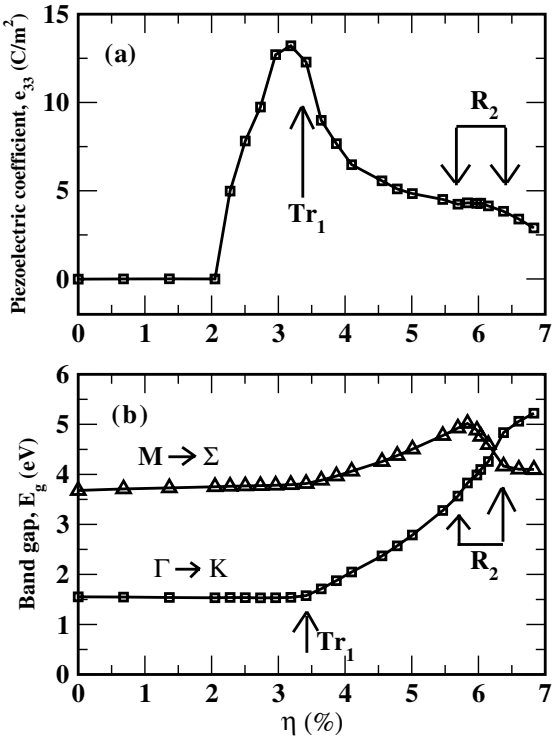

FIG. 3. Electromechanical and optical properties of hexagonal ScN as a function of the compressive strain η. (a) and (b) display the e_{33} piezoelectric coefficient and the lowest-in-energy optical transitions from occupied to unoccupied electronic levels, respectively. These optical transitions are estimated by increasing the LDA predictions by a constant value of 1.3 eV, which is the energetic difference between the experimental [15] and LDA [16] band gaps in rocksalt ScN.

band gap when increasing the strain in the region joining Tr_1 to R_2. As a result, the band gap crosses the *entire range of the visible light spectrum* when η increases from 3.4% to 6.4%. This rapid variation of the band gap is due to the drastic structural changes—and the resulting change in electronic charge distribution—undergone by hexagonal ScN in the region joining Tr_1 to R_2 [see Figs. 1(b) and 1(c)]. Hexagonal ScN and/or related materials may thus be of primary technological importance for generating new light-emitting devices, in addition to having a high prospect in the development of applications taking advantage of their large piezoelectricity. Furthermore, we also find that our investigated material has two other interesting optical features: its valence-band maximum *and* its conduction band minimum, both change location in the first Brillouin zone in R_2. The former is located at the M point, while the latter lies along the Σ line joining the Γ to the M point, for $\eta \geq 6.4\%$. This is in agreement with the finding of Ref. [22] for wurtzite ScN. Figure 3(b) also shows that the band gap is roughly equal to 4 eV (which corresponds to ultraviolet radiations) and is independent of η, for the largest studied compressive strains, which is also in agreement with Ref. [22].

Having demonstrated that compressively strained hexagonal ScN can exhibit optimized electromechanical and optical properties by undergoing structural changes, it is now obvious that the suggestions of Ref. [4] should be correct. As a matter of fact, alloying hexagonal ScN with a wurtzite material having a wide band gap (e.g., GaN) should lead to the structural path schematized in Fig. 1; that is, an evolution from a fivefold coordinated nonpolar structure with a relatively small band gap to a fourfold coordinated polar phase with a much larger band gap should occur, when progressively decreasing the Sc concentration in the alloy. A paraelectric-to-ferroelectric Tr_1 transition (yielding a large piezoelectric response) and a R_2 region associated with a change of coordination (leading to a band gap engineering) should thus occur along this path for some specific Sc compositions. Interestingly, varying x in hexagonal disordered $(Sc_{1-x}Ga_x)N$ alloys is likely more promising than varying the compressive strain in hexagonal ScN to practically grow materials bridging the semiconductor and ferroelectric fields. This, for at least two reasons. First of all, the equilibrium hexagonal phase of ScN is a *metastable* phase having a total energy higher by $\simeq 316$ meV/2 atoms [4] from the ground-state rocksalt phase of ScN [15,16,22]. Alloying ScN with GaN should overcome this energetic problem by favoring the emergence of hexagonal structures rather than rocksalt phases, since GaN has a rocksalt structure $\simeq 887$ meV/2 atoms [4] *higher in energy* than its hexagonal ground state. Second, ScN hexagonal structures close to the Tr_1 transition and the R_2 region are probably quite challenging to synthesize since they require a relatively large compressive strain (3.4% and 6.4%, respectively). On the other hand, realization of many technologically used materials [e.g., (Al,Ga,In)N/(Ga,In)N quantum wells] requires an interplay between the composition in the active layers and the strain induced by the substrate on top of which the active layers are grown. Consequently, we would like to suggest that the realization of multifunctional devices can be accomplished by *simultaneously* varying the compressive strain *and* the composition in *epitaxially grown* hexagonal $(Sc_{1-x}Ga_x)N$ alloys. For instance, one can imagine a disordered $(Sc_{1-x_1}Ga_{x_1})N$ solid solution for which the x_1 concentration yields a paraelectric phase *at the border* of undergoing the Tr_1 transition. Epitaxially growing such compound on a hexagonal substrate having a *slightly smaller* in-plane lattice constant will produce a compressive strain able to induce this Tr_1 transition, and thus will lead to large electromechanical responses. Similarly, it is possible to find the right combination between composition and small compressive strain induced by a substrate in epitaxially grown $(Sc_{1-x_1}Ga_{x_1})N$ alloys to have desired optical properties.

Finally, let us also point out that MgO-based materials may also result in the anomalies presently reported, because MgO also exhibits a fivefold coordinated hexagonal structure that is similar to the equilibrium phase of hexagonal ScN [8]. Many materials with different and simultaneously optimized properties may thus have been overlooked in the past. We thus hope that this Letter will encourage the experimental investigation of such fascinating compounds.

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[13] Note that the phonon calculations we performed predict that all the studied hexagonal structures exhibit phonon with positive frequencies and, therefore, are stable.
[14] The $P6_3/mmc$ space group phase exhibits a transverse optical mode at Γ having a negative frequency square (while exhibiting no soft modes at the zone boundaries), for strain $\geq 3.4\%$. The difference in the total energy between the $P6_3/mmc$ structure and the $P6_3/mc$ phase ranges between 0 and 0.34 eV per two atoms when η ranges between 3.4% and 6.8%, respectively.
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