Supporting Information

Ferroelectricity and Large Piezoelectric Response of AlN/ScN Superlattice

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Comparison Between Different Structures

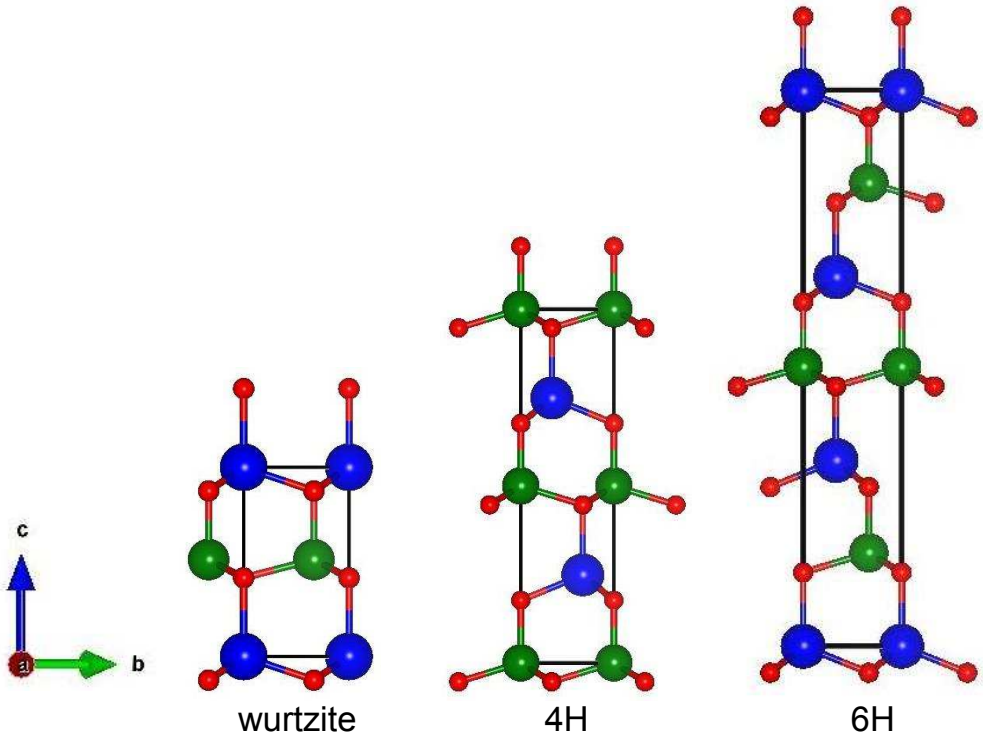

Figure S.1: Three different allotropes of ScAlN superlattice.

Our studied w-ScAlN consists of ScN and AlN buckled monolayers repeating along the c-direction in wurtzite structure . However, different structures (different allotropes) are also possible, for example, 4H and 6H structures are common for SiC. Note that wurtzite structure is also known as 2H structure in the literature. Here we compare energy of these three structures (shown in figure S1) for predicting their relative stability. We find that wurtzite structure is 0.040 eV/atom and 0.035 eV/atom more stable than 4H and 6H, respectively.

Comparison Between Different Functionals

Table 1: Calculated structural parameters and spontaneous polarization of w-ScAlN using LDA, GGA, and hybrid (HSE06) functionals.

Functional	a=b (Å)	c (Å)	u_{Al}	u_{Sc}	P_3(C/m^2)
LDA	3.301	5.062	0.369	0.421	1.084
GGA	3.333	5.207	0.363	0.416	1.115
Hybrid	3.332	5.181	0.363	0.417	1.105

Piezoelectric constants e_{ij}

Table 2: All independent piezoelectric constants in C/m^2.

Structure	e_{33}	e_{31}	e_{14}	e_{15}	e_{16}
w-AlN	1.46173	-0.58130	-0.29388	-0.29388	-
w-ScAlN	1.78755	-0.65032	-0.35337	-0.36219	-0.36442
w-ScAlN (5%)	3.82170	-0.64016	-0.10979	-0.12785	-0.51154

Partial Density of States (PDOS)

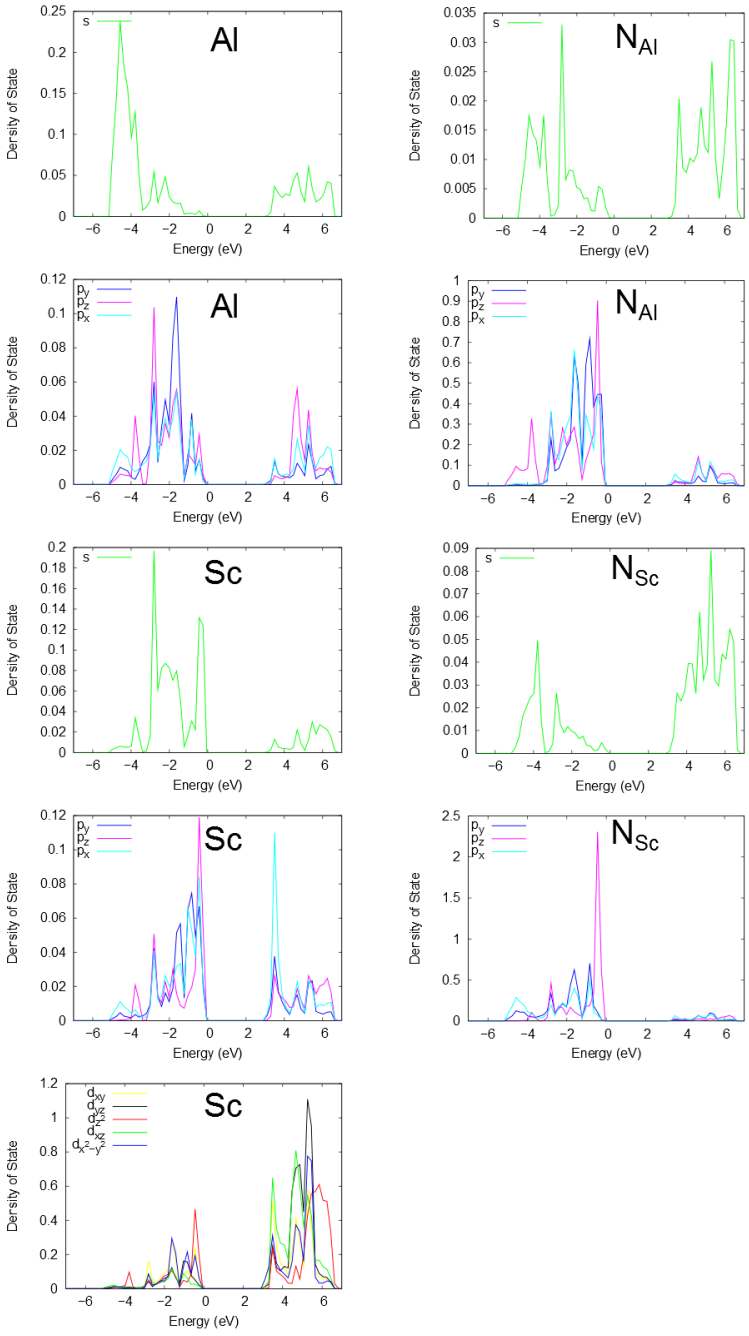

Figure S.2: Angular momentum decomposed partial densities of states (PDOS) of Al, N and Sc in w-ScAlN. N_{Al} (N_{Sc}) represents the N on top of Al (Sc).

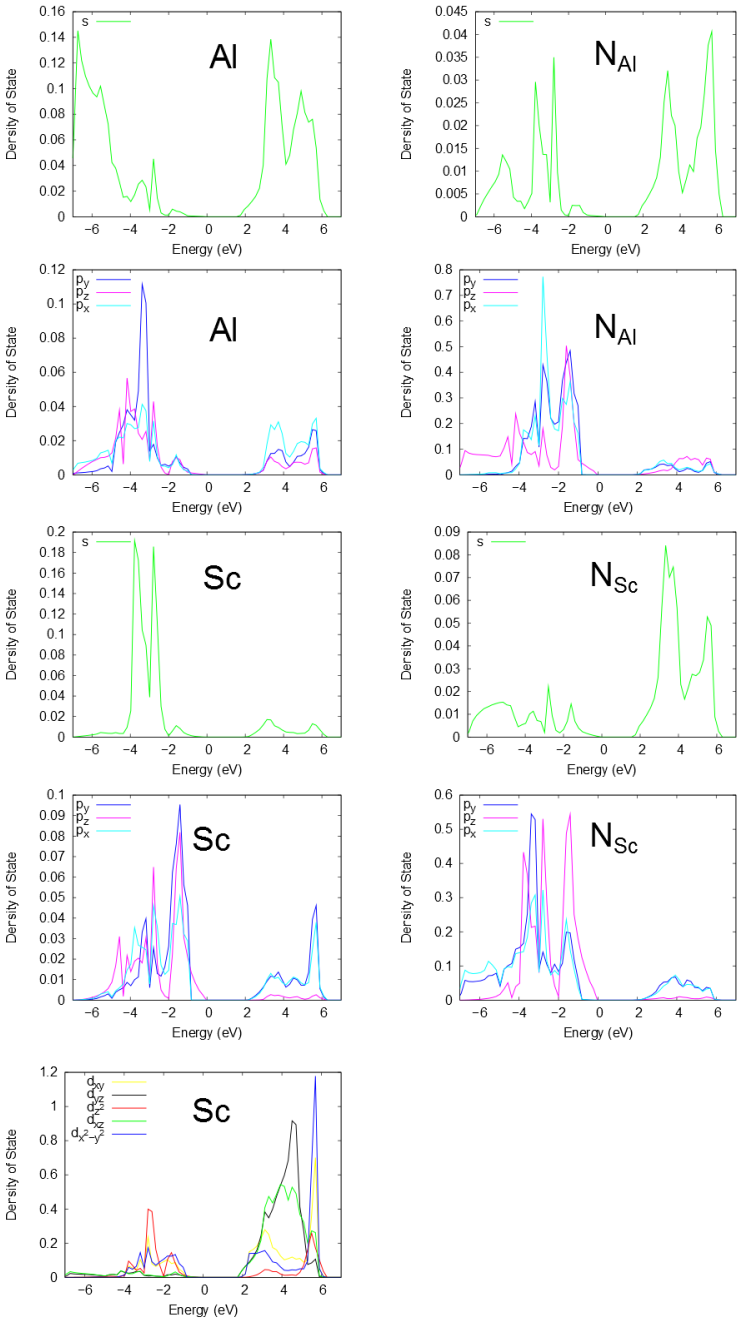

Figure S.3: Angular momentum decomposed PDOS of Al, N and Sc in h-ScAlN. N_{Al} (N_{Sc}) represents the N on top of Al (Sc).

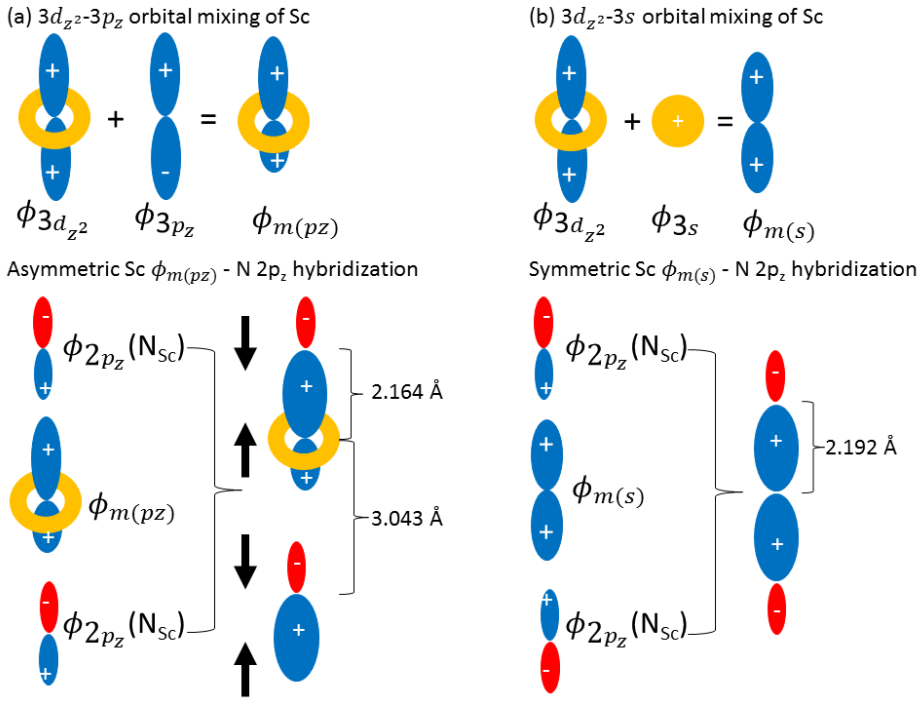

Figure S.4: (a) Schematic diagram of asymmetric Sc $\phi_{m(p_z)}$-N $2p_z$ hybridization in w-ScAlN and (b) schematic diagram of symmetric Sc $\phi_{m(s)}$-N $2p_z$ hybridization in h-ScAlN.

Phonon Modes Under Epitaxial Strain

The space group of w-ScAlN is P3m1 and the primitive unit cell consists of 4 atoms. From the group theory analysis, there are 9 optical modes at Γ with irreducible representation: $\Gamma_{\text{opt}} = 3\text{E} + 3\text{A}_1$, where E modes are doubly degenerate. The representation for each phonon band is shown in Fig. S5(a). L, M and H in bracket are used for labeling low, medium, and high frequency for both E and A_1 modes (Fig. S5(a)). The A_1 modes represent atomic vi-

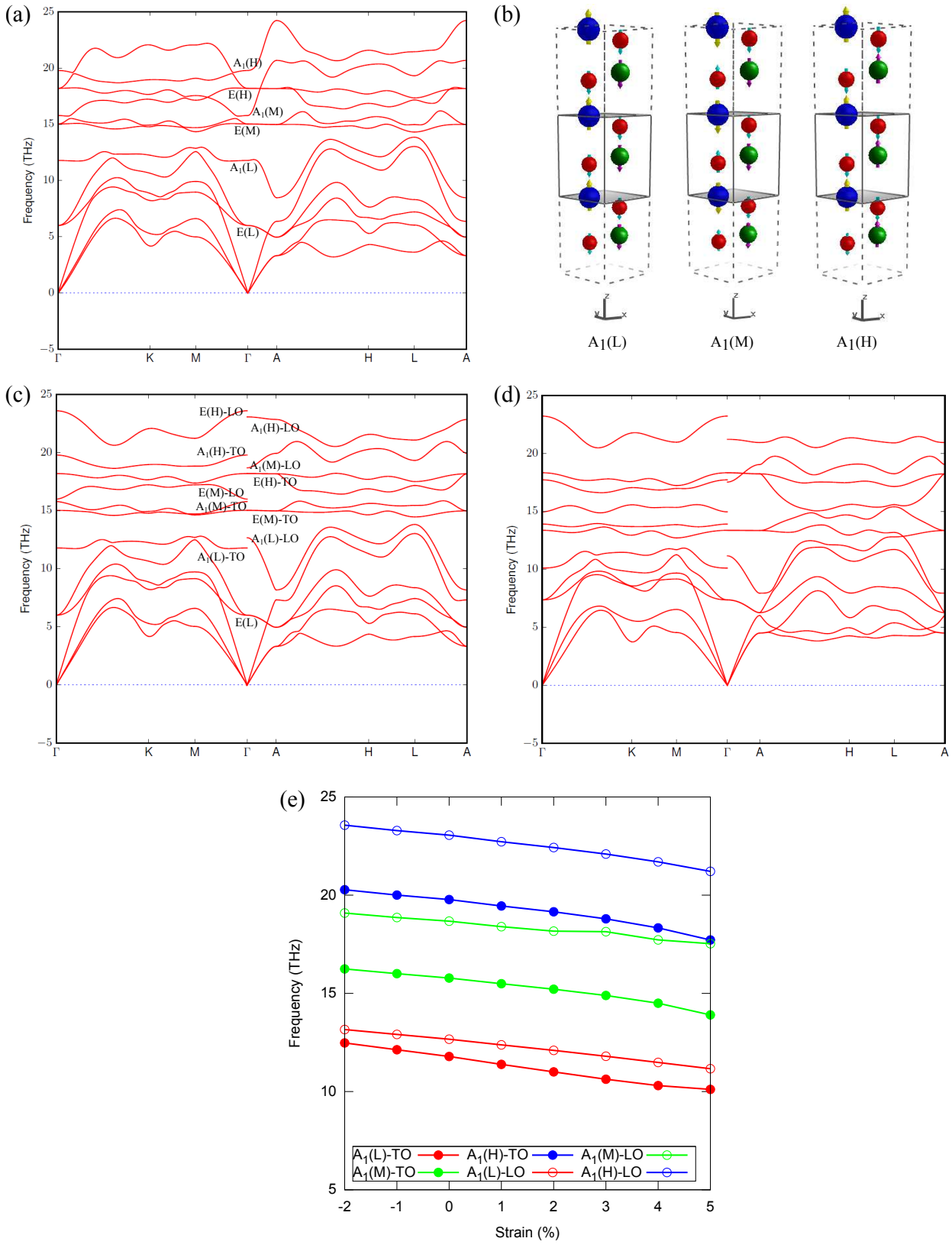

Figure S.5: (a) Phonon dispersion of unstrained w-ScAlN without considering the nonanalytic correction term arising from the long-range nature of the Coulomb interaction in the polar materials, (b) Schematic view of the displacement vectors for the three A_1 modes (c) phonon dispersion of unstrained w-ScAlN with considering the nonanalytic correction term and TO and LO bands are labeled, (d) phonon dispersion of w-ScAlN at 5% epitaxial tensile strain with considering the nonanalytic correction term, and (e) frequency of A_1modes (both TO and LO modes) as a function of epitaxial strain.

bration along the c-direction (along the z axis), while atoms vibrate in the xy plane for the E modes. Three A_1 modes along ΓA direction in the first Brillouin zone are shown in Fig. S5(b). A non-analytical term is added to dynamical matrix as implemented in the phonopy code to treat the long-range Coulomb interaction of macroscopic electric field induced by polarization of collective ionic motions near the Γ-point[1]. As a result of non-analytical term, E(M), E(H), and three A_1 modes are split into transverse optical (TO) and longitudinal optical (LO) components (Fig. S5(c)). Our calculated phonon dispersion for w-ScAlN with 5% epitaxial tensile strain shows no imaginary frequency in the whole first Brillouin zone ((Fig. S5(d))), indicating that the wurtzite structure remains dynamically stable even at 5% epitaxial tensile strain. However, phonon modes (we are mainly interested in A_1 modes as they represent atomic vibration along the c-direction parallel to the spontaneous polarization) become softer for tensile strain (shown in Fig. S5(e)). Note that similar softening of modes for biaxial strain is found for pure w-AlN[2]. Interestingly, leading to a structural instability to enhance piezoelectric response, phonon modes softening in Sc doped w-AlN has also been observed experimentally[3].

References

(1) Togo, A.; Tanaka, I. First principles Phonon Calculations in Materials Science. *Scr. Mater.* **2015**, *108*, 1–5.

(2) Wagner, J.-M.; Bechstedt, F. Properties of Strained Wurtzite GaN and AlN: Ab Initio Studies. *Phys. Rev. B* **2002**, *66*, 115202.

(3) Deng, R.; Jiang, K.; Gall, D. Optical Phonon Modes in Al1-xScxN. *Journal of Applied Physics* **2014**, *115*, 013506.