Stabilization of Wurtzite $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$ in Pseudomorphic Epitaxial $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ Superlattices

Agnė Žukauskaitė, Christopher Tholander, Ferenc Tasnádi, Björn Alling, Justinas Pališaitis, Jun Lu, Per O. Å. Persson, Lars Hultman and Jens Birch

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Agnė Žukauskaitė, Christopher Tholander, Ferenc Tasnádi, Björn Alling, Justinas Pališaitis, Jun Lu, Per O. Å. Persson, Lars Hultman and Jens Birch, Stabilization of Wurtzite $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$ in Pseudomorphic Epitaxial $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ Superlattices, 2015, Acta Materialia, (94), 101-110.

<http://dx.doi.org/10.1016/j.actamat.2015.04.033>

Copyright: Elsevier

<http://www.elsevier.com/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-103831>

Stabilization of Wurtzite $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$ in Pseudomorphic Epitaxial $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ Superlattices

Agnė Žukauskaitė^{1,2}, Christopher Tholander¹, Ferenc Tasnádi³, Björn Alling¹, Justinas Palisaitis¹, Jun Lu¹, Per O. Å. Persson¹, Lars Hultman¹, and Jens Birch¹

¹ Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden.

² Fraunhofer Institute for Applied Solid State Physics, Tullastr. 72, 79108 Freiburg, Germany

³ Theoretical Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden.

Abstract

Pseudomorphic stabilization in wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices ($x=0.2, 0.3$, and 0.4 ; $y=0.2-0.72$), grown by reactive magnetron sputter epitaxy was investigated. X-ray diffraction and transmission electron microscopy show that in $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ superlattices the compressive biaxial stresses due to positive lattice mismatch in $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}$ and $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$ lead to the loss of epitaxy, although the structure remains layered. For the negative lattice mismatched In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices, a tensile biaxial stress promotes the stabilization of wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ even for the highest investigated concentration $x=0.4$. *Ab initio* calculations with fixed in-plane lattice parameters show a reduction in mixing energy for wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ under tensile stress when $x \geq 0.375$ and corroborate the experimental results.

Keywords: Ab initio calculations; Sputter deposition; Nitrides; Superlattice; Metastable phases.

1. Introduction

Metastable wurtzite scandium aluminum nitride ($\text{Sc}_x\text{Al}_{1-x}\text{N}$) alloys have attracted a lot of attention recently. A 400% increase in piezoelectric response for $x=0.43$ [1] as well as an improved electromechanical coupling (k_t^2) [2-5] make this material a potential alternative to the commonly used pure AlN in telecommunication industry [6]. The anomalously large piezoelectric modulus d_{33} of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ was proposed to be related to softening of the material caused by a competition between Sc and Al atoms for the bonding coordination of nitrogen, due to a metastable layered hexagonal phase of ScN [7]. Mixing enthalpy calculations indicate that wurtzite phase is favored up to $x=0.55-0.56$ [8,9]. This suggests that further improvement in application-relevant material properties would be possible by increasing the Sc concentration. However, experimental studies show a driving force for promoting phase separation into more stable wurtzite AlN and cubic rock-salt ScN at elevated growth temperatures and Sc concentration $x \geq 0.3$ [10]. Band gap energy measurements indicate a structural instability around $x=0.2$, leading to rock-salt ScN grains within $\text{Sc}_x\text{Al}_{1-x}\text{N}$ matrix in samples deposited at 850 °C [11].

Our previous *ab initio* theoretical study of ternary group IIIA-IIIB nitrides shows that the energy minimum in the potential-energy landscape shifts towards lower c/a values [12]. Furthermore, a general volume matching argument has been introduced to select alloying elements for giant piezoelectric response [12]. The in-plane lattice parameter a increases due to larger atomic volume of ScN as compared to AlN, leading to distortions in bond angle β [11,13], thus changing the c/a ratio. It has been theoretically predicted that epitaxial stabilization of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ up to $x=0.4$ could hinder the material disintegration through spinodal decomposition [8]. However, phase separation through nucleation and growth of semicoherent wurtzite AlN phases in domain boundaries of cubic ScN has been demonstrated during annealing of cubic solid solutions [14] and might be a limiting factor for alloy formation during thin film growth.

Ab initio calculations show that the structural properties of ScN in GaN/ScN and InN/ScN superlattices with overall Sc concentration less than 50% are closer to wurtzite than the layered hexagonal phase [15]. Additionally, the epitaxial stabilization approach was successfully utilized to stabilize cubic AlN in a TiN/AlN superlattice [16,17]. Recently, this technique was also used to stabilize cubic $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in sandwiched TiN/ $\text{Sc}_x\text{Al}_{1-x}\text{N}$ /TiN structures with up to $x=0.82$, and subsequently – in cubic TiN/(Al,Sc)N multilayers [18,19]. Theoretical critical thickness calculations of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{GaN}$

heteroepitaxial systems using an energy balance model show that the critical thickness can vary between 2 nm and infinity, depending on lattice mismatch [20]. Highest critical thickness values were obtained for lattice matched $\text{Sc}_{0.18}\text{Al}_{0.82}\text{N}/\text{GaN}$, however, it should be noted, that kinetic limitations and other processes occurring during growth can allow thicker layers to be deposited, and that even small changes in the in-plane lattice parameters contribute to large uncertainties in these calculations. Also, the non-existent metastable ScN phases were not taken into account. Here we use epitaxial superlattice structures to explore the pseudomorphic (epitaxial) stabilization of wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ with up to $x=0.4$.

The effects of the stress, induced by different stabilizing layers, on the nucleation and phase stability of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ ($x=0.2, 0.3, 0.4$) can be investigated by introducing zero, positive, and negative in-plane lattice mismatch, thus influencing the nominal c/a ratio in ideally strained epitaxial $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers. For this purpose, three types of epitaxial superlattice structures were produced: 1) $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$, where the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers are subjected to compressive stress due to a larger in-plane lattice parameter as compared to wurtzite AlN; 2) nearly lattice matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$, where the In concentration was tuned to match $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in-plane; and 3) $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In-rich In}_y\text{Al}_{1-y}\text{N}$, where $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers experience biaxial tensile stress due to smaller in-plane lattice parameter compared to $\text{In}_y\text{Al}_{1-y}\text{N}$. In addition, *ab initio* mixing enthalpy calculations within the density functional theory (DFT) [21] framework were carried out to investigate the effect of different stress states on stability of wurtzite and layered hexagonal $\text{Sc}_x\text{Al}_{1-x}\text{N}$ with respect to phase separation, caused by different fixed values of the in-plane lattice parameter.

Strain is typically present in the films due to stresses caused by lattice mismatch between the layers. The more Sc is incorporated in the $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ superlattice, the larger the lattice mismatch becomes, laterally compressing the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers more and more if non-relaxed epitaxy is sustained. On the other hand, if the in-plane lattice parameter of $\text{In}_y\text{Al}_{1-y}\text{N}$ is tune [22], lattice match to $\text{Sc}_x\text{Al}_{1-x}\text{N}$ can be achieved, or, in the case of In-rich $\text{In}_y\text{Al}_{1-y}\text{N}$, tensile biaxial stress can be induced in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ during the initial stages of the growth. However, as the individual stress and strain states in the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers are unknown, we will refer only to the lattice mismatch further on.

2. Experimental details

A series of samples with varying Sc concentration and different superlattice periods was prepared onto $\text{Al}_2\text{O}_3(0001)$ substrates at heater temperatures T_H of 500-700 °C in a ultra high

vacuum (UHV) deposition system with a base pressure of 4×10^{-6} Pa. Magnetically unbalanced reactive DC magnetron sputtering in Ar/N₂ gas mixture (99.999999% pure) at a total process pressure of 0.66 Pa was performed. Separate elemental targets of In (99.995% pure), Al (99.9995% pure), and Sc (99.99% pure) were used in a constant power mode.

The Al₂O₃(0001) substrates were ultrasonically cleaned in trichloroethylene, acetone, and isopropanol, as well as blown dry with N₂ prior to placing them in the growth chamber through a load-lock system. After thermal degassing at the selected T_H for 1 h, Al and Sc targets were clean-sputtered in Argon for 5 min before starting the deposition. Sc_xAl_{1-x}N/AlN superlattices were deposited on 50 nm thick high temperature (HT) AlN(0001) seed layers. Cubic HT ScN(111) with $d_{\{110\}} = 3.18$ Å was used as a seed layer in the case of Sc_xAl_{1-x}N/In_yAl_{1-y}N due to closer in-plane lattice match to In_yAl_{1-y}N in comparison to wurtzite AlN $a = 3.11$ Å. Also, during growth of Sc_xAl_{1-x}N/In_yAl_{1-y}N, a negative potential of 15 V was applied to the substrate to enhance the ad-atom mobility [23,24].

X-ray reflectivity (XRR) and x-ray diffraction (XRD) measurements of separately grown thin films of AlN, In_yAl_{1-y}N and Sc_xAl_{1-x}N were performed to estimate the growth rate as well as the composition. The magnetron powers were later adjusted to produce superlattice samples with $x = 0.2, 0.3$, and 0.4 in Sc_xAl_{1-x}N layers with periods $\Lambda = 8$ and 16 nm. Total superlattice thickness was kept constant at 240 nm, while the number of periods was varied between 15 and 30 for $\Lambda = 16$ and $\Lambda = 8$ nm, respectively. In_yAl_{1-y}N in-plane lattice constants were obtained using Vegard's rule, based on a study of magnetron sputtered InN by Hsiao *et al.* [22]. Concentrations x and y were chosen such that the in-plane lattice mismatch $\delta = (a_{\text{ScAlN}} - a_{\text{InAlN}}) / a_{\text{InAlN}}$ varied from -3% to $+7\%$ throughout the deposition series. A list of grown superlattice samples, showing the nominal compositions, estimated in-plane lattice parameters, and lattice mismatch values, can be found in Table I.

Table I. Layer compositions, in-plane lattice parameters, calculated lattice mismatch δ values, and stress states based on δ of investigated superlattices.

x in Sc _x Al _{1-x} N	y in In _y Al _{1-y} N	ScAlN a [Å] from [9]	InAlN a [Å]	Lattice mismatch δ [%]	Stress state
0.2	0	3.23	3.11	3.86	Compressive stress in Sc _x Al _{1-x} N layers
0.3	0	3.28	3.11	5.47	
0.4	0	3.33	3.11	7.07	
0.2	0.2	3.23	3.20	0.94	Nearly lattice matched to In _y Al _{1-y} N
0.3	0.37	3.28	3.28	0.14	
0.4	0.45	3.33	3.31	0.55	
0.2	0.38	3.23	3.28	-1.55	Tensile stress in Sc _x Al _{1-x} N layers
0.3	0.52	3.28	3.34	-1.92	
0.4	0.72	3.33	3.43	-3.03	

XRD for phase analysis and superlattice characterization and XRR measurements were done with a Philips Bragg-Brentano diffractometer in the $\theta/2\theta$ mode. Average in-plane lattice parameters were investigated by reciprocal space mapping (RSM) of the $10\bar{1}5$ reflection using a Philips X'Pert MRD diffractometer in low-resolution mode. Microstructural analysis was performed using a Tecnai TF20 UT FEG transmission electron microscope (TEM) operated at 200 kV. Cross-sectional electron transparent samples were prepared by mechanical cutting and polishing, followed by Ar⁺ ion milling. Scanning TEM (STEM) and energy dispersive x-ray spectroscopy (EDX) maps were acquired using a ~ 1 nm² probe size.

The Sc_xAl_{1-x}N alloys were modeled at compositions $x=0.125, 0.25, 0.375$, and 0.5 , according to the special quasirandom structure (SQS) [25] method using 128 atom supercells. In the simulations the projected augmented wave (PAW) [26] method implemented in the Vienna Ab-initio Simulation Package (VASP) [27,28] was used with Perdew, Burke, Ernzerhof generalized gradient approximation (PBE-GGA) [29] for the exchange-correlation functional. We applied a $3\times 3\times 3$ Monkhorst-Pack [30] k-mesh and an energy cutoff of 400 eV in all calculations. Fixed in-plane lattice parameters $a_0=3.1318$ Å, 3.2884 Å, 3.4450 Å, and 3.6227 Å were used. The lowest one corresponds to the in-plane lattice parameter of wurtzite AlN ($\delta>0$), the second and the third are an additional 5% ($\delta=0$) and 10% ($\delta<0$) increase, and the largest one corresponds to wurtzite InN. For these parameters, we calculate the total energy of the wurtzite (B4), layered-hexagonal (B_k), and cubic rock-salt (B1) phases of ScN and AlN, to see which phases are favored at the different in-plane lattice parameters. To have the most relevant comparison between the B1 phase and the hexagonal phases, a B1 based supercell with suitable geometry was constructed so that the free c -parameter of the cell correspond to the cubic [111] direction while the other two lattice constants, $d_{\{110\}}=a_0$ lay in the close-packed (111) plane and were being subjected to the constrains. For each considered in-plane lattice parameter a_0 , the mixing energies were calculated with all phases and compositions being constrained in-plane according to:

$$\Delta E_{a_0}^{B4/B_k}(x) = E(\text{Sc}_x\text{Al}_{1-x}\text{N})_{a=a_0}^{B4/B_k} - xE(\text{ScN})_{a=a_0}^{\text{ref}} - (1-x)E(\text{AlN})_{a=a_0}^{\text{ref}}, \quad (1)$$

where $E(\text{Sc}_x\text{Al}_{1-x}\text{N})_{a=a_0}^{B4/B_k}$ is the energy of the alloy in structure B4 or B_k with the constrained in-plane lattice parameter value of a_0 . $E(\text{ScN})_{a=a_0}^{\text{ref}}$ is the reference energy of the most favorable phase of pure ScN given the constrained value of a_0 , and $E(\text{AlN})_{a=a_0}^{\text{ref}}$ is the corresponding reference energy of pure AlN in its most favorable phase at $a=a_0$.

3. Results

3.1 Growth study

Fig. 1 shows XRD scans of three superlattices samples with $\Lambda=8$ nm: $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$ ($\delta>0$), $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ ($\delta\approx 0$), and $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$ ($\delta<0$). All observed diffraction peaks correspond to wurtzite c -axis (0001) superlattice structures and the Al_2O_3 substrate. No additional crystal orientations were observed in the films. In Fig. 1, the bottom scan shows a diffraction pattern from the $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$. The peak intensity is rather low, and only the AlN seed layer and the average superlattice peak could be indexed, marked as “seed layer” and “0” in Fig. 1 (bottom). The lattice matched $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ XRD pattern (Fig. 1, middle) shows a definite improvement over $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$ both in terms of intensity and the number of observed superlattice peaks. Here, the average superlattice peak and its negative and positive satellites are indexed with 0, $-n$, and $+n$, respectively. The top-most scan in Fig. 1 is from In-rich $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$. From all three investigated cases, the peak intensities were highest in this structure, and more satellite peaks could be resolved.

FIG. 1. X-ray diffraction patterns of $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$ (bottom), $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ (middle), and $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$ (top) superlattice samples with period thickness $\Lambda=8$ nm.

For each investigated lattice mismatch case, a composite stacked superlattice sample was prepared for the (S)TEM and EDX analyses. Consecutively grown $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ superlattices with different Sc concentrations ($x=0.2, 0.3$, and 0.4) were separated by 50 nm thick buffer layers of $\text{AlN}(0001)$. Buffer layers of cubic $\text{ScN}(111)$ were used in $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$. For each Sc concentration, a Λ -series of 5-10 periods for $\Lambda=4, 8$, and 16 nm were deposited on top of each other.

A STEM micrograph of the resulting $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ sample is shown in Fig. 2(a). The image exhibits strong mass contrast, hence the Sc-containing layers are identified as bright. For all three investigated Sc concentrations, the superlattice structures can be clearly resolved

for $\Lambda=8$ and 16 nm. The layer waviness as well as cumulative roughness is low, but increases with higher Sc concentration. At the lowest Sc concentration the sample microstructure has some indications of columnar growth, but at $x=0.3$ and 0.4 the columns are hardly discernible. The accumulated surface roughness is an indication of limited ad-atom mobility. In the case of lattice-matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ (Fig. 2(b)), pronounced columnar growth is present both for $x=0.2$ and $x=0.3$, however, the roughness of the layers is very high already starting from $x=0.2$, despite the application of negative substrate bias that should be beneficial for the flattening of the layers during growth. The roughness is transferred through the buffer layer into the next sample section, leading to the presence of both cumulative and correlated roughness. At the highest investigated Sc concentration $x=0.4$ the superlattice structure becomes strongly distorted. Fig. 2(c) shows results from In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$. Columnar growth is present throughout the sample, but the layer waviness and sample roughness is lower than for the lattice-matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ (see Fig. 2(b)).

FIG. 2. Scanning TEM micrographs for cross-section of composite stacked superlattice samples: (a) positive lattice mismatched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ with $x=0.2, 0.3$ and 0.4 , (b) lattice matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ with $x=0.2, y=0.2, x=0.3, y=0.37$, and $x=0.4, y=0.45$, and (c) negative lattice mismatched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ with $x=0.2, y=0.38, x=0.3, y=0.52$, and $x=0.4, y=0.72$.

The homogeneity of the superlattices with $\Lambda=16$ nm, shown in Fig. 2, was investigated using STEM-EDX elemental maps of $50 \times 50 \text{ nm}^2$. The larger period thickness was preferred for this type of measurement due to possible overlapping and beam broadening effects caused by roughness. The results from $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ with $x=0.3$ and $x=0.4$ are displayed in Fig. 3(a) and Fig. 3(b), respectively. For $x=0.3$, the thickness of the AlN layers appears to be smaller than the intended 8 nm, making it difficult to estimate the distribution of Sc. In the case of

$x=0.4$ (Fig. 3(b)) the layer boundaries are sharp, and Sc seems to be contained within the $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$ layers. The superlattices with lattice matched and negative lattice mismatched $\text{Sc}_x\text{Al}_{1-x}\text{N}$ also retain good elemental separation of In and Sc for samples with $x=0.3$ (Fig. 3(c) and Fig. 3(e)). However, when the Sc concentration is increased to $x=0.4$ the lattice-matched SL becomes very disordered and the multilayer structure is lost (Fig. 3(d)). In the In-rich sample ($\delta < 0$) well-separated $\text{In}_y\text{Al}_{1-y}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers are maintained (Fig. 3(f)). These results corroborate the XRD results shown in Fig. 1, where In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattice structures maintain higher layer integrity.

FIG. 3. Cross-sectional energy dispersive spectroscopy maps, where indium is mapped in purple, and scandium in green for $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ (a) $x=0.3$, (b) $x=0.4$, lattice matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ (c) $x=0.3$ $y=0.37$, (d) $x=0.4$ $y=0.45$, and negative lattice mismatched (e) $x=0.3$ $y=0.52$ and (f) $x=0.4$ $x=0.72$ superlattice samples with $\Lambda=16$ nm.

FIG. 4. Cross-sectional HRTEM micrographs of $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ along the $[01\bar{1}0]$ zone axis with (a) $x=0.2$, (b) $x=0.3$, and (c) $x=0.4$; In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ with (d) $x=0.2$ $y=0.38$, (e) $x=0.3$ $y=0.52$, and (f) $x=0.4$ $y=0.72$.

The cross-sectional high resolution TEM (HRTEM) micrographs in Fig. 4 show samples with $\delta > 0$ and $\delta < 0$ in the left and in the right columns, respectively. Due to similar electron density of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ and AlN, the multilayer contrast is vague in Fig. 4(a)–(c) (left column), while $\text{In}_y\text{Al}_{1-y}\text{N}$ layers are slightly darker than $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in Fig. 4(d)–(f) (right column). At low Sc content ($x=0.2$), both $\text{Sc}_{0.2}\text{Al}_{0.8}\text{N}/\text{AlN}$ (Fig. 4(a)) and $\text{Sc}_{0.2}\text{Al}_{0.8}\text{N}/\text{In}_{0.38}\text{Al}_{0.62}\text{N}$ (Fig. 4(d)) show well-ordered epitaxial crystal structures, where lattice fringes are continuous through the individual layers. When the Sc content is increased to $x=0.3$, the crystal quality of the $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$ superlattice is deteriorated (Fig. 4(b)), and the structure is composed of crystallites with no visible preferred orientation. On the other hand, when $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers are negative lattice mismatched at $x=0.3$, the $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$ superlattice (Fig. 4(e)) maintains the crystalline coherency between the layers and well-ordered c -axis oriented growth is observed. However, the roughness is higher than in the case of $\text{Sc}_{0.2}\text{Al}_{0.8}\text{N}/\text{In}_{0.38}\text{Al}_{0.62}\text{N}$. At the highest investigated Sc concentration ($x=0.4$), the crystalline

quality of $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}/\text{AlN}$ deteriorates even further (Fig. 4(c)). In $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}/\text{In}_{0.72}\text{Al}_{0.28}\text{N}$ (Fig. 4(f)) an apparent epitaxial growth is retained with visibly distorted basal planes.

The diffraction patterns for superlattices with $\delta > 0$ and $\delta < 0$ for three different Sc concentrations ($x=0.2$, 0.3 , and 0.4) are displayed in Fig. 5. For the positive lattice mismatched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ superlattice (Fig. 5(a)), well-developed superlattice satellite peaks could only be seen and indexed at the lowest investigated Sc concentration $x=0.2$. At Sc content $x=0.3$ some peaks are visible, but their intensities are low, and they cannot be assigned to the superlattice structure. At even higher Sc content, only the 0002 peak from the AlN seed layer remains. Fig. 5(b) shows XRD patterns for In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices. Due to the increasing amount of In to match the increasing amount of Sc, the zero order superlattice peak (indexed as 0) shifts towards lower angle values when x goes from 0.2 to 0.4 . At the same time the peak intensities decrease, although the superlattice satellite peaks (indexed as $+n$ and $-n$) in the diffraction pattern clearly show that an ordered superlattice structure is still present at $x=0.4$. These results are in agreement with observations made from STEM and HRTEM micrographs (Fig. 2 and Fig. 4).

FIG. 5. X-ray diffraction patterns of $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$, $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.37}\text{Al}_{0.63}\text{N}$, and $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$ superlattice samples with period thickness $\Lambda=8$ nm.

Similar XRD analysis of $\Lambda=16$ nm superlattices was also performed, but is not shown here, as the same trends were observed: the peak intensities decrease with increased Sc concentration, there are no superlattice satellite peaks in the case of $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}/\text{AlN}$, and distinct superlattice satellites indicating good crystalline quality in the case of In-rich $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}/\text{In}_{0.72}\text{Al}_{0.28}\text{N}$ are present.

The XRD scans (Fig. 1 and Fig. 5), as well as additional scans from lattice matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ (not shown) were also used to calculate the superlattice period Λ using the following expression: $\Lambda = \lambda / 2(\sin \theta_{n+1} - \sin \theta_n)$ [31]. Here, $\lambda = 1.5406 \text{ \AA}$ is the characteristic X-ray wavelength for Cu $K\alpha_1$, θ_{n+1} and θ_n – adjacent satellite peak positions, and n – the satellite order. For samples with intended $\Lambda = 8 \text{ nm}$ and $\Lambda = 16 \text{ nm}$, the actual values varied in the range of 7.5-8.5 nm, and 15.0-17.5 nm, respectively.

FIG. 6. Reciprocal space maps of $10\bar{1}5$ reflection in In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$: (a) $x=0.2$ $y=0.38$, (b) $x=0.3$ $y=0.52$, and (c) $x=0.4$ $y=0.72$.

In order to determine the average in-plane lattice parameters of superlattices with negative lattice mismatch, XRD RSM of the asymmetric $10\bar{1}5$ reflection from In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ were recorded. The results are shown in Fig. 6. A mosaicity due to crystal imperfections, as is evident by the spread in the ω direction, is present for all x . In the sample with $x=0.2$ (Fig. 6(a)), 5 peaks originating from the superlattice can be distinguished, and the average in-plane lattice parameter $a=3.24 \text{ \AA}$ could be extracted from the main superlattice peak. Upon increasing x and y , the structure factor changes and superlattice peaks separate into two groups due to the combined effect of an increasing negative lattice mismatch and an increasing amount of In in relation to Sc. The RSM of the sample with $x=0.3$ is shown in Fig. 6(b), here, in addition to peaks from the superlattice, the $11\bar{2}12$ reflection from the Al_2O_3 substrate is also visible on the right side. The position of the main superlattice peak corresponds to average in-plane lattice parameter $a=3.32 \text{ \AA}$. Fig. 6(c) shows RSM from $x=0.4$, the in-plane lattice parameter at the main superlattice peak position is $a=3.37 \text{ \AA}$. These experimental values are in agreement with the corresponding theoretical average lattice parameters: a_{avg} for $(x=0.2; y=0.38)$, $(x=0.3; y=0.52)$, and $(x=0.4; y=0.72)$ is $3.26 \text{ \AA}$, $3.31 \text{ \AA}$, and $3.38 \text{ \AA}$ respectively, as calculated from data in Table I.

3.2 Phase stability calculations

To qualitatively explain how in-plane lattice strain affects the phase separation tendency, an *ab initio* theoretical phase stability study based on mixing energies (eq. 1) of the cubic (B1), wurtzite (B4), and hexagonal (B_k) $Sc_xAl_{1-x}N$ alloys was performed for $x= 0.125, 0.25, 0.375$, and 0.5 . The in-plane lattice parameter a_0 was fixed at values $3.1318, 3.2884, 3.4450$, and $3.6227 \text{ \AA}$ to reflect the scope of the experimental part of this study, with lattice mismatch $\delta>0, \delta=0$, and $\delta<0$. On the other hand, the c parameter was allowed to relax. For all considered values of a_0 , B1-ScN is the most favorable reference phase at $x=1.00$. For pure AlN ($x=0.00$) the B4 phase is the most favorable reference when $a=3.1318$, and $3.2884 \text{ \AA}$, while for $a=3.4450 \text{ \AA}$, the B_k phase is lowest in energy. The largest in-plane parameter $a=3.6227 \text{ \AA}$ adheres to the B_k -ScN and B_k -AlN as the most stable phases.

FIG. 7. Calculated mixing enthalpy of $Sc_xAl_{1-x}N$ with fixed in-plane lattice parameters: wurtzite B4- $Sc_xAl_{1-x}N$ when $a=3.1318 \text{ \AA}$ (■), $a=3.2884 \text{ \AA}$ (●), $a=3.4450 \text{ \AA}$ (▼), and hexagonal B_k - $Sc_xAl_{1-x}N$ when $a=3.4450 \text{ \AA}$ (▲), and $a=3.6227 \text{ \AA}$ (x). Relaxed B4- $Sc_xAl_{1-x}N$ values (◇) are taken from C. Höglund *et al.*, Ref. [9]. The lines are guides for the eye.

Fig. 7 shows the resulting mixing energies ΔE_{mix} of the B4 phase calculated according to (eq. 1), for all four investigated in-plane lattice spacings. The B_k phase is included for the two largest lattice spacings since it is only there that it is competitive with the B4 phase. As a comparison, we are also including ΔH_{mix} of B4- $Sc_xAl_{1-x}N$ from the previously published $Sc_xAl_{1-x}N$ study by C. Höglund *et al.* [9], where both c and a parameters were allowed to relax independently for each composition. ΔE_{mix} was positive in all investigated cases, confirming that $Sc_xAl_{1-x}N$ is metastable with a tendency for phase separation. B4- $Sc_xAl_{1-x}N$ with $a=3.1318 \text{ \AA}$, corresponding to a_0 of pure B4-AlN, has the highest ΔE_{mix} that increases linearly as a function of x , exceeding the energy of the relaxed wurtzite structure. This

correlates with our experimental XRD and TEM results, where we show that the crystalline quality of $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ superlattice deteriorates rapidly when $x > 0.2$. However, for both $a = 3.2884 \text{ \AA}$ and $a = 3.4450 \text{ \AA}$ the mixing enthalpy is lower than the values obtained in Ref. [9]. These in-plane lattice parameters are close to nominal a of the $\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ and $\text{In}_{0.72}\text{Al}_{0.28}\text{N}$ (Table I) that are nearly lattice-matched to $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}$ and a negative lattice mismatch in $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$, respectively. $\text{Sc}_x\text{Al}_{1-x}\text{N}$ with the largest in-plane parameter, corresponding to B4-InN, is only stable for $x \geq 0.5$, and only in the B_k phase.

Table II. Theoretical in-plane lattice parameters of wurtzite (B4) and hexagonal (Bk) AlN and ScN, and cubic (B1) ScN in ascending order. *Wurtzite ScN parameter was obtained from a local minimum in the energy landscape by using fixed $c/a = 1.6$ ratio of a wurtzite structure.

Crystal structure	a	c/a
B4-AlN	3.1318	1.602
B1-ScN(111)	3.1822	1.732
Bk-AlN	3.3146	1.263
B4-ScN*	3.4681	1.600
Bk-ScN	3.7143	1.214

To understand the trend of decreasing mixing energies of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys with increasing in-plane lattice spacing, we must consider the equilibrium lattice parameters of both the alloys and the competing pure ScN and AlN phases. According to [9], the calculated a -parameter of B4 $\text{Sc}_x\text{Al}_{1-x}\text{N}$ goes from $3.13 \text{ \AA}$ ($x=0.0$) to $3.38 \text{ \AA}$ ($x=0.5$) more or less linearly. The calculated lattice a -parameters of the competing pure B4, B_k AlN and B1, B4, as well as B_k ScN phases are presented in Table II. (111)-oriented B1-ScN has in-plane spacing $d_{110} = 3.1822 \text{ \AA}$, while B4-AlN has $a = 3.1318 \text{ \AA}$ and B_k -AlN has $a = 3.3146 \text{ \AA}$. The latter comes into relevance only at the two largest investigated in-plane lattice spacings. It should be noted, that a metastable B4-ScN with $a = 3.4681 \text{ \AA}$ can only exist with a fixed in-plane lattice parameter. Therefore, we used a local minimum in the energy landscape at fixed $c/a = 1.6$ for this comparison.

4. Discussion

The XRD pattern for $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ (Fig. 1 middle), $\delta \approx 0$, implies a clear improvement in crystalline quality as well as layer definition in comparison to $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{AlN}$ (Fig.1 bottom), $\delta > 0$. A shift of the zero order superlattice peak towards lower 2θ values is also evident, which is attributed to an increase in the average lattice parameters of the superlattice, as $\text{In}_{0.37}\text{Al}_{0.63}\text{N}$ has a larger unit cell than AlN. The highest peak intensity and well resolved satellite peaks in the case of $\text{Sc}_{0.3}\text{Al}_{0.7}\text{N}/\text{In}_{0.52}\text{Al}_{0.48}\text{N}$ (Fig.1 top), $\delta < 0$, indicate that a negative lattice mismatch has a positive effect on the crystalline quality as well as layer definition of $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices.

These experimental results support mixing enthalpy results for relaxed and differently strained $\text{Sc}_x\text{Al}_{1-x}\text{N}$ (Fig. 7). As expected from the calculations, growth under conditions of $\delta > 0$ results in an even more pronounced destabilization of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers, than the close-to fully relaxed state with $\delta \approx 0$. The increase in mixing energies when the a -parameter is fixed and small can be understood as the Sc-containing B4 alloys getting under increasingly compressive stress with increasing x . On the other hand, the competing B4-AlN and B1-ScN are on spot or near to their equilibrium values. This combination results in an increased value of ΔE_{mix} and consequently larger difficulties in growing the solid solutions. The intermediate in-plane lattice constant $a = 3.2884 \text{ \AA}$ is, as was the purpose, close to the equilibrium value for the B4 alloy with $x = 0.25$ [9]. On the other hand, the competing pure nitrides are less favorable as they are destabilized by biaxial tensile stress. This leads to a weaker driving force for phase separation in terms of lower positive mixing energies, as compared to the case with smaller in-plane lattice constant, as well as the fully relaxed situation. For the larger in-plane lattice constant, $a = 3.4450 \text{ \AA}$, the pure AlN phase is under such high tensile stress, that the normally very unfavorable $\text{B}_k\text{-AlN}$ becomes the most competitive structure. Though cubic B1-ScN is still the most energetically competitive phase at $x = 1.0$, in this case the lattice spacing is closer to that of hypothetical B4-ScN. At this large in-plane lattice constant the binaries are considerably less competitive due to very large tensile stress while the alloys, although strained, are relatively less distorted from their equilibrium lattice constants. This results in an even smaller positive value of the mixing energies. However, at even higher in-plane lattice parameter $a = 3.6227 \text{ \AA}$, only the $\text{B}_k\text{-ScN}$ and $\text{B}_k\text{-AlN}$ are stable. This presents an upper limit of the in-plane parameter, between $a = 3.4450 \text{ \AA}$ and $a = 3.6227 \text{ \AA}$, where B4-ScN becomes unstable and thus also any $\text{B4-Sc}_x\text{Al}_{1-x}\text{N}$.

Previous studies of $\text{In}_y\text{Al}_{1-y}\text{N}$ show a tendency for random compositional fluctuations during the early stages of growth, which leads to a wavy surface [32], and may explain the higher degree of roughness observed in our $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ samples that is not present in $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$. In our previous study of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ thin films, we demonstrated a correlation between columnar microstructure and good crystalline quality [10], suggesting that the columnar microstructure in the present $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices also indicates an improved crystalline quality. Even for the highest investigated Sc concentration ($x=0.4$) the layered structure is present and well defined. It should be noted that EDX elemental mapping showed no intermixing, even between the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ and AlN layers (Fig. 3(a) and (b)), indicating that the deterioration of crystalline quality inside individual layers due the positive lattice mismatch does not lead to elemental intermixing between layers. The deterioration of the superlattices with increasing x , observed in the low magnification STEM micrographs (Fig. 2(b)), and EDX elemental maps (Fig. 3(c) and (d)) shows that no epitaxial stabilization of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in lattice matched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices was obtained. Therefore, further investigations were focused the other two extreme cases of positive lattice mismatched $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ and negative lattice mismatched In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$, $\delta>0$ and $\delta<0$, respectively. According to the lattice period thickness calculations, there are no correlations with the Sc concentration or the choice of the stabilizing layer. However, in all of the investigated samples, the XRD peak intensity was decreasing when the Sc concentration increased, and in the case of $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{AlN}$ with $x=0.3$ and 0.4 the satellite peak positions could not be used for accurate calculations.

It is interesting to notice that for small Sc content, the large tensile stress results in stabilization of the B_k -phase that has a larger a -parameter as compared to the B_4 phase. However, at the compositions $x=0.375$ and 0.5 , the increasing Sc-content restabilizes the B_4 -alloys since the Sc atoms are so much larger than the Al atoms and would need an even larger in-plane lattice constant to prefer the B_k -phase. For instance, pure B_k -ScN has an equilibrium a -parameter of $3.7143 \text{ \AA}$.

The qualitative result of *ab-initio* calculations that the large negative in-plane lattice mismatch reduces the tendency for phase separation by destabilizing the pure binary nitrides and consequently stabilizing the wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys agrees well with our experimental observations. Additionally, low mixing enthalpy values suggest that it should be possible to synthesize layered hexagonal B_k - $\text{Sc}_x\text{Al}_{1-x}\text{N}$ with a correct combination of Sc content and in-plane lattice parameter of stabilizing layer. This crystal phase may already be present in our

In-rich $\text{Sc}_x\text{Al}_{1-x}\text{N}/\text{In}_y\text{Al}_{1-y}\text{N}$ superlattices; however, further studies, including HRTEM simulations, are needed for confirmation, as will be published elsewhere.

5. Conclusions

We demonstrated the effects of lattice mismatch and resulting stresses on formation and stability of metastable wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ in superlattices with AlN and $\text{In}_y\text{Al}_{1-y}\text{N}$. Three cases – negative (In-rich $\text{In}_y\text{Al}_{1-y}\text{N}$), zero (Al-rich $\text{In}_y\text{Al}_{1-y}\text{N}$), and positive (AlN) lattice mismatch were investigated. Both experimental results and *ab initio* mixing enthalpy calculations confirm that stabilizing layers with larger in-plane lattice parameter (giving negative lattice mismatch), where $\text{Sc}_x\text{Al}_{1-x}\text{N}$ layers are affected by tensile biaxial stress, promote the epitaxial stabilization. The layers with the highest investigated Sc concentration, $\text{Sc}_{0.4}\text{Al}_{0.6}\text{N}$, were stabilized by $\text{In}_{0.72}\text{Al}_{0.28}\text{N}$, as shown in TEM and XRD analysis. These experimental findings are supported by the theoretically predicted destabilization of the competing phase separated pure wurtzite AlN and rock-salt ScN binaries with tensile strain and corresponding stabilization of wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys. A further decrease of mixing energies in wurtzite structure at $x=0.5$ in the case of negative lattice mismatch suggests, that the epitaxial stabilization can be used to alloy even more Sc into $\text{Sc}_x\text{Al}_{1-x}\text{N}$ maintaining the wurtzite crystal structure, when pseudomorphic stabilizing layers are tuned to provide the negative lattice mismatch for suppression of phase separation and crystal degradation.

ACKNOWLEDGEMENTS

We acknowledge the financial support by the Linköping Linnaeus Initiative on Nanoscale Functional Materials (LiLiNFM) supported by the Swedish Research Council (VR) under grant No.349-2008-6582. B.A. and L.H. acknowledges funding from the VR through grants 621-2011-4417 and 621-2013-4018, respectively. The calculations were performed using computer resources provided by the Swedish national infrastructure for computing (SNIC) at the National Supercomputer Centre (NSC) and the Center for High Performance Computing (PDC).

REFERENCES

- [1] M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, Y. Takeuchi, N. Kawahara, Enhancement of piezoelectric response in scandium aluminum nitride alloy thin films prepared by dual reactive cosputtering, *Adv Mater.* 21 (2009) 593.
- [2] G. Wingqvist, F. Tasnádi, A. Zukauskaite, J. Birch, H. Arwin, L. Hultman, Increased electromechanical coupling in w- $\text{Sc}_x\text{Al}_{1-x}\text{N}$, *Appl. Phys. Lett.* 97 (2010) 112902.
- [3] M.A. Moreira, J. Bjurström, I. Katardjev, V. Yantchev, Aluminum scandium nitride thin-film bulk acoustic resonators for wide band applications, *Vacuum.* 86 (2011) 23.
- [4] M.A. Moreira, J. Bjurström, V. Yantchev, I. Katardjev, Synthesis and characterization of highly c-textured $\text{Al}_{1-x}\text{Sc}_x\text{N}$ thin films in view of telecom applications, *IOP Conf. Ser. Mater. Sci. Eng.* 41 (2012) 012014.
- [5] R. Matloub, A. Artieda, C. Sandu, E. Milyutin, P. Muralt, Electromechanical properties of $\text{Al}_{0.9}\text{Sc}_{0.1}\text{N}$ thin films evaluated at 2.5 GHz film bulk acoustic resonators, *Appl. Phys. Lett.* 99 (2011) 092903.
- [6] G. Piazza, V. Felmetger, P. Muralt, R.H. Olsson III, R. Ruby, Piezoelectric aluminum nitride thin films for microelectromechanical systems, *MRS Bull.* 37 (2012) 1051.
- [7] F. Tasnádi, B. Alling, C. Höglund, G. Wingqvist, J. Birch, L. Hultman, I.A. Abrikosov, Origin of the anomalous piezoelectric response in wurtzite $\text{Sc}_x\text{Al}_{1-x}\text{N}$ alloys, *Phys. Rev. Lett.* 104 (2010) 137601.
- [8] S. Zhang, D. Holec, W.Y. Fu, C.J. Humphreys, M.A. Moram, Tunable optoelectronic and ferroelectric properties in Sc-based III-nitrides, *J. Appl. Phys.* 114 (2013) 133510.
- [9] C. Höglund, J. Birch, B. Alling, J. Bareño, Z. Czigány, P.O.Å Persson, G. Wingqvist, A. Zukauskaite, L. Hultman, Wurtzite structure $\text{Sc}_{1-x}\text{Al}_x\text{N}$ solid solution films grown by reactive magnetron sputter epitaxy: Structural characterization and first-principles calculations, *J. Appl. Phys.* 107 (2010) 123515.
- [10] A. Zukauskaite, G. Wingqvist, J. Palisaitis, J. Jensen, P.O.A. Persson, R. Matloub, P. Muralt, Y. Kim, J. Birch, L. Hultman, Microstructure and dielectric properties of piezoelectric magnetron sputtered w- $\text{Sc}_x\text{Al}_{1-x}\text{N}$ thin films, *J. Appl. Phys.* 111 (2012) 093527.
- [11] R. Deng, S.R. Evans, D. Gall, Bandgap in $\text{Al}_{1-x}\text{Sc}_x\text{N}$, *Appl. Phys. Lett.* 102 (2013) 112103.
- [12] C. Tholander, I.A. Abrikosov, L. Hultman, F. Tasnádi, Volume matching condition to establish the enhanced piezoelectricity in ternary $(\text{Sc},\text{Y})_{0.5}(\text{Al},\text{Ga},\text{In})_{0.5}\text{N}$ alloys, *Phys. Rev. B Condens. Matter Mater. Phys.* 87 (2013) 094107.
- [13] C. Constantin, H. Al-Brithen, M.B. Haider, D. Ingram, A.R. Smith, ScGaN alloy growth by molecular beam epitaxy: Evidence for a metastable layered hexagonal phase, *Phys. Rev. B Condens. Matter Mater. Phys.* 70 (2004) 193309.
- [14] C. Höglund, B. Alling, J. Birch, M. Beckers, P.O.Å Persson, C. Baehtz, Z. Czigány, J. Jensen, L. Hultman, Effects of volume mismatch and electronic structure on the decomposition of ScAlN and TiAlN solid solutions, *Phys. Rev. B Condens. Matter Mater. Phys.* 81 (2010) 224101.
- [15] V. Ranjan, S. Bin-Omran, D. Sichuga, R.S. Nichols, L. Bellaiche, A. Alsaad, Properties of GaN/ScN and InN/ScN superlattices from first principles, *Phys. Rev. B Condens. Matter Mater. Phys.* 72 (2005) 085315.

- [16] A. Madan, I.W. Kim, S.C. Cheng, P. Yashar, V.P. Dravid, S.A. Barnett, Stabilization of cubic AlN in epitaxial AlN/TiN superlattices, *Phys. Rev. Lett.* 78 (1997) 1743.
- [17] I.W. Kim, Q. Li, L.D. Marks, S.A. Barnett, Critical thickness for transformation of epitaxially stabilized cubic AlN in superlattices, *Appl. Phys. Lett.* 78 (2001) 892.
- [18] B. Saha, S. Saber, G.V. Naik, A. Boltasseva, E.A. Stach, E.P. Kvam, T.D. Sands, Development of epitaxial $\text{Al}_x\text{Sc}_{1-x}\text{N}$ for artificially structured metal/semiconductor superlattice metamaterials, *Physica Status Solidi (B)*. 252 (2014) 251.
- [19] B. Saha, S.K. Lawrence, J.L. Schroeder, J. Birch, D.F. Bahr, T.D. Sands, Enhanced hardness in epitaxial TiAlScN alloy thin films and rocksalt TiN/(Al,Sc)N superlattices, *Appl. Phys. Lett.* 105 (2014) 151904.
- [20] S. Zhang, W.Y. Fu, D. Holec, C.J. Humphreys, M.A. Moram, Elastic constants and critical thicknesses of ScGaN and ScAlN, *J. Appl. Phys.* 114 (2013) 243516.
- [21] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133.
- [22] C.L. Hsiao, J. Palisaitis, M. Junaid, P.O. Å Persson, J. Jensen, Q. Zhao, L. Hultman, L. Chen, K. Chen, J. Birch, Room-temperature heteroepitaxy of single-phase $\text{Al}_{1-x}\text{In}_x\text{N}$ films with full composition range on isostructural wurtzite templates, *Thin Solid Films*. 524 (2012) 113.
- [23] T. Seppänen, P.O. Å Persson, L. Hultman, J. Birch, G.Z. Radnóczy, Magnetron sputter epitaxy of wurtzite $\text{Al}_{1-x}\text{In}_x\text{N}$ ($0.1 < x < 0.9$) by dual reactive dc magnetron sputter deposition, *J. Appl. Phys.* 97 (2005) 083503.
- [24] T. Seppänen, L. Hultman, J. Birch, 248 nm cathodoluminescence in $\text{Al}_{1-x}\text{In}_x\text{N}$ (0001) thin films grown on lattice-matched $\text{Ti}_{1-y}\text{Zr}_y\text{N}$ (111) seed layers by low temperature magnetron sputter epitaxy, *Appl. Phys. Lett.* 89 (2006) 181928.
- [25] A. Zunger, S. Wei, L.G. Ferreira, J.E. Bernard, Special quasirandom structures, *Phys. Rev. Lett.* 65 (1990) 353.
- [26] P.E. Blöchl, Projector augmented-wave method, *Phys. Rev. B*. 50 (1994) 17953.
- [27] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*. 6 (1996) 15.
- [28] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B Condens. Matter Mater. Phys.* 54 (1996) 11169.
- [29] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865.
- [30] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B*. 13 (1976) 5188.
- [31] M.A. Moram, M.E. Vickers, X-ray diffraction of III-nitrides, *Rep. Prog. Phys.* 72 (2009) 036502.
- [32] R. Butté, J. Carlin, E. Feltin, M. Gonschorek, S. Nicolay, G. Christmann, D. Simeonov, A. Castiglia, J. Dorsaz, H.J. Buehlmann, S. Christopoulos, G. Baldassarri Höger Von Högersthal, A.J.D. Grundy, M. Mosca, C. Pinquier, M.A. Py, F. Demangeot, J. Frandon, P.G. Lagoudakis, J.J. Baumberg, N. Grandjean, Current status of AlInN layers lattice-matched to GaN for photonics and electronics, *J. Phys. D*. 40 (2007) 6328.