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Ab initio calculations and experimental study of piezoelectric $Y_x\text{In}_{1-x}\text{N}$ thin films deposited using reactive magnetron sputter epitaxy

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Abstract

By combining theoretical prediction and experimental verification we investigate the piezoelectric properties of yttrium indium nitride ($Y_x\text{In}_{1-x}\text{N}$). *Ab-initio* calculations show that the $Y_x\text{In}_{1-x}\text{N}$ wurtzite phase is lowest in energy among relevant alloy structures for $0 \leq x \leq 0.5$. Reactive magnetron sputter epitaxy was used to prepare thin films with Y content up to $x = 0.51$. The composition dependence of the lattice parameters observed in the grown films is in agreement with that predicted by the theoretical calculations confirming the possibility to synthesize a wurtzite solid solution. An AlN buffer layer greatly improves the crystalline quality and surface morphology of subsequently grown $Y_x\text{In}_{1-x}\text{N}$ films. The piezoelectric response in films with $x = 0.09$ and $x = 0.14$ is observed using piezoresponse force microscopy. Theoretical calculations of the piezoelectric properties predict $Y_x\text{In}_{1-x}\text{N}$ to have comparable piezoelectric properties to $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

Keywords: YInN, Thin films, Sputter deposition, Piezoelectricity, Ab initio calculations

1. Introduction

The interest in semiconductor alloys of group IIIA (AlN, InN, GaN) and IIIB (ScN, YN) nitrides has been flourishing since it was discovered that AlN, a superior piezoelectric material for bulk acoustic wave (BAW) devices [1], could be alloyed with ScN to produce scandium aluminum nitride ($\text{Sc}_x\text{Al}_{1-x}\text{N}$) which significantly increases the piezoelectric response [2]. The origin of the giant amplification of the piezoelectric response upon Sc alloying is the phase competition between layered hexagonal (B_k) ScN and wurtzite (B_4) AlN [3]. This phase competition is caused by a morphotropic phase boundaries that separate the polar B_4 and nonpolar B_k phases of the material [4]. The resulting instability leads to the increase

of e_{33} and decrease of C_{33} , simultaneously. The combined effect dramatically enhances the clamped piezoelectric coefficient $d_{33,f} = e_{33}/C_{33}$. The discovery has attracted attention to the $\text{Sc}_x\text{Al}_{1-x}\text{N}$ material system with research focused on piezoelectric [5, 6, 7, 8, 9, 10, 11] as well as optoelectronic properties [12, 13, 10].

Inspired by the results for $\text{Sc}_x\text{Al}_{1-x}\text{N}$, we investigated theoretically the six ternary nitrides $\text{A}_{0.5}\text{B}_{0.5}\text{N}$ ($\text{A}=\text{Sc}, \text{Y}; \text{B}=\text{Al}, \text{Ga}, \text{In}$) and showed that increase in the piezoelectric response is a general feature for wurtzite group IIIA nitrides alloyed with group IIIB nitrides [14]. However, the increase is not always as high as in the case of $\text{Sc}_x\text{Al}_{1-x}\text{N}$. It was found that poor volume matching of the parent binaries results in a less pronounced increase of the piezoelectric response.

Based on our findings, we predicted $Y_x\text{In}_{1-x}\text{N}$ as a candidate material for possessing a large piezoelectric response. Indium nitride (InN) and the

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hexagonal modification of yttrium nitride (YN) have similar atomic volume, in addition, InN has a piezoelectric response comparable to AlN by itself, with 4.03 compared to 5.18 pC/N, respectively [14].

$Y_xIn_{1-x}N$ alloy characterization is in its infancy. Only one experimental study by Zoita *et al.* [15] reports synthesis of $Y_xIn_{1-x}N$, and this with low levels of Y ($x < 0.1$). In addition, in a theoretical study by Benyounes *et al.* [16] YN was suggested as a possible alloy to tune the direct and indirect bandgap in metastable zincblende (B3) InN.

The parent binary components are considerably more investigated. InN is a IIIA-nitride semiconductor which has been thoroughly studied for bandgap engineering in combination with GaN and/or AlN in development of blue and UV LEDs, and laser diodes [17]. It is also possible to grow nanowires of InN for optoelectronic and piezoelectric applications [18, 19]. Experimental [20, 21, 22] and theoretical [23, 24, 25] studies also suggest YN for alternative optoelectronic applications.

In this work we investigate the $Y_xIn_{1-x}N$ alloy system by addressing the mixing enthalpies from a theoretical point of view for relevant crystal structures and their lattice parameters, and experimental verification using reactive magnetron sputter epitaxy (MSE) to grow $Y_xIn_{1-x}N$ thin films. Finally, we compare the piezoelectric response of $Y_xIn_{1-x}N$ thin films to pure InN thin films using piezoresponse force microscopy and theoretical calculations.

2. Method

2.1. Computational details

Density functional theory [26] (DFT) is used to study the hexagonal wurtzite (B4), layered hexagonal (B_k), cubic rock-salt (B1), and cubic zincblende (B3) $Y_xIn_{1-x}N$ alloys. The structures are modelled with the special quasi-random structure (SQS) method [27]. The B4, and B_k alloys are modelled with the same 128-atom supercells used by Tasnádi *et al.* [3], and the B1 and B3 are the same as used by Alling *et al.* [28]. The alloys were modelled at compositions $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75$, and 0.875 using supercells comprised of $(4 \times 2 \times 4)$ or $(4 \times 4 \times 2)$ unit cells in order to minimize the short-range order parameters on the first 8 coordination shells.

The calculations are performed with the Vienna ab-initio simulation package [29, 30] (VASP).

The standard projector augmented wave [31, 32] (PAW) approach is used together with the Perdew-Burke-Ernhofer generalized gradient approximation [33, 34] (PBE-GGA) for the exchange correlation functional. The semicore electron 4d-states are included as valence electrons for In, and the 4s-states for Y. A $(3 \times 3 \times 3)$ Monkhorst-Pack k -mesh and 400 eV plane-wave energy cutoff was used in all calculations.

The mixing enthalpies at zero pressure are calculated for $x = 0, 0.125, 0.25, 0.375, 0.5, 0.625, 0.75$, and 1, with respect to B4-InN and B1-YN according to

$$\Delta H_{mix}(x) = H_{Y_xIn_{1-x}N} - (xH_{B1-YN} + (1-x)H_{B4-InN}), \quad (1)$$

where $H_{Y_xIn_{1-x}N}$ is the energy of the alloy, and H_{B1-YN} and H_{B4-YN} are the energies for the pure binaries, all calculated at their respective optimal lattice parameter.

The piezoelectric properties of the InN-rich B4- $Y_xIn_{1-x}N$ with $x = 0, 0.125, 0.25, 0.375$, and 0.5 are studied at the respective equilibrium structures. To find the equilibrium structure, the cell shape and internal atomic positions of the structures are relaxed at fixed volumes. Finally, the equilibrium c/a and a are determined by relaxing the atomic positions at fixed volume and c/a . Because $[0001]$ is the standard growth direction of wurtzite bulk and superlattice nitrides the focus is on the properties along this crystal direction [35].

The piezoelectric constant e_{33} is obtained from the relation derived by Bernardini *et al.* [35]:

$$e_{33}(x) = e_{33}^{clamped-ion}(x) + \frac{4eZ^*(x)}{\sqrt{3}a_0(x)^2} \frac{du(x)}{d\epsilon}, \quad (2)$$

where $e_{33}^{clamped-ion}$ is the clamped-ion part of e_{33} , e is the elemental charge, Z^* is the c -axial component of the dynamical Born charge tensor $Z^{(T)}$, a_0 is the equilibrium lattice constant, and $du/d\epsilon$ is the change in the internal parameter u due to strain in the c -direction, and it is calculated by straining the supercell in the c -direction while the in-plane lattice parameter is preserved and internal relaxation of the atoms is allowed. $e_{33}^{clamped-ion}$ is calculated from the response in the electronic polarization in the c -direction P_3 due to strain ϵ in the same direction without internal relaxation of the atoms in the supercell,

$$e_{33}^{clamped-ion}(x) = \frac{\partial P_3(x)}{\partial \epsilon}. \quad (3)$$

The Born charge Z^* is calculated using the relation

$$Z^*(x) = \frac{\sqrt{3}a_0(x)^2}{4e} \frac{\partial P_3}{\partial u}, \quad (4)$$

where $\partial P_3/\partial u$ is determined by calculating the change in polarization from shifting the nitrogen atoms in the c -direction while keeping the cell-shape fixed.

The elastic constant C_{33} is calculated from the second derivative of the total energy per volume using a finite difference technique where the unit cell is distorted $\pm 2\%$ and $\pm 4\%$ in the c -direction. C_{33} and e_{33} are used together with the assumption that the distortion in-plane is negligible due to epitaxial constraints in the thin film, to approximate the piezoelectric response with the clamped piezoelectric response $d_{33,f}$:

$$d_{33,f} = e_{33}/C_{33}. \quad (5)$$

This approximation provides a qualitative illustration of the effects of composition on the combined change in polarizability and elastic constants which give rise to the piezoelectric response.

2.2. Experimental details

Thin films of $\text{Y}_x\text{In}_{1-x}\text{N}$ were grown by magnetically unbalanced reactive dc MSE, in Ar/N_2 plasma discharge, on $\text{Al}_2\text{O}_3(0001)$ and $\text{Si}(100)$ substrates with and without an $\text{AlN}(0001)$ buffer layer. An ultra-high vacuum (UHV) chamber with base pressure 4×10^{-6} Pa was used. Two separate elemental targets, 50 mm 99.995 % pure In and 99.99% pure Y were used in constant power mode at a total process pressure of 0.67 Pa. Two different process gas Ar/N_2 ratios were used (40% and 60% N_2), while keeping the total process pressure constant. The relative amounts of Y and In were controlled by adjusting applied target powers. Prior to deposition, the $\text{Al}_2\text{O}_3(0001)$ and $\text{Si}(100)$ substrates were cleaned in ultrasonic baths of trichloroethylene, acetone, and isopropanol and blown dry with N_2 . Thermal degassing was done prior to growth at a substrate temperature of $T_s = 900^\circ\text{C}$ for samples with an AlN buffer layer. During growth, -30 V dc substrate bias was applied. $\text{Y}_x\text{In}_{1-x}\text{N}$ films were grown at a relatively low temperature of $T_s = 300^\circ\text{C}$ to avoid desorption of In from the surface of $\text{Y}_x\text{In}_{1-x}\text{N}$ [36, 37]. AlN(0001) buffer layer was deposited at $T_s = 900^\circ\text{C}$ in pure N_2 atmosphere. A 5 nm AlN capping layer was deposited at room temperature in a pure N_2 atmosphere on

all samples to avoid potential oxidation of the films due to the high susceptibility to oxygen observed in YN films [20].

The elemental composition was determined by Rutherford backscattering spectrometry (RBS) measured at the Tandem Laboratory in Uppsala, Sweden, using a primary beam of 2.0 MeV $^4\text{He}^+$ ions with an incoming angle relative to the surface normal of 6° and a scattering angle of 172° . The data was evaluated with the program SIMNRA version 6.06.

X-ray diffraction (XRD) measurements were performed in a Philips X'Pert MRD diffractometer in low-resolution mode for acquisition of pole figures and lattice parameters. A Philips Bragg-Brentano diffractometer was operated in $\theta/2\theta$ mode for crystal quality evaluation.

For the transmission electron microscopy (TEM) characterization, cross-section samples were prepared from the as-deposited structures by a traditional "sandwich" method, which includes mechanical cutting, stabilizing in Ti grid and polishing from both sides. The samples were ion milled from both sides at 5 keV ion energy and a 5° angle with gradually reduced energy to 2 keV to reduce the surface damage in the final sample. The milling was performed in a Gatan-PIPS system at liquid nitrogen temperature in order to preserve the structure during milling. Scanning TEM (STEM) high angle annular dark field (HAADF), high resolution (HR)TEM and selective area electron diffraction (SAED) analysis were performed in a Tecnai G2 TF20 UT FEG microscope operated at 200 kV.

The piezoelectric phase polarity was evaluated using piezoresponse force microscopy (PFM) in a Dimension 3100 atomic force microscope with a Nanoscope-IVa controller. An NSG01 conductive Pt-coated Si tip with a resonance frequency $f_r = 135$ kHz was used at an excitation voltage of 10 V and ac frequency of 5.6 kHz as described in more detail in Ref. [38].

3. Results and Discussion

3.1. Mixing thermodynamics and thin film growth

The mixing enthalpies for relevant phases of $\text{Y}_x\text{In}_{1-x}\text{N}$ are presented in Fig.1. The mixing enthalpies are positive for all investigated phases, showing that the alloy is thermodynamically unstable, at least at low temperatures, with respect

Figure 1: Mixing enthalpies for $Y_x\text{In}_{1-x}\text{N}$ as a function of composition x for B4 (wurtzite), B_k (layered hexagonal), B1 (rock-salt), and B3 (zincblende).

to phase separation into B1-YN and B4-InN. Considering mean-field configurational entropy contributions [39] at growth temperature would only result in a negligible equilibrium intersolubility. However, since bulk diffusion can be practically frozen out during low-temperature PVD deposition, prohibiting phase separation, a metastable alloy could be formed, preferably with the lowest energy alloy structure. The B4 phase is found to be lowest in energy up to $x = 0.5$, after which the B1 phase is lowest. Although there could exist a metastable B_k phase at lower concentrations, a transition into the more stable B4 minimum would require very little energy. The flat energy landscape makes it numerically difficult to distinguish a metastable phase from a saddle point [3, 14]. Therefore, we only consider the lowest energy B_k or B4 phase of each composition, the B4 phase up to $x = 0.625$ after which it is B_k phase.

Compared to $\text{Sc}_x\text{Al}_{1-x}\text{N}$ [5, 12] and $Y_x\text{Al}_{1-x}\text{N}$ [40, 41] the B4- $Y_x\text{In}_{1-x}\text{N}$ mixing enthalpies are lower at all compositions (B4 at $x=0.5$ are 0.35, 0.5, and 0.22 eV, respectively), indicating that its driving force towards phase separation through surface diffusion during growth is smaller than that of $\text{Sc}_x\text{Al}_{1-x}\text{N}$ and $Y_x\text{Al}_{1-x}\text{N}$. However, a notable difference between InN and AlN is that in InN the B3 phase is much closer in energy to that of the B4 phase. We see that adding Y increases the difference in mixing enthalpy between these the B4 and B3 phases, increasing the stability of the B4 phase. As the wurtzite phase is the most interesting for electroacoustic and optoelectronic applications, this trend of destabilizing the zincblende phase by alloying InN with YN could be useful in its own rights in cases where B3 competition is found problematic

for InN applications.

Figure 2: AFM measurements of the surface roughness in $Y_{0.31}\text{In}_{0.69}\text{N}$; (a) directly on the Al_2O_3 (roughness RMS value 23.1 nm) and (b) with AlN buffer layer (roughness RMS value 2.2 nm).

$Y_x\text{In}_{1-x}\text{N}$ with $0.00 \leq x \leq 0.51$ thin films were grown with a thickness of 150-250 nm on $\text{Al}_2\text{O}_3(0001)$ and $\text{Si}(100)$ substrates with and without an $\text{AlN}(0001)$ buffer layer. The nominal lattice mismatch between $\text{Al}_2\text{O}_3(0001)$ and $\text{InN}(0001)$ is as much as 25% [17]. Initial growth experiments of $Y_x\text{In}_{1-x}\text{N}$ layers directly on Al_2O_3 thus resulted in a material with very poor crystalline quality and high surface roughness ($\text{RMS} > 20 \text{ nm}$). Previous studies show that by introducing an AlN buffer layer through nitridation of the Al_2O_3 surface, the mismatch to InN can be reduced to 13% [17]. Such lattice parameter engineering can also effect the phase stability [42]. For that reason, a 50 nm AlN buffer layer was introduced prior to further growth of $Y_x\text{In}_{1-x}\text{N}$. As a result, the roughness measured by AFM decreased to 2-3 nm, see Fig.2. The comparison between XRD $\theta/2\theta$ scans from samples with and without the AlN buffer layer also confirm the improved crystalline quality (not shown).

Figure 3: X-ray diffraction patterns for $Y_x\text{In}_{1-x}\text{N}$ films deposited using 40 % and 60 % N_2 flow.

During the growth experiments, two different Ar/N₂ ratios were employed, while maintaining a constant total process gas pressure. At 40 % N₂ flow, the crystalline quality of the films was rather low and XRD measurements exhibit a wurtzite (10 $\bar{1}$ 1) peak in addition to (0002). By increasing the nitrogen flow to 60%, the crystalline quality improved. However, it should be noted, that based on RBS measurements, the Y:In ratio in the films was also influenced by the gas ratio. For the same applied magnetron powers, Y content was higher in samples prepared using 40 % N₂ flow gas mixture, which also has affects the crystalline quality of the material. In the example (Fig.3), at 40 % N₂ the Y content of $x = 0.31$, and at 60 % N₂ $x = 0.22$ was measured, respectively. Based on the superior quality, all of the following characterization is performed on films grown with 60 % N₂ flow.

The $\theta/2\theta$ XRD scans from Y_xIn_{1-x}N/AlN/Al₂O₃ are displayed in Fig.4 (a)-(g). The concentrations in the figure are obtained from RBS measurements. For all investigated concentrations, peaks corresponding to Y_xIn_{1-x}N(0002) and AlN(0002) are present confirming growth of *c*-axis oriented wurtzite Y_xIn_{1-x}N. In the case of pure InN thin films, an additional peak at 32.96°, corresponding to pure In(111) can be seen in Fig.4 (a). Through inspection of the InN thin films using optical light microscopy and AFM it was found that small droplets of In formed on the film surface during growth. Most likely these droplets are the source of the In(111) peak visible in Fig.4, as In droplet formation is a common phenomenon during InN growth [17]. However, the formation of these metal droplets is not observed upon alloying with Y. These film surfaces became smooth and homogeneous for all investigated Y concentrations, as shown in Fig.2 (b). It can also be seen from XRD scans in Fig.4 (b) and (c) that at low concentrations of Y (up to $x = 0.15$), the crystalline quality of Y_xIn_{1-x}N improves in comparison to $x = 0$ samples (InN) – peak intensity increases and the metal In peak disappears. At $x \geq 0.24$, however, the crystalline quality is degrading rapidly, as was also previously observed in other group IIIA-IIIB alloys such as Sc_xAl_{1-x}N [5, 7] and Y_xAl_{1-x}N [41].

One possible reason for low XRD peak intensity of pure InN is the phase mixture. According to mixing enthalpy calculations (Fig.1), at $x = 0$ the energy difference between zinkblende and wurtzite is very small. However, d-spacing of wurtzite (0002)

and zinkblende (111) is almost identical and the peaks would overlap in a symmetric $\theta/2\theta$ scan. For this reason, XRD pole figures were recorded to determine the crystal phase of Y_xIn_{1-x}N. At $2\theta = 60.5^\circ$ wurtzite (11 $\bar{2}$ 2) and zinkblende (311) InN reflections can be measured simultaneously [43]. Results from the samples grown on Al₂O₃(0001) substrates are presented in Fig.5. All pole figures up to $x = 0.24$ contain 6-fold hexagonal reflections at $\psi = 60^\circ$, the discrete spots confirm *c*-axis oriented wurtzite and epitaxial relationship with the substrate and the buffer layer. However, additional peaks at $\psi = 30^\circ$ can also be distinguished, with very sharp reflections at $x = 0$ and more diffuse features at $x = 0.15$ and 0.24 that can be attributed to 3-fold symmetry with twinning, corresponding to zinkblende (B3) (311) reflection. At higher Y concentrations the crystalline quality of the films is too degraded for phase identification analysis. Pole figures at *d*-spacing of wurtzite (10 $\bar{1}$ 4) were also recorded (not shown) and confirm the formation of wurtzite Y_xIn_{1-x}N.

The TEM results are shown in Fig.6. Overview STEM-HAADF images confirm that the samples are comprised of AlN buffer, Y_xIn_{1-x}N, and AlN capping layer grown on Al₂O₃ substrates. The STEM-HAADF images were recorded ensuring high mass contrast conditions, thus Y_xIn_{1-x}N layers exhibit increased contrast, as can be seen by comparing Fig.6 (a) to (b) and (c). However, STEM-HAADF contrast is varying within each layer, the primary reasons for such variations is likely attributed to the microstructural quality of the films, and particularly to high point defect density. AlN buffer layers have similar thickness (~50 nm), dense columnar structures and moderately smooth interfaces with Y_xIn_{1-x}N in all studied samples. Y_xIn_{1-x}N layer thicknesses for samples with $x = 0$ (InN) is ~50 nm while for $x = 0.09$ and 0.14 it is ~150 nm, which can be explained by In forming droplets, instead of InN, in the pure InN sample. Additionally, Y_xIn_{1-x}N layers with $x = 0.09$ and 0.14 developed pronounced columnar microstructure with clear resolved boundaries and rough faceted surfaces. Thin AlN capping layers follow the terrain line of Y_xIn_{1-x}N layers and is ~4 nm thick. SAED patterns obtained along [1 $\bar{1}$ 00] zone axis reveal sets of discrete diffraction spots which are attributed to the different lattice parameter layers and the substrate. The Y_xIn_{1-x}N layers have wurtzite structure and are epitaxially grown on AlN. Within the columns, the acquired

Figure 4: (a)-(g) X-ray diffraction patterns for $Y_x\text{In}_{1-x}\text{N}$ films through a range of x . At $x = 0.40$ and 0.51 the intensity is additionally multiplied by a factor 100 to promote peak identification.

Figure 5: X-ray pole figures with $(11\bar{2}2)$ wurtzite ($\psi = 60^\circ$) and the (311) zincblende ($\psi = 30^\circ$) reflections of $Y_x\text{In}_{1-x}\text{N}$ films for (a) $x = 0$, (b) $x = 0.14$, and (c) $x = 0.24$.

HRTEM images show ordered but wavy lattices in all studied $Y_x\text{In}_{1-x}\text{N}$ layers, where a number of cubic inclusions were observed in $x = 0$ (InN) layer (not shown). These inclusions could explain the appearance of the B3(311) peaks in the InN pole figure, Fig.5 (a).

XRD was also used to extract $Y_x\text{In}_{1-x}\text{N}$ a and c lattice parameters from the position of the asymmetric $(10\bar{1}4)$ reflection. The experimentally obtained data together with calculated B4, B_k , B1, and B3 equilibrium lattice parameters a_0 and c/a ratios are presented in Fig.7. The small but finite size difference between InN and YN is sufficient to increase the lattice parameter a_0 with increasing Y-content. The B1 and B3 lattice parameters increase linearly when x goes from 0 to 1, in the B1 phase from 4.71 to 4.92 Å, and in the B3 phase from 5.05 to 5.30 Å, respectively, see Fig.7 (a). In the composition range $x = 0$ to 0.625 the B4 a_0 increases from 3.59 to 3.81 Å, and $B_k a_0$ increases from 3.98 for

$x = 0.625$ to 4.04 Å for $x = 1$, Fig.7 (b). The experimentally determined B4- $Y_x\text{In}_{1-x}\text{N}$ in-plane lattice parameter a increases with increasing x up to the highest measured concentration $x = 0.34$, following the trend predicted by the calculations, with only a slight deviation from the calculated values.

Calculations show that the B4 c/a ratio decreases from 1.61 to 1.44 with increasing Y-concentration up to $x = 0.625$. The B_k ratio is steady at ~ 1.22 for $0.625 \leq x \leq 1$. The experimental c/a ratio agrees better with calculation than a but starts to slightly deviate from the calculations at $x = 0.24$, where the crystalline quality of the material is degrading rapidly, as observed by XRD (Fig.4). The experimental deviation from the c/a can not be caused by the expected systematic overestimation by GGA since the overestimation in c would be cancelled out by the overestimation in a_0 . Thus, the small difference between the measured and calculated values is most likely caused by in-plane strain in the samples.

3.2. Piezoelectric properties

The results from calculations of the piezoelectric properties of $Y_x\text{In}_{1-x}\text{N}$ alloys with x from 0 (pure InN) to 0.5 are plotted in Fig.8 together with the corresponding $\text{Sc}_x\text{Al}_{1-x}\text{N}$ values obtained from Ref.[3] and [11] in order to allow a comparison with $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

The concentration dependence of the piezoelectric coefficient e_{33} for $Y_x\text{In}_{1-x}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$ is presented in Fig.8 (a). In $Y_x\text{In}_{1-x}\text{N}$ e_{33} increases

Figure 6: Overview STEM-HAADF images and corresponding SAED patterns along $[1\bar{1}00]$ zone axis (left column) of as-grown structures together with HRTEM images from the $Y_x\text{In}_{1-x}\text{N}$ layers of corresponding samples (right column).

exponentially from 0.94 to 2.20 C/m² following the same trend as in $\text{Sc}_x\text{Al}_{1-x}\text{N}$, where e_{33} increases from 1.55 to 3.04 C/m². However, the absolute values of e_{33} in $Y_x\text{In}_{1-x}\text{N}$ are ~ 0.6 C/m² lower than for $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

The two terms which make up e_{33} (defined in Eq.(2)) are plotted in Fig.8 (b). Here we see that the main contribution to the increase of e_{33} comes from the non-clamped-ion part in both $Y_x\text{In}_{1-x}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$, which increase from 1.83 to 2.86 and 2.02 to 3.55 C/m² respectively. However, in $Y_x\text{In}_{1-x}\text{N}$ $e_{33}^{\text{clamped-ion}}$ is increasing from -0.88 to -0.66 C/m², while in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ $e_{33}^{\text{clamped-ion}}$ is decreasing slightly from -0.47 to -0.51 C/m² compensating the slight difference between the two alloys in the non-clamped-ion part.

The contribution to the polarization change caused by internal relaxation is dependent on the

dynamical Born charge Z^* and $du/d\epsilon$ presented in Fig.8 (c) and (d). Because both factors influence the non-clamped-ion part through multiplication, the y -axis of the figures are chosen so that they represent comparable effects on e_{33} . With $Z^* \approx 3$ in both $Y_x\text{In}_{1-x}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$, the increase in e_{33} comes primarily from the $du/d\epsilon$ term which increases from 0.35 ($x = 0$) to 0.92 ($x = 0.5$) C/m² in $Y_x\text{In}_{1-x}\text{N}$ similar to $\text{Sc}_x\text{Al}_{1-x}\text{N}$.

The elastic constant C_{33} is presented in Fig.8 (e). The results show a linearly decreasing C_{33} from 205 ($x = 0$) to 94 ($x = 0.5$) GPa with increasing x in $Y_x\text{In}_{1-x}\text{N}$. Although this decrease with Y concentration is slightly less pronounced than in $\text{Sc}_x\text{Al}_{1-x}\text{N}$, where it decreases from 367 ($x = 0$) to 131 ($x = 0.5$) GPa, the elastic constant is over all much lower. Because the elasticity is inversely proportional to piezoelectric constant $d_{33,f}$ (Eq.5), a softer material will have a higher piezoelectric response for the same amount of mechanical stress than a more rigid material with the same polarization sensitivity.

Because both e_{33} and C_{33} affects the piezoelectric response, the relation between them is of importance. This relation is approximated using Eq.(5) and presented in Fig.8 (f). It is here evident that $Y_x\text{In}_{1-x}\text{N}$ alloys provides a similar piezoelectric response as $\text{Sc}_x\text{Al}_{1-x}\text{N}$ for all considered values of x . The polarization in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ is much more sensitive to distortion (high e_{33}), and $Y_x\text{In}_{1-x}\text{N}$ is much softer and easier to distort (low C_{33}). The resulting $d_{33,f}$ in $Y_x\text{In}_{1-x}\text{N}$ is 23.31 pC/N, which agrees well with our previous study [14] with only a $\sim 10\%$ difference. With respect to $\text{Sc}_x\text{Al}_{1-x}\text{N}$, the $d_{33,f}$ in $Y_x\text{In}_{1-x}\text{N}$ is as high as in $\text{Sc}_x\text{Al}_{1-x}\text{N}$ calculated by Tasnádi *et al.* [3], 23.31 vs 23.28 pC/N. Caro *et al.* [11] get a slightly higher 26.13 pC/N from their configurational sampling of $\text{Sc}_x\text{Al}_{1-x}\text{N}$. Although there are slight differences in the piezoelectric response at 0.5, at lower concentrations the differences between them are indistinguishable.

Piezoelectric polarity distribution in the $Y_x\text{In}_{1-x}\text{N}$ thin films with $x=0$, 0.09, and 0.14 was investigated using piezoresponse force microscopy (PFM) in mapping mode. The resulting two dimensional maps are shown in Fig.9. The oscillation of the piezoelectric film can be either in-phase ($+90^\circ$) or out-of-phase (-90°) with the applied ac signal. In the case of wurtzite nitrides, metal-face and N-face material would exhibit opposite contrast, and 0° would represent regions without a piezoelectric response in out-of-plane

Figure 7: (a) B1 and B3 a_0 lattice parameters, (b) experimentally determined and theoretical B4 and B_k hexagonal a_0 lattice parameters, and (c) experimentally determined and theoretical B4 and B_k hexagonal c/a lattice parameter ratios.

direction. In the pure InN thin films (Fig.9 (a)) the piezoelectric phase was close to 0° , indicating no or very weak piezoelectric response, while both $x=0.09$ and $x=0.14$ showed a positive piezoelectric response, with the piezoelectric phase closer to $+90^\circ$ in sample with higher Y concentration, i.e., the piezoelectric domains are polarized in one direction only. This indicates an increased piezoelectric response with increasing x , which is in line with the theoretical predictions. From this initial study we thus affirm that $Y_xIn_{1-x}N$ is a competitive alternative to $Sc_xAl_{1-x}N$ in terms of $d_{33,f}$ values.

4. Conclusions

Our calculations show positive mixing enthalpies for rock-salt, zincblende, layered hexagonal, and wurtzite $Y_xIn_{1-x}N$ alloys with respect to rock-salt YN and wurtzite InN. The wurtzite phase alloys are lowest in energy for $x \leq 0.5$, while for $x > 0.5$ rock-salt structure is the most stable. With respect to the layered hexagonal phase, the wurtzite phase is lowest in energy for $x \leq 0.625$. c -oriented wurtzite $Y_xIn_{1-x}N$ alloy thin films in the range $0 \leq x \leq 0.51$ were deposited using reactive magnetron sputter epitaxy. Both XRD pole figures and TEM analysis showed that by alloying up to $x = 0.14$ Y, the material quality was improved due to destabilization of the zincblende phase and elimination of metal In droplets. Moreover, the films greatly benefited from AlN(0001) buffer layers, resulting in a tenfold reduced surface roughness and improved

crystalline quality. Experimental lattice parameters match well with the theoretical predictions up to the highest measured concentration at $x = 0.34$. PFM measurements show an increasing positive piezoelectric response in the films with $x=0.09$ and 0.14 , compared to pure InN that show no piezoelectric response or very small randomly oriented piezoelectric domains. This is explained by calculations of the piezoelectric properties of $Y_xIn_{1-x}N$, which show an increased piezoelectric response as a consequence of a e_{33} increase from 0.94 ($x = 0$) to 2.20 ($x = 0.5$) C/m² and a C_{33} decrease from 205 ($x = 0$) to 94 ($x = 0.5$) GPa. This results in an increase of $d_{33,f}$ up to 23.31 pC/N at $x = 0.5$, making $Y_xIn_{1-x}N$ comparable to $Sc_xAl_{1-x}N$, and a possible candidate for future electroacoustic applications.

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Figure 8: Piezoelectric coefficients for B4 $Y_x\text{In}_{1-x}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$ ($\text{Sc}_x\text{Al}_{1-x}\text{N}$ data obtained from Ref. [3] and [11]) (a) e_{33} , (b) e_{33} components, the non clamped-ion part of e_{33} at the top, and the clamped-ion $e_{33}^{\text{clamped-ion}}$ part at the bottom, (c) Born effective charge Z^* , (d) sensitivity of the internal structure parameter u $du/d\epsilon$, (e) elastic constant C_{33} , and (f) clamped piezoelectric response $d_{33,f}$.

Figure 9: Piezoresponse force microscopy phase images of $Y_x\text{In}_{1-x}\text{N}$ in a $5 \times 5 \mu\text{m}$ area for (a) $x=0$, (b) $x=0.09$, and (c) $x=0.14$.

carried out using supercomputer resources provided by the Swedish national infrastructure for computing (SNIC) at the National Supercomputer Center (NSC), and the resources Lindgren and Beskow based in Sweden at the Center for High-Performance Computing (PDC) at the KTH Royal Institute of Technology.

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