Bandgap in $\text{Al}_{1-x}\text{Sc}_x\text{N}$

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Aluminum scandium nitride ($\text{Al}_{1-x}\text{Sc}_x\text{N}$) layers deposited by reactive magnetron co-sputtering on sapphire 0001 substrates at 850 °C are epitaxial single-crystals for $x \leq 0.20$. Their in-plane lattice constant increases linearly ($3.111 + 0.744x{\AA}$) while the out-of-plane constant remains at 4.989 ± 0.005 Å. Optical absorption indicates a band gap of 6.15–9.32 eV and a linearly increasing density of defect states within the gap. The average bond angle decreases linearly with $x$, suggesting a trend towards the metastable hexagonal-ScN structure. However, an anomalous decrease at $x = 0.20$ indicates a structural instability which ultimately leads to phase separated rock-salt ScN grains for $x > 0.4$. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4795784]

III-metal-N ternary compounds are studied extensively because they facilitate band gap engineering for optoelectronic devices when the metal is another iso-electric group III element, and they show promise as diluted magnetic semiconductor for spintronics if the metal element is a rare earth or transition metal with a net magnetic moment. The use of Sc as the alloying element is interesting because (i) Sc is iso-electric with group III metals, suggesting an alternate route for nitride band gap engineering. For example, Little and Kordesch reported an apparent band gap $E_{g}(x) = 4 - 1.5x$ eV for polycrystalline Ga$_{1-x}$Sc$_x$N layers over the entire $x = 0–1$ composition range, without evidence for a phase separation which is attributed to the low deposition temperature of 400 °C. In contrast, Constantin et al. reported a phase separation for $x > 0.17$ for Ga$_{1-x}$Sc$_x$N films deposited by Molecular Beam Epitaxy at 650 °C, and a single phase wurtzite solid-solution optical band gap of $E_{g}(x) = 3.37 - 1.07x$ eV for $x \leq 0.17$. ScN crystallizes in the rock salt structure such that substitutional Sc within a wurtzite structure III-nitride compound destabilizes the four-fold tetrahedral bonding, leading to an anomalous strengthening of the electromechanical response with promise for applications in piezoelectric acoustic-wave actuators and sensors. Such an enhanced piezoelectric response has been predicted for ordered Ga$_{1-x}$Sc$_x$N and In$_{1-x}$Sc$_x$N by Alsaad and Ahmad, who studied these compounds by first-principle calculations and attributed the effect to a strain induced phase transition from the wurtzite structure to a metastable non-polar hexagonal structure, which was previously predicted for ScN. More recently, Akiyama et al. reported a measured piezoelectric coefficient $d_{33}$ for Al$_{1-x}$Sc$_x$N layers that is up to four times larger than that of pure AlN. This enhancement of the piezoelectric response in Al$_{1-x}$Sc$_x$N has been experimentally confirmed by multiple other research groups and has been attributed, based on first-principles calculations, to a softening of the wurtzite AlN structure. More specifically, Sc atoms within wurtzite-type Al$_{1-x}$Sc$_x$N tend towards nearly five-fold-coordinated atomic positions, similar to what is predicted for metastable hexagonal ScN. This reduces the stiffness constant $C_{33}$ and simultaneously increases the internal strain sensitivity and therefore the piezoelectric constant $e_{33}$, yielding an overall enhancement of $d_{33} \approx e_{33}/C_{33}$. Despite the recent interest in Al$_{1-x}$Sc$_x$N due to its intriguing electromechanical properties, this compound still remains relatively unexplored. In particular, no reliable data exists regarding its composition dependent band gap, which is of key interest for potential optoelectronic applications.

In this letter, we present the measured band gap $E_{g}$, optical absorption coefficient $\alpha$, and lattice constants $a$ and $c$ as a function of $x = 0–0.45$, for Al$_{1-x}$Sc$_x$N layers deposited by reactive magnetron co-sputtering on c-plane sapphire substrates. The layers are epitaxial single-crystals for compositions $0 \leq x \leq 0.20$. For this composition range, $E_{g}$ decreases linearly, $a$ increases linearly, and $c$ remains nearly constant, suggesting a decreasing bond angle due to substitutional Sc incorporation. However, a discontinuity in $E_{g}$, $a$, and $c$ at $x = 0.20$ indicates a structural instability. Phase separation at larger $x$ causes the nucleation of rock salt ScN grains within the Al$_{1-x}$Sc$_x$N matrix, leading to a linear region in $x$ vs photon energy $h\nu$ associated with a ScN direct interband transition. The layers were deposited in an ultrahigh vacuum sputter deposition system at 850 °C, using 99.99% pure Al and Sc targets, pulsed and regular dc power, respectively, continuously rotating $1 \times 1$ cm$^2$ sapphire 0001 substrates, 5 mTorr 99.999% pure N$_2$, and a deposition rate of 6–13 nm/min depending on composition $x = 0–0.45$, which was determined by X-ray photoelectron spectroscopy (PHI 5000 VersaProbe). The thickness was measured by cross-sectional scanning electron microscopy (Carl Zeiss Supra), which is in agreement (within 6%) with the thickness determined by spectral ellipsometry (J. A. Woollam VASE).

Fig. 1 shows X-ray Diffraction (XRD) results from Al$_{1-x}$Sc$_x$N layers with $x = 0–0.45$, obtained using a PANalytical X’Pert Pro diffractometer with a hybrid X-ray mirror and two-crystal monochromator yielding Cu K$\alpha_1$ radiation (1.5406 Å) with 0.0068° divergence, and with a 0.27° acceptance parallel plate collimator in front of a scintillator point detector. Samples with $x \leq 0.24$ exhibit only two detectable peaks in $\theta$–2$\theta$ scans for $2\theta = 33°–75°$, which are due to a peak in the sapphire substrate 0006 and Al$_{1-x}$Sc$_x$N 0002 reflections. This result, in combination with XRD phi scans (not shown), indicate that the layers grow epitaxially on sapphire(0001) for $x \leq 0.20$ while epitaxy cannot be confirmed for $x > 0.2$, due to insufficient peak intensities. Small sections of typical $\theta$–2$\theta$
The result in Fig. 1(a), increasing the Sc concentration from 0.16, indicating a decreasing crystalline quality. This trend continues in-plane and out-of-plane lattice constants for AlN, which is 1.0 % increase over the range where c remains constant within 0.2%. The data are well described by a linear fit corresponding to $a(x) = 3.111 + 0.744x$ Å, plotted as dashed line in Fig. 1(c). However, $a = 3.30$ Å for $x = 0.20$, which is 1.2% above the expected value from the linear trend, confirming the onset of a structural instability at $x = 0.20$.

The observation that $a$ increases linearly with $x$ while $c$ remains nearly constant is similar to what has been reported for AlN by Akiyama et al.8 and Höglund et al.9 for GaN. It indicates a decrease in the average bond angle $\beta$ in the (1120) plane. This bond angle is known to be $\beta = 108.2^\circ$ for wurtzite AlN (Ref. 20) but is $90^\circ$ for both the stable six-fold coordinated rock-salt ScN, and the predicted nearly five-fold coordinated metastable hexagonal ScN with a layered structure,12 while wurtzite ScN with a predicted $\beta = 108.4^\circ$ (Ref. 26) is expected to be unstable.12 Therefore, we attribute the anisotropic expansion and the associated change in bond angle to a destabilization of the wurtzite structure by substitutional Sc atoms, associated with a transition from directionally sp$^3$-hybridized to isotropic ionic bonding. We calculate the bond angle using our measured $a$ and $c$ for $x \leq 0.16$ and find (i) $\beta = (108.4-12.1x)^\circ$ assuming all bonds have equal length, (ii) $\beta = (108.2-12.2x)^\circ$ assuming that the bond length ratio remains identical to that of AlN, or (iii) $\beta = (108.2-13.9x)^\circ$ assuming a linear combination of the bond length ratio between wurtzite AlN and hexagonal ScN. Extrapolating these relationships to $x = 1$ yields $\beta = 96.3$, 96.0, or 94.3°, which are all well above 90°, suggesting a non-linear exacerbated anisotropic deformation for $x > 0.16$. In fact, Al$_{0.80}$Sc$_{0.20}$N which is outside the linear regime in Fig. 1(c) exhibits a $\beta = 104.7^\circ \pm 0.3^\circ$, which is 1.0° smaller than 105.7 ± 0.3° predicted from our linear relationships, indicating an increasing destabilization of the wurtzite structure. That is, $x = 0.20$ represents an interesting composition, where the Sc concentration is large enough to cause non-linear structural changes while still small enough to suppress phase separation such that the resulting layer is single-phase but structurally unstable, representing a promising composition for a potentially large piezoelectric response.11,23 Here

![FIG. 1. XRD results from Al$_{1-x}$Sc$_x$N layers deposited on sapphire 0001. (a) $2\theta$–$\theta$ spectra showing the wurtzite phase 0002 and the rock-salt phase 111 peaks for $x = 0.0, 0.09, 0.20$, and 0.45, (b) asymmetric $2\theta$ scans showing the wurtzite phase 1013 reflection for $x = 0.0, 0.09, 0.20$, and 0.24. (c) measured in-plane $a$ and out-of-plane $c$ lattice constants of the wurtzite phase. The lines indicate the linear trends for $x \leq 0.16$.](image-url)
we also note that our measured $da/dx = 0.774$ Å is considerably larger than $\sim 0.25$ Å reported in Ref. 9 for layers deposited on Si(001) in an Ar/N$_2$ mixture at 580°C and $\sim 0.45$ Å for deposition on an AlN buffer on sapphire at 850°C in pure N$_2$. These differences may be attributed to different deposition conditions which may lead to variations in the strain as well as N-vacancy concentrations.

Fig. 2(a) is a plot of the absorption coefficient $x$ vs. photon energy $h\nu$ for Al$_{1-x}$Sc$_x$N layers with $x = 0.0$–0.45. Transmittance and reflectance spectra were measured using a Perkin-Elmer Lambda 950 spectrophotometer in the wavelength range from 185 to 600 nm and were calibrated using a metal mirror which was cross-calibrated with the measured reflectance from a polished sapphire surface, and with the measured specular transmission at the rough substrate back side, respectively. The substrate optical constants are taken from Palik’s handbook, and $x$ is determined using the method described in Refs. 28 and 29, which neglects multiple reflections within the layer. This approach is accurate if the majority of light is absorbed within a single path through the layer and leads for our layer thicknesses to uncertainties in $x$ of $<1 \times 10^4$ cm$^{-1}$, which is less than 8% for the $x$-range used to determine the band gap in this study.

The absorption for pure AlN ($x = 0$) in Fig. 2(a) exhibits a steep increase around 6.2 eV, consistent with a measured band gap of 6.15 eV, as discussed below. The shoulder at 6.0 eV is likely caused by N-vacancy defect states and is absent for AlN samples deposited at a higher temperature $T_s = 950$°C (not shown). The curve for Al$_{0.956}$Sc$_{0.044}$N exhibits a similar steep onset in $x$, however at a smaller $h\nu \approx 5.4$ eV, indicating a decreasing band gap with the addition of Sc. Increasing Sc further continues this trend, with the absorption edge decreasing monotonically to $\sim 2.5$ eV for $x = 0.45$. In addition, the absorption below the gap increases monotonically with increasing $x$, suggesting an increasing density of defect states within the band gap. This is quantified by measuring the slope $d/\mu(h\nu)$, as indicated by the dashed lines in Fig. 2(a) and plotted as a function of $x$ in Fig. 2(b). This plot shows a moderate increase in $d/(h\nu)$ with increasing $x$ for $x < 0.20$, followed by a more pronounced increase for $x > 0.20$, as illustrated by the dashed and solid lines in Fig. 2(b). This suggests a transition in the absorption process at $x \approx 0.20$, which coincides with the composition where the lattice constant vs. $x$ plot in Fig. 1(c) also shows a discontinuity. We attribute the absorption at large $x$ to segregated rock-salt ScN. This is most evident for the sample with $x = 0.45$ since rock-salt ScN is detected by XRD and the dashed line in Fig. 2(a) intercepts the $x$-axis at $h\nu = 2.5$ eV, which is within the reported range of the ScN optical transition at 2.1–2.6 eV. In fact, the intercept for all Al$_{1-x}$Sc$_x$N layers with $x \geq 0.24$ is at $h\nu = 2.51 \pm 0.02$ eV, suggesting the presence of segregated rock-salt ScN grains within these samples, even if they are too small to be detected by XRD for $x \leq 0.34$. Consequently, the linear increase in Fig. 2(b) for $x > 0.2$ is evidence that the amount of segregated ScN within Al$_{1-x}$Sc$_x$N increases linearly with $x$. For $x \leq 0.2$, the sub-bandgap absorption is small, and the positions of the intercepts with the $x$-axis are less well defined and are in the range of 2.4–3.0 eV. We attribute this absorption to Sc-induced defect states within the gap which may be associated with lattice distortions and/or N-vacancies. The linear increase in Fig. 2(b) for $x < 0.2$ suggests that the defect density is approximately proportional to the Sc concentration.

Fig. 3 shows a plot of the optical band gap as a function of $x$, as determined from the absorption coefficient using two different methods. The squares are obtained using the Tauc plot for a direct band gap, as illustrated in the inset for Al$_{0.956}$Sc$_{0.044}$N. The plotted ($z/\mu(x)^2$ vs. $h\nu$) curve in the inset increases steeply near the band gap and exhibits a linear region which, as illustrated with the dotted line, yields a band gap for $x = 0.022$ of 5.96 eV. The circles in Fig. 3 indicate the photon energies where $x = 7 \times 10^4$ cm$^{-1}$, which is the measured absorption coefficient of AlN at an energy corresponding to the AlN band gap determined from the Tauc plot. Thus, the circles represent an alternative method to determine the gap, which uses as an approximation the assumption that all changes in $x$ are due to changes in $E_g$. This method has the advantage to be relatively insensitive to sub-band gap absorption which causes the linear region in the Tauc plot to become less prominent with increasing $x$. The two methods yield similar results, with the largest deviation being 7%.

The measured bandgap for pure AlN is 6.15 eV, which is within the range of previously reported values, 6.0–6.3 eV. It is also close to the reported true direct gap at 10 K of 6.11 eV ($\Gamma_7 \rightarrow \Gamma_{7\text{bm}}$ transition), which is 0.2 eV lower than the 6.3 eV $\Gamma_7 \rightarrow \Gamma_{7\text{vb}}$ transition measured in perpendicular
incident geometry where the light wave vector is parallel to the c-axis.\textsuperscript{36} This suggests that crystal imperfections in our samples break the selection rule, yielding the true band gap. The band gap of Al\textsubscript{1-x}Sc\textsubscript{x}N decreases approximately linearly with increasing x for x < 0.20, drops even steeper between x = 0.20 and 0.34, from 4.37 to 2.94 eV, but approaches a nearly constant value for x > 0.34. The drop in the bandgap at x > 0.2 may be an indication of a structural transition consistent with the discontinuities observed in Figs. 1(c) and 2(b) and may also be attributed to absorption of segregated ScN which lowers the apparent band gap of Al\textsubscript{1-x}Sc\textsubscript{x}N, similar to what has been reported for Ga\textsubscript{1-x}Sc\textsubscript{x}N with x = 0.3–0.5.\textsuperscript{6} At large x, the apparent band gap approaches a constant value because absorption is dominated by segregated rock-salt ScN with a direct transition around 2.5 eV.

The decrease in the band gap in the single-phase region (x ≤ 0.20) is well described with a linear relationship $E_g(x) = 6.15 - 9.32x$ eV, as indicated by the line through the data points in Fig. 3. The rather strong composition dependence suggests, using an extrapolation to x = 1, that the unstable wurtzite or hexagonal ScN would be metallic, with a band overlap of 3.2 eV. This is in strong contrast to the predicted semiconducting properties of hexagonal ScN (Ref. 12) as well as similar extrapolations of the measured band gap of Ga\textsubscript{1-x}Sc\textsubscript{x}N layers, suggesting hexagonal ScN to be semiconducting with a 2.3–2.5 eV gap.\textsuperscript{6,7} That apparent contradiction between our results and these previously reported studies indicates that linear interpolation from wurtzite AlN to hexagonal ScN is not applicable. This is similar to our measured composition dependence of the band angle, which exhibits a highly non-linear region for x ≥ 0.20, suggesting that the compound becomes structurally unstable, even if still exhibiting a single-phase wurtzite structure. In addition, extrapolation of our measured lattice constants yields a unit cell volume of 64.1 Å$^3$ for h-ScN, which is 25% larger than 51.25 Å$^3$ predicted by simulation for relaxed pure h-ScN.\textsuperscript{12} Thus, the extrapolated band overlap from our study may be due to the considerably larger lattice constant of the hexagonal ScN as extrapolated from Al\textsubscript{1-x}Sc\textsubscript{x}N, in comparison to the reported extrapolation from Ga\textsubscript{1-x}Sc\textsubscript{x}N or prediction from simulated pure hexagonal ScN. A similar extrapolated band overlap of ~1.5 eV has recently also been reported for hexagonal YN, based on ternary Al\textsubscript{1-x}Y\textsubscript{x}N layers.\textsuperscript{37}

To summarize, reactive co-sputtering of Al\textsubscript{1-x}Sc\textsubscript{x}N on sapphire 0001 substrates at 850 °C yields single-phase epitaxial layers for x ≤ 0.20. The crystalline quality, as determined by x-ray diffraction decreases with increasing x, which is attributed to the destabilization of the wurtzite structure by substitutional Sc atoms. A rock-salt ScN 111 XRD peak for Al\textsubscript{0.55}Sc\textsubscript{0.45}N indicates phase separation. The out-of-plane lattice constant remains constant for x ≤ 0.16, while the in-plane constant increases linearly with x, indicating a decreasing bond angle. The bond angle shows a discontinuity at x = 0.20, suggesting an exacerbated destabilization of the wurtzite structure. This discontinuity also results in a steep increase in the sub-band-gap optical absorption. The optical band gap of wurtzite Al\textsubscript{1-x}Sc\textsubscript{x}N decreases according to $E_g(x) = 6.15 - 9.32x$ eV for x ≤ 0.20. At larger x, the structural instability and phase separation leads to an increasing dominance of absorption associated with a 2.5 eV direct transition.

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