Optical and electron transport properties of rock-salt Sc\textsubscript{1-x}Al\textsubscript{x}N

Ruopeng Deng, P. Y. Zheng, and D. Gall
Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

(Received 30 April 2015; accepted 16 June 2015; published online 7 July 2015)

Epitaxial single-crystal Sc\textsubscript{1-x}Al\textsubscript{x}N ternary alloy layers deposited by magnetron co-sputtering on MgO(001) substrates at 950 °C exhibit a solid solution rock-salt phase for x = 0–0.2 without decomposition. Optical absorption indicates a linear increase in the optical gap from 2.51 eV for ScN to 3.05 eV for Sc\textsubscript{0.8}Al\textsubscript{0.2}N and, after correction due to the Moss-Burstein shift, a direct X point interband transition energy \( E_g(\Gamma) = 2.15 + 2.75 \times x \) (eV). Correspondingly, the direct transition at the zone center increases with Al concentration according to \( E_g(\Gamma) = 3.80 + 1.45 \times x \) (eV), as determined from a feature in the reflection spectra. All layers are degenerate n-type semiconductors with a room temperature mobility that decreases from 22 to 6.7 to 0.83 cm\textsuperscript{2}/Vs as x increases from 0 to 0.11 to 0.20. The corresponding carrier densities are \( 9.2 \times 10^{20} \), \( 7.9 \times 10^{20} \), and \( 0.95 \times 10^{20} \) cm\textsuperscript{-3} as determined from Hall measurements and consistent with optical free carrier absorption below photon energies of 1 eV. Temperature dependent transport measurements indicate metallic conduction for ScN, but weak localization that leads to a resistivity minimum at 85 and 210 K for x = 0.051 and 0.15, respectively, and a negative temperature coefficient over the entire measured 4–300 K range for Sc\textsubscript{0.8}Al\textsubscript{0.2}N. The decreasing mobility is attributed to alloy scattering at randomly distributed Al atoms on cation sites, which also cause the weak localization. The carrier density is primarily due to unintentional F doping from the Sc target and decreases strongly for x > 0.15, which is attributed to trapping in defect states due to the deterioration of the crystalline quality, as evidenced by the x-ray diffraction peak width that exhibits a minimum of 0.14° for x = 0.11 but increases to 0.49° for x = 0.20. This is consistent with asymmetric x-ray diffraction analyses, indicating a relaxed lattice constant that decreases from 4.511 ± 0.005 Å to 4.411 ± 0.004 Å as x = 0–0.2, and a biaxial in-plane compressive strain that decreases from −1.1% to −0.2% as x increases from 0 to 0.11, which is attributed to the higher Al adatom mobility, but increases again to −1.8% for x = 0.20, as x approaches the critical composition for phase separation, which causes structural instability and a higher defect density. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4923429]

I. INTRODUCTION

Ternary nitride alloys combining transition metal nitrides and Group-III metal nitrides are already well known as protective coating material, with, for example, Ti\textsubscript{1-x}Al\textsubscript{x}N or Cr\textsubscript{1-x}Al\textsubscript{x}N exhibiting excellent wear and high temperature oxidation resistance.\textsuperscript{1–3} More recently, alloys combining ScN and Group-III nitrides have gained interest since Sc is isoelectric with Group-III metals, providing opportunities for bandgap engineering in alloys like Ga\textsubscript{1-x}Sc\textsubscript{x}N (Refs. 4 and 5) and Al\textsubscript{1-x}Sc\textsubscript{x}N,\textsuperscript{6,7} leading to potential applications in light-emitting diodes. In addition, Al\textsubscript{1-x}Sc\textsubscript{x}N shows promise for piezoelectric device applications as its piezoelectric coefficient has been reported to be up to 400% higher than that of pure AlN.\textsuperscript{8–12} This Al-rich Al\textsubscript{1-x}Sc\textsubscript{x}N alloy crystallizes in the wurtzite phase with Sc atoms substitutionally replacing Al, leading to an anisotropic expansion and softening of the alloy structure,\textsuperscript{6,8,13–15} which is attributed to substitutional Sc favoring a five-fold coordinated bonding as predicted in a meta-stable hexagonal ScN phase.\textsuperscript{16} Alternatively, the Al-ScN alloy system can also be stabilized in a cubic rock-salt structure, particularly for Sc-rich compositions, as the thermodynamically stable phase of pure ScN is rock-salt\textsuperscript{17–19} and AlN also exhibits a meta-stable rock-salt phase that can be synthesized at high pressure\textsuperscript{20} or stabilized in epitaxial multi-layers.\textsuperscript{21} In fact, phase-pure cubic Sc\textsubscript{1-x}Al\textsubscript{x}N layers have been deposited by magnetron co-sputtering over a large composition range 0 ≤ x ≤ 0.82, and their structure and phase stability studied by both experimental and theoretical methods.\textsuperscript{22–28} Density functional calculations predict that the band gap of cubic Sc\textsubscript{1-x}Al\textsubscript{x}N increases with x,\textsuperscript{29,30} providing potential for band gap engineering. ScN has also been proposed as a high-temperature thermoelectric candidate material,\textsuperscript{31–33} and alloying ScN with other nitrides could possibly provide approaches for tuning electrical and thermal conductivity.\textsuperscript{26} However, despite the potentially promising properties, relatively little is known about the optical and electronic transport properties of cubic Sc\textsubscript{1-x}Al\textsubscript{x}N.

In this paper, we report on the optical and electron transport properties of rock-salt Sc\textsubscript{1-x}Al\textsubscript{x}N ternary alloys deposited on MgO(001) by magnetron co-sputtering over the composition range x = 0–0.2. This investigation builds on our recently reported study on ScN,\textsuperscript{34} which exhibits a fundamental 0.92 ± 0.05 eV indirect band gap from the valence band maximum at the \( \Gamma \) point to the conduction band minimum at the X point, and direct band gaps at the X and \( \Gamma \) points which can be directly investigated using optical methods. In particular, absorption spectra indicate a direct
transition at the X point which increases from 2.18 to 2.70 eV due to a Burstein–Moss shift as the electron density increases from \( N = 1.12 \times 12.8 \times 10^{20} \text{cm}^{-3} \). In contrast, a feature at 3.80 \( \pm 0.02 \text{eV} \) in the ScN reflection spectrum that is associated with the direct transition at the \( \Gamma \) point is unaffected by \( N \). Correspondingly, for the present investigation on Sc\(_{1-x}\)Al\(_x\)N, we study both direct transitions at the X and \( \Gamma \) points as a function of Al concentration \( x \) by optical spectroscopy and find an approximately linear increase of the band gaps. The relatively high deposition temperature of 950 °C in this study results in a large adatom mobility and, in turn, epitaxial layers with good crystalline quality but also a tendency for phase separation into rock-salt ScN and wurzite AlN. Therefore, we limit the composition here to \( 0 \leq x \leq 0.2 \), which results for all layers in single phase epitaxial cubic Sc\(_{1-x}\)Al\(_x\)N ternary alloys. The crystalline quality increases with increasing \( x \) due to an enhanced adatom mobility and a decreasing lattice mismatch, but degrades quickly for \( x > 0.15 \), which also causes a steep decrease in the mobility and carrier density due to defect scattering and electron trapping in defect states. The random distribution of Sc and Al on cation sites causes weak carrier localization and a resulting minimum in the resistivity at a critical temperature that increases with \( x \).

II. EXPERIMENTAL PROCEDURE

Sc\(_{1-x}\)Al\(_x\)N layers were deposited by reactive magnetron co-sputtering in a load-locked ultra-high vacuum deposition system with a base pressure of \( 10^{-9} \text{Torr} \). Double-side polished 10 \( \times 10 \times 0.5 \text{mm}^3 \) single-crystal magnesium oxide MgO(001) substrates were cleaned in sequential ultrasonic baths of trichloroethylene, acetone, and isopropyl alcohol, for 15 min each, rinsed in de-ionized water, blown dry with nitrogen, mounted onto a Mo substrate holder using silver paint, and inserted into the deposition system. Prior to deposition, substrates were degassed at 1000 °C for 1 h. The substrate temperature was measured with a pyrometer that was cross-calibrated by a thermocouple underneath the substrate holder and was lowered to 950 °C for deposition by reactive sputtering from 5-cm-diameter nominally 99.99% pure Sc and Al targets in 20 mTorr 99.999% pure N\(_2\). The targets faced the substrate surface at a 45° angle and at a 9 cm distance from the substrate that was continuously rotated at 60 rpm to ensure composition and thickness uniformity. Both magnetrons were simultaneously operated with separate power supplies providing a constant DC power, which was kept constant at 300 W for the Sc target, resulting in a ScN deposition rate of 10 nm/min, and which was varied from 0 to 400 W for the Al target to control the Al concentration in the alloy layers. The deposition time for each sample was adjusted according to the Al power, in order to obtain comparable film thicknesses ranging from 250 to 300 nm, as measured by cross-sectional scanning electron microscopy (SEM) in a Carl Zeiss Supra microscope.

The composition and particularly the Al-to-Sc ratio was determined after deposition by Auger electron spectroscopy (ULVAC-PHI 700) and photoelectron spectroscopy (PHI 5000 VersaProbe). In addition, these methods were also used to detect fluorine impurities which stem from the Sc target and are the primary source of the free carriers, as reported in detail for the case of pure ScN in Ref. 34. The F impurity level in the Sc\(_{1-x}\)Al\(_x\)N layers is 2 ± 1 at. %, which is just slightly above the detection limit and, within the experimental error, independent of \( x \).

X-ray diffraction (XRD) was done in a PANalytical X'Pert Pro Diffractometer with a hybrid X-ray mirror and a two-crystal monochromator yielding Cu \( Kz_2 \) radiation (1.5406 Å) with a 0.0068° divergence, and with a 0.27° acceptance parallel plate collimator in front of a scintillator point detector. Symmetric and asymmetric \( \omega-20 \) spectra were acquired to determine both in-plane and out-of-plane lattice constants; \( \omega-\)rocking curve scans were collected to inspect crystalline quality; and \( \phi \)-scans at constant \( \omega \) and 20 angles corresponding to cubic 222 reflections were acquired to determine in-plane crystalline orientations and confirm epitaxy, similar to \( \phi \)-scans used to confirm the epitaxy of CrN(001) and Cu(001) deposited on MgO(001).

Ultraviolet-to-visible (UV-Vis) optical spectra were collected in a Perkin-Elmer Lambda 950 spectrophotometer over a wavelength range from 190 to 3000 nm in 1 nm steps. Transmittance \( T \) measurements were carried out at normal incidence, and reflectance \( R \) measurements were done with a 6° incident angle and an Al mirror reference which was calibrated with the polished surface of a sapphire substrate and optical constants of sapphire from Palik’s handbook. Both collected \( T \) and \( R \) spectra were treated to account for effects from the MgO substrate, using optical constants of MgO obtained from substrate \( T \) and \( R \) spectra measured in the same system.

Electronic transport measurements were done in a van der Pauw geometry. For this purpose, 1.5 \( \times \) 1.5 mm\(^2\) Al, Cu, or Au contacts were sputter deposited on the corners of each sample and were contacted to wire leads with silver paint. Room-temperature Hall measurements were done using an Accent HL5500 Hall system with a 0.518 T magnetic field. The temperature-dependent resistivity was measured in vacuum in a liquid-H\(_2\)O cryostat during warm-up from 4 K to ambient temperature. The temperature measurement/control system resulted in minor discontinuities in the slope of the measured resistivity \( \rho \) vs \( T \) curves at 50, 200, and 250 K, which have negligible effect on the quantitative data analysis in this paper. For each sample, resistances \( R_{12-34}, R_{34-12}, R_{14-32}, \) and \( R_{32-14} \) in both current directions were measured at room temperature and 4 K to accurately solve for the sheet resistance \( R_s \). The geometric factor \( g = R_{12-34}/R_s \) at the two temperatures was nearly identical, with a difference of <3% for all samples. The average \( g \) was subsequently applied to the measured \( R_{12-34} \) during the temperature sweep to obtain \( R_s \) as a function of temperature. All deposited films are sufficiently resistive to render thermoelectric voltage effects negligible, with zero current offsets being much smaller (<3%) than the voltage drop across the layer due to the measurement current. The latter was chosen to be small enough to have a negligible effect on the measured voltage due to local heating. The resistivity was determined from the measured \( R_s \) and the thickness from SEM measurements.
III. RESULTS AND DISCUSSION

X-ray diffraction $\omega$-2$\theta$ spectra showing the rock-salt 002 reflection from Sc$_{1-x}$Al$_x$N layers with $x = 0$–0.2 are plotted in Fig. 1(a) as both the measured data points and the Lorentzian fitting curves. The peak from the ScN film ($x = 0$) is centered at $39.72 \pm 0.02^\circ$, corresponding to a perpendicular (out-of-plane) lattice constant $a_\perp = 4.535 \pm 0.002$ Å. This value is larger than the reported ScN relaxed lattice constant of 4.501 Å,

\[ a \]  

indicating an in-plane biaxial compressive stress within the layer. The alloy with the largest Al concentration, $x = 0.018$, exhibits a peak with a 42% smaller intensity which is shifted to the right, corresponding to a reduced lattice constant of $a_\perp = 4.528 \pm 0.002$ Å. Increasing the Al concentration further to $x = 0.051$, 0.11, and 0.15 leads to a continuous peak shift to larger 2$\theta$-values of 40.00 ± 0.01°, 40.195 ± 0.005°, and 40.550 ± 0.005°, respectively, indicating that $a_\perp$ decreases, which is expected because rock-salt AlN has a smaller reported lattice constant than ScN. 20 In addition, the peak intensity from these layers is 2.1, 5.8, and 40.195 times stronger than for pure ScN, respectively, indicating that a 6% decrease, which is expected because rock-salt AlN has a smaller reported lattice constant than ScN. 20 For all layers, $a_\parallel$ is larger than $a_\perp$, indicating a biaxial in-plane compressive strain with a magnitude that decreases from 1.1% to 0.8%, 0.4%, and 0.2% for $x = 0$, 0.018, 0.051, and 0.11, respectively, and increases again to 0.3% and 1.8% for $x = 0.15$ and 0.20. The smallest strain of 0.2% is observed for the Sc$_{0.89}$Al$_{0.11}$N sample which also shows the largest x-ray diffraction intensity. This correlation of small strain with high diffraction intensity suggests that a larger atomic mobility which increases the crystalline quality also facilitates stress relaxation. The relaxed lattice constant for ScN is 4.511 ± 0.005 Å. This is slightly (0.2%) larger than the reported 4.501 Å for relaxed ScN. 40

![FIG. 1. X-ray diffraction (a) symmetric and (b) asymmetric $\omega$-2$\theta$ scans showing the 002 and 113 reflections, respectively, from epitaxial Sc$_{1-x}$Al$_x$N/MgO(001) layers with $x = 0$–0.2 as labeled.](image)

![FIG. 2. (a) Out-of-plane $a_\perp$, in-plane $a_\parallel$, and relaxed $a_\perp$ lattice constants vs Al concentration $x$ in Sc$_{1-x}$Al$_x$N/MgO(001) layers, and (b) full-width at half-maximum of XRD peaks from $\alpha$ rocking curves ($\Gamma_0^{002}$ and $\Gamma_0^{113}$) of the 002 and 113 reflections.](image)
which is attributed to Fluorine impurity atoms which stem from the Sc source material\(^{24}\) and occupy N lattice sites, causing a lattice expansion\(^{24,25}\) as well as a Burstein-Moss shift in the ScN direct optical transition,\(^{34}\) as discussed below. The relaxed lattice constant decreases with increasing \(x\), reaching \(a_o = 4.511 \pm 0.005, 4.495 \pm 0.003, \) and \(4.479 \pm 0.001 \) Å for \(x = 0.018, 0.051, \) and 0.11, respectively. These values are considerably above what would be expected using Vegard’s linear mixing rule, as indicated in Fig. 2(a) with a dashed line labeled \(a_{\text{Vegard}}\) which is determined using rock-salt ScN and AlN lattice constants of 4.501 and 4.045 Å, respectively.\(^{20,40}\) At higher Al concentrations, the measured \(a_o = 4.439 \pm 0.001\) and \(4.411 \pm 0.004 \) Å for \(x = 0.15\) and 0.20 approaches \(a_{\text{Vegard}}\). A similar non-linear \(a_o\) vs \(x\) dependence has also been reported by Höglund \textit{et al.}\(^{22}\) for Sc\(_{1-x}\)Al\(_x\)N solid solution films deposited on MgO(111) substrates at 600 °C with, opposite to our results, a deviation from \(a_{\text{Vegard}}\) for all compositions \(x \leq 0.6\).

Figure 2(b) is a plot of the x-ray diffraction peak widths vs composition \(x\) of Sc\(_{1-x}\)Al\(_x\)N(001) layers. More specifically, the plot shows the full-widths at half-maximum \(\Gamma_{02}^{002}\) and \(\Gamma_{20}^{002}\) of the 002 and 113 peaks from symmetric and asymmetric \(\omega-2\theta\) scans shown in Fig. 1 as well as the width \(\Gamma_{20}^{002}\) of the 002 \(\omega\) rocking-curves. All three measured peak widths are an indication of the crystalline quality where smaller \(\Gamma_{02}^{002}\) and \(\Gamma_{20}^{002}\) values indicate a larger x-ray coherence length perpendicular and parallel to the substrate surface, respectively, while \(\Gamma_{13}^{113}\) is affected by both the in-plane and out-of-plane coherence lengths with the former being more dominant. Peak broadening is due to the lattice distorting strain fields around dislocations and, for \(\Gamma_{02}^{002}\) and partially \(\Gamma_{13}^{113}\), also due to the mosaic spread associated with low-angle grain boundaries. The three plotted widths exhibit all a similar dependence on the Al concentration. In particular, \(\Gamma_{02}^{002}\) increases from 1.8° for ScN to 2.5° for Sc\(_{0.982}\)Al\(_{0.018}\)N, but decreases to 1.4°, 0.9°, and 0.8° for \(x = 0.051, 0.11,\) and 0.15, respectively, followed by a considerable increase to 1.5° for Sc\(_{0.8}\)Al\(_{0.2}\)N. Likewise, \(\Gamma_{13}^{113}\) increases from 0.98° to 1.2°, then decreases to 0.52° for \(x = 0.15\), and increases again to 1.0° for \(x = 0.20\), while \(\Gamma_{20}^{002}\) increases from 0.47° to 0.62° for \(x = 0.0–0.018\), decreases to a minimum of 0.14° for \(x = 0.11\), and increases to 0.49° for Sc\(_{0.8}\)Al\(_{0.2}\)N.

The overall trend of increasing crystalline quality with increasing \(x \leq 0.15\) is attributed to the combination of (i) the larger adatom mobility of Al vs Sc atoms which is due to both the lower metallic bond energy of Al vs Sc with melting points of 934 and 1812 K, respectively, and the lower atomic mass of Al which results in a considerably better mass-match with impinging N\(_2^+\)-ions and therefore a higher momentum transfer and, in turn, a higher Al surface diffusivity, and (ii) the decreasing lattice constant with increasing \(x\) which reduces the lattice mismatch with the MgO substrate from 7.1% for ScN to 5.4% for Sc\(_{0.85}\)Al\(_{0.15}\)N, leading to a lower misfit strain and dislocation density. The trend of increasing crystalline quality with increasing \(x\) is reversed for the highest Al concentration, \(x = 0.20\). This is attributed to this composition approaching the phase separation point above which wurzite AlN clusters form. Therefore, the single phase solid solution rock-salt structure of the Sc\(_{0.8}\)Al\(_{0.2}\)N layer has a reduced stability, which, in turn, leads to lower formation energies for crystalline defects and also allows larger strains, as evident from the rapid increase in strain between \(x = 0.15\) and \(x = 0.20\) in Fig. 2(a). We note that Höglund \textit{et al.}\(^{22}\) reported a single-phase rock-salt structure for Sc\(_{1-x}\)Al\(_x\)N up to \(x = 0.6\) and Saha \textit{et al.}\(^{28}\) stabilized the cubic phase by epitaxial constraints up to \(x = 0.82\). These larger critical Al compositions are attributed to the lower deposition temperatures of 600 °C and 750 °C in these studies, while the 950 °C in our investigation is expected to overcome kinetic barriers for phase separation at a lower Al concentration, slightly above \(x = 0.20\). The data points in Fig. 2(b) for the smallest Al concentration of \(x = 0.018\) deviate from the decreasing trend, showing a lower crystalline quality than for pure ScN although the strain, as shown in Fig. 2(a) is lower. This is not well understood but may be related to a deposition instability related to the formation of an AlN surface layer on the Al target which forms due to the low Al deposition power for this sample and causes the well-known hysteresis problem\(^{44,45}\) in reactive sputtering and, therefore, a non-uniform Al concentration in this layer.

Figures 3(a) and 3(b) show sections of transmittance \(T\) and reflectance \(R\) spectra, which are used to determine the direct optical transition energies in the Sc\(_{1-x}\)Al\(_x\)N ternary alloy. The \(T\) spectra in Fig. 3(a) indicate a relatively high transparency for photon energies \(h\nu\) between approximately 1 and 2.5 eV, leading to interference fringes with three maxima for all spectra. At low \(h\nu < 1\) eV, the transmittance decreases with decreasing \(h\nu\) due to free carrier absorption. This effect is strongest for the ScN layer and decreases with increasing \(x\), due to a decreasing free carrier density. More specifically, the transmittance at 0.5 eV is 5.9% for ScN and increases to 13% for Sc\(_{0.89}\)Al\(_{0.11}\)N and 36% for Sc\(_{0.8}\)Al\(_{0.2}\)N, indicating a decreasing absorption due to free carriers. At high \(h\nu, T\) decreases with increasing \(h\nu\), which is attributed to absorption from interband transitions. The transition energy increases with increasing Al concentration, as highlighted in Fig. 3(a) with a dashed line. More specifically, the transmission edge, defined as the photon energy for which \(T = 0.1\%\), is 2.79 eV for ScN, and shifts to 3.0 eV for Sc\(_{0.8}\)Al\(_{0.2}\)N.

FIG. 3. Optical (a) transmittance and (b) reflectance spectra vs photon energy \(h\nu\) from 250 to 300 nm thick Sc\(_{1-x}\)Al\(_x\)N layers on MgO(001) substrates with \(x = 0–0.2\).
x = 0.051, 3.15 eV for x = 0.11, and 3.62 eV for x = 0.2. This trend indicates an increasing direct band gap at the X point, discussed in detail below, as Al atoms substitutionally replace Sc to form a ternary alloy.

The R spectra in Fig. 3(b) are plotted for the high photon energy range from hν = 2–5.5 eV. Interference fringes dominate the spectra at low photon energies but disappear above ~2.5 eV for ScN to ~3 eV for Sc0.8Al0.2N, consistent with the decreasing transparency observed in Fig. 3(a). The spectra exhibit a relatively weak peak near 4 eV, which is due to direct interband transitions near the Γ point where valence and conduction bands are nearly parallel, yielding a high joint density of states.34 The position of this feature is highlighted by the tilted vertical line, indicating a shift from 3.8 eV for ScN to 4.0 eV for Sc0.8Al0.2N to 4.1 eV for Sc0.8Al0.2N. This shift indicates an increasing band gap with increasing Al concentration, as discussed more quantitatively below. The amplitude of the feature decreases with increasing x, which is attributed to the relaxation of k-vector conservation as an increasing fraction of cation sites are randomly occupied by Al atoms.

Figure 4(a) is a plot of the optical absorption coefficient α vs photon energy hν = 0.5–3.5 eV, as determined from T and R spectra using the method described in Ref. 17. The absorption spectra below 1 eV are dominated by the free carrier absorption. This absorption is largest for ScN, with α = 7.0 × 10^4 cm^{-1} at hν = 0.5 eV, and decreases to 6.3 × 10^4 and 5.3 × 10^4 cm^{-1} for x = 0.018 and 0.051, increases again to 6.3 × 10^4 cm^{-1} for x = 0.11, and continues to decrease to 5.0 × 10^4 and 2.6 × 10^4 cm^{-1} for x = 0.15 and 0.2. The general trend of a decreasing free carrier absorption is consistent with the above discussion of the transmission spectra and is primarily attributed to the decreasing free carrier density and mobility discussed below, while the reversal of the trend for the x = 0.11 sample is due to a larger free carrier concentration for this particular sample, as also presented below. The spectra also show an onset of strong absorption above 2 eV, which is due to interband transitions at the X point of the Brillouin zone. Increasing the Al concentration leads to a nearly parallel shift of the spectra to higher photon energies. For instance, the curve for ScN reaches α = 1.0 × 10^5 cm^{-1} at hν = 2.52 eV, while the photon energy to reach the same level of absorption increases to 2.56, 2.62, 2.73, 2.82, and 2.96 eV as the Al concentration increases to x = 0.018, 0.051, 0.11, 0.15, and 0.2, respectively.

Figure 4(b) is a plot of the optical gap energies as a function of Al concentration in Sc1−xAlxN. The data points are obtained using a quantitative analysis of the optical spectra. In particular, the optical gap E_g,opt, which is associated with direct interband transitions at the X point, is determined for each Al concentration from the α vs hν data, using the Tauc’s plot method as described in Ref. 6, while the value for the direct interband transition at the Γ point is obtained from the peak in the reflectance spectra in Fig. 3(b). In order to accurately determine this peak position, the reflectance spectra between 3 and 5 eV are fitted using a 10th-order polynomial, which provides smooth curves that retain the relevant peak. Subsequently, the peak position is obtained from the minimum of the second derivative of these smooth spectra, corresponding to the largest negative curvature of the original spectrum.

The obtained optical gap for the ScN layer is 2.52 eV, which is considerably larger than the reported intrinsic X point gap of 2.07 ± 0.05 eV.34 This larger measured value is due to the Burstein–Moss effect caused by free carriers35 which fill the bottom of the conduction band at the X point and therefore increase the optical gap. In fact, using the data for the optical gap vs carrier concentration N from Ref. 34, we estimate that this ScN layer with E_g,opt = 2.52 eV should have a N = 9.1 × 10^{20} cm^{-3}, which is very close to the 9.2 × 10^{20} cm^{-3} from the Hall measurements presented below. The Γ point transition energy E_g(Γ) for the ScN layer is 3.81 eV, in excellent agreement with the previously reported 3.80 ± 0.02 eV.34 The free carriers have negligible effect on this second transition, since the conduction band bottom is not at the Γ point and all samples in this study are n-type. Both optical transition values increase with increasing Al concentration, to E_g,opt = 2.55, 2.63, 2.74, 2.84, and 3.05 eV, and to E_g(Γ) = 3.83, 3.86, 3.95, 4.05, and 4.08 eV for x = 0.018, 0.051, 0.11, 0.15, and 0.2, respectively. This increase is approximately linear in x, as indicated by the dashed lines in Fig. 4(b), which are obtained by linear fitting and yield E_g,opt = 2.50 + 2.51 x (eV) and E_g(Γ) = 3.80 + 1.45 x (eV). In addition, Fig. 4(b) also contains X point gap values which are obtained by correcting the measured optical gap by a Burstein–Moss shift of N × (−4.3 × 10^{−22} eV cm^3) as reported for ScN,34 where N is the measured carrier concentration as presented below for each
Sc$_{1-x}$Al$_x$N layer. This analysis assumes that increasing $x$ causes negligible changes in the density of states at the bottom of the conduction band. The resulting X point gap $E_g(X)$ values increase approximately linearly with $x$, as indicated by the dotted line which corresponds to $E_g(X) = 2.15 + 2.75 x$ (eV). However, the data point for the largest Al concentration ($x=0.20$) is well above this line. We attribute this either to (i) the breakdown of a linear relationship which may be associated with the structural instability which also causes a dramatic decrease in the crystalline quality, as observed by the XRD results presented in Figs. 1 and 2, or (ii) an overestimation of the Burstein–Moss shift for the $x<0.20$ samples which have a large carrier concentration that is considerably reduced for $x=0.20$ due to trapping by defect states, as presented below. Extrapolation of the lines in Fig. 4(b) to $x=1$ suggests $E_g(X) = 4.90$ eV, $E_g_{opt} = 5.01$ eV, and $E_g(\Gamma) = 5.25$ eV for rock-salt AlN. These values are slightly larger than a previously reported extrapolation for the direct gap to 4.7 $\pm$ 0.2 eV, but smaller than the results from first-principles calculations for rock-salt AlN, which predict, similar to ScN, a valence band top at the $\Gamma$ point and a conduction band bottom at the X point, with $E_g(\Gamma) = 6.3$–7.2 eV and $E_g(X) = 7.6$–8.3 eV. However, we note here that the random arrangement of Al and Sc atoms on the cation sublattice are expected to relax the momentum conservation selection such that contributions from indirect interband transitions to the optical absorption spectrum may increase with increasing $x$. With this argument, extrapolation of $E_g$ values to $x=1$ points to the indirect $\Gamma \rightarrow X$ band gap of rock-salt AlN, which has been predicted to be 4.6–5.9 eV in good agreement with the 4.90–5.25 eV from our extrapolation.

Figure 5 is a plot of the carrier concentration $N$ and carrier mobility $\mu$ vs Al concentration $x$ in Sc$_{1-x}$Al$_x$N layers, as determined by room temperature Hall measurements. All samples exhibit an n-type carrier density which decreases and then increases slightly from $N = 9.2 \times 10^{20}$ cm$^{-3}$ for ScN to $7.4 \times 10^{20}$, $6.3 \times 10^{20}$, and $7.9 \times 10^{20}$ cm$^{-3}$ for $x = 0.018, 0.051$, and 0.11, respectively, followed by a considerable drop to $5.6 \times 10^{20}$ cm$^{-3}$ for Sc$_{0.85}$Al$_{0.15}$N and $0.95 \times 10^{20}$ cm$^{-3}$ for Sc$_{0.8}$Al$_{0.2}$N. The relatively large carrier densities indicate that the layers are highly degenerate semiconductors, consistent with the transport results presented below. The carriers are primarily attributed to unintentional F doping, as discussed above. The measured changes in $N$ are attributed to carrier trapping by deep level states associated with crystalline defects as well as localized states due to the random Al occupation of cation sites. In particular, the initial decrease in $N$ is attributed to increasing carrier localization with increasing $x$, while the high $N$ for the Sc$_{0.89}$Al$_{0.11}$N layer is due to the high crystalline quality as shown in Figs. 1 and 2, and the subsequent steep decrease in $N$ is due to both localization associated with the increasing Al concentration as well as carrier trapping due to a deteriorating crystalline quality. The measured mobility for ScN is $\mu = 22$ cm$^2$/V s, which is within the range of previously reported values for epitaxial ScN, ranging from 10–284 cm$^2$/V s. The mobility decreases with increasing Al concentration to $\mu = 17.5, 7.5, 6.7, 2.2$, and 0.83 cm$^2$/V s for the corresponding compositions from $x = 0.018$ to 0.20. The continuous decrease is primarily attributed to alloy scattering, that is, increasing electron scattering at the random arrangement of Sc and Al atoms which are expected to form a solid solution on cation sites. In addition, the decreasing crystalline quality particularly for $x = 0.20$ likely also contributes to the decreasing $\mu$ through scattering at crystalline defects.

Figure 6 shows temperature-dependent resistivity $\rho(T)$ curves from four Sc$_{1-x}$Al$_x$N samples with $x = 0, 0.051, 0.15$, and 0.2. The resistivity of the ScN layer in Fig. 6(a) remains nearly constant at 0.26 $\times$ 10$^2$ $\mu$Q cm for $T = 4$–70 K, and then increases linearly with $T$ to reach 0.30 $\times$ 10$^2$ $\mu$Q cm at 280 K. This temperature profile is characteristic for metallic conduction, indicating that this ScN layer is a highly degenerate semiconductor where the temperature dependence of $\rho$ is dominated by phonon scattering. In addition, the resistivity is lower than previously reported, which is attributed to the large carrier density in the ScN of the present study. The resistivity in Fig. 6(b) from the Sc$_{0.9}$Al$_{0.05}$N layer is...
approximately four times larger than for pure ScN, consistent with the considerably lower mobility and slightly lower carrier density shown in Fig. 5. It decreases from $1.22 \times 10^3 \mu\Omega$ cm at 4 K to a minimum of $1.21 \times 10^3 \mu\Omega$ cm at 85 K and increases to $1.31 \times 10^3 \mu\Omega$ cm at 290 K. The negative slope at low temperature is attributed to weak localization caused by Al-alloying induced disorder while the nearly linear positive slope at higher temperatures is due to phonon scattering. Similar localization has previously been reported for epitaxial Sc$_{1-x}$Al$_x$N(001).55 Ti$_{x}$W$_{1-x}$N(001),59 TaN$_{x}$(001).65,66 HfN$_{x}$(001),62 and CrN(001).63,64 The $\rho$ vs $T$ curves for Sc$_{0.85}$Al$_{0.15}$N and Sc$_{0.8}$Al$_{0.2}$N in Figs. 6(c) and 6(d) exhibit a negative slope over most of the measured temperature range, with $\rho = 5.25 \times 10^3$ and $153 \times 10^3 \mu\Omega$ cm at 4 K and $\rho = 4.90 \times 10^3$ and $79 \times 10^3 \mu\Omega$ cm at 290 K, respectively, and a minimum of $4.87 \times 10^3 \mu\Omega$ cm near 210 K for $x = 0.15$ and an expected minimum at $T > 300$ K for $x = 0.20$. The insets in these figures are plots of the conductivity $\sigma$ vs $T^{1/2}$. The curves are well described by the dashed straight lines due to the fast temperature rise associated with the low heat capacity at low $T$, while the deviation at high $T$ is attributed to phonon scattering. The linear trend with $\sigma = \sigma_0 + C T^{1/2}$ suggests that the transport is dominated by weak carrier localization due to the disorder from Al incorporation, where $\sigma_0$ is the zero-temperature conductivity and the constant $C$ is determined by the Fermi momentum, electron mean free path, and phase-breaking length $L_p$.65 The Fermi level is above the disorder-induced band tail for the degenerate n-type semiconductor ScN, and it does not move into the band tail with the addition of Al (up to $x = 0.2$), as this would cause strong localization and related hopping conduction at low temperature.63,64 That is, the ternary alloy conductors like a metal, except that the additional Al impurity atoms cause interference between coherent electron wave paths through back-scattering, increasing the overall resistivity. Weak localization occurs in Sc$_{1-x}$Al$_x$N if $L_p$ is larger than the average spacing between Al impurity atoms which is proportional to $x^{-1/3}$. Therefore, the minima $T_C$ in Figs. 6(b) and 6(c) are expected to be proportional to $x^{2/3}$, since $L_p$ is proportional to $T^{1/2}$.65 This is confirmed by comparing the two alloy samples Sc$_{0.9}$Al$_{0.1}$O$_{5.1}$N and Sc$_{0.85}$Al$_{0.15}$N which have a ratio in $x^{2/3}$ of 0.49, in reasonable agreement with 0.40, the ratio of the transition temperatures of 85 and 210 K.

### IV. CONCLUSIONS

Sc$_{1-x}$Al$_x$N ternaries deposited on MgO(001) substrates at 950°C form epitaxial layers over the entire investigated composition range $x = 0–0.2$ and exhibit a single cubic rock-salt phase. Increasing the Al concentration from $x = 0–0.11$ causes an increasing crystalline quality as quantified by the XRD peak widths. This is attributed to the higher adatom mobility of Al vs Sc atoms as well as the decreasing lattice mismatch to the substrate. However, $x = 0.20$ leads to a considerably lower crystalline quality, indicating that this composition approaches the phase separation point above which wurtzite AlN clusters form at the growth temperature of 950°C. Similarly, the measured biaxial compressive strain decreases from ~1.1% to ~0.2% but increases again to ~1.8% as $x$ increases from 0 to 0.11 to 0.20, suggesting that the increased atomic mobility facilitates strain relaxation but a composition close to the phase separation point suppresses relaxation. The relaxed lattice constant decreases with increasing $x$, while the band gap increases with increasing $x$, as quantified by (i) the optical band gap, (ii) the direct transition energy at the X point which is determined from the optical band gap corrected for the Burstein–Moss effect, and (iii) the direct transition energy at the Γ point, determined from the optical reflection spectra. All layers are degenerate n-type semiconductors that exhibit metallic conduction with weak carrier localization due to the randomness associated with the solid solution of Sc and Al atoms on cation sites. The mobility decreases from 22 to 0.83 cm$^2$/V-s as $x$ increases from 0 to 0.20. This is primarily attributed to alloy scattering and, for $x > 0.15$, also to scattering and trapping by crystalline defects. The carrier concentration of $6–9 \times 10^{20}$ cm$^{-3}$ for $x \leq 0.11$ is due to unintentional F impurities. It decreases steeply for $x > 0.15$ to $N = 0.95 \times 10^{17}$ cm$^{-3}$ for Sc$_{0.8}$Al$_{0.2}$N, which is attributed to trapping in defect states.

### ACKNOWLEDGMENTS

This research is supported by NSF through Grant Nos. 1309490 and 1234872. The authors would like to thank Swatilekha Saha and Professor Kim M. Lewis for their help with temperature-dependent resistivity measurements.

---


