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Gas source molecular beam epitaxy of scandium nitride on silicon carbide and gallium nitride surfaces

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Scandium nitride (ScN) is a group IIIB transition metal nitride semiconductor with numerous potential applications in electronic and optoelectronic devices due to close lattice matching with gallium nitride (GaN). However, prior investigations of ScN have focused primarily on heteroepitaxial growth on substrates with a high lattice mismatch of 7%-20%. In this study, the authors have investigated ammonia (NH₃) gas source molecular beam epitaxy (NH₃-GSMBE) of ScN on more closely lattice matched silicon carbide (SiC) and GaN surfaces (<3% mismatch). Based on a thermodynamic analysis of the ScN phase stability window, NH₃-GSMBE conditions of 10⁻⁵-10⁻⁴ Torr NH₃ and 800-1050 °C where selected for initial investigation. *In-situ* x-ray photoelectron spectroscopy (XPS) and ex-situ Rutherford backscattering measurements showed all ScN films grown using these conditions were stoichiometric. For ScN growth on 3C-SiC (111)- $(\sqrt{3} \times \sqrt{3})$ R30° carbon rich surfaces, the observed attenuation of the XPS Si 2p and C 1s substrate core levels with increasing ScN thickness indicated growth initiated in a layer-by-layer fashion. This was consistent with scanning electron microscopy (SEM) images of 100-200 nm thick films that revealed featureless surfaces. In contrast, ScN films grown on 3C-SiC (111)- (3×3) and 3C-SiC (100)- (3×2) silicon rich surfaces were found to exhibit extremely rough surfaces in SEM. ScN films grown on both 3C-SiC (111)-($\sqrt{3} \times \sqrt{3}$)R30° and 2H-GaN (0001)-(1 × 1) epilayer surfaces exhibited hexagonal (1×1) low energy electron diffraction patterns indicative of (111) oriented ScN. X-ray diffraction ω -2 θ rocking curve scans for these same films showed a large full width half maximum of 0.29° (1047 arc sec) consistent with transmission electron microscopy images that revealed the films to be poly-crystalline with columnar grains oriented at $\approx 15^{\circ}$ to the [0001] direction of the 6H-SiC (0001) substrate. In-situ reflection electron energy loss spectroscopy measurements determined the band-gap for the NH₃-GSMBE ScN films to be 1.5 ± 0.3 eV, and thermal probe measurements indicated all ScN films to be n-type. The four point probe sheet resistance of the ScN films was observed to increase with decreasing growth temperature and decreased with unintentional oxygen incorporation. Hg probe capacitance-voltage measurements indicated N_D-N_A decreased with decreasing growth temperature from 10^{19} to 10^{20} /cm³ for the lowest resistivity films to $\approx 5 \times 10^{16}$ /cm³ for the highest resistivity films. *In-situ* ultraviolet photoelectron spectroscopy measurements additionally showed the valence band maximum moving from 1.4 to 0.8 eV below the Fermi level with decreasing growth temperature consistent with the increased resistivity and reduction in carrier concentration. These results suggest that additional reductions in ScN carrier concentrations can be achieved via continued optimization of ScN growth conditions and selection of substrate orientation and surface termination. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4894816]

I. INTRODUCTION

Scandium nitride (ScN) is a group IIIB transition metal nitride semiconductor with an indirect band gap $(E_g = 1.3 \pm 0.3 \text{ eV})^{1-3}$ and rock salt (NaCl) crystal structure $[a_o = 0.4503 \pm 0.002 \text{ nm} \text{ (Refs. 4-8)]}$. ScN exhibits many

excellent physical properties typical of transition metal nitrides such as high hardness, mechanical strength, and high temperature stability (see Table I for a summary of reported ScN properties).^{1–32} The reasonably close lattice matching to cubic and wurtzite GaN (see Table II),^{33,34} demonstrated ability to grow large crystals,^{6,7} and low resistivity^{18–21} has recently made ScN an interesting choice as a possible conductive substrate,^{6,15} dislocation reducing interfacial buffer layer,^{35–43} semiconductor heterojunction,^{44,45} and Ohmic contact^{44–46} for GaN based devices. As an alloying agent with GaN and other group IIIA (AlN) and IIIB (MnN, YN) nitride semiconductors, ScN is of further interest for

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TABLE I. Properties of ScN.

Property	Value		
Crystal structure	Rock salt (NaCl)(Refs. 4–10)		
Lattice constant (nm)	0.4503 ± 0.0002 (Refs. 4–10)		
Bandgap, Eg (eV)	1.3 ± 0.3 indirect, 2.4 ± 0.3 direct (Ref. 1)		
Conductivity type	n-type (Refs. 4, and 10–21)		
Carrier	10^{18} -10 ²¹ (Refs. 4, and 10–21)		
concentration (cm^{-3})			
Electron mobility (cm ² /V s)	28–200 (Refs. 4, 10, and 18–21)		
Doping	n-type: O (Ref. 15)		
	p-type: none clearly identified (Refs. 4 and 10) ^a		
Resistivity (Ω cm)	2×10^{-6} -0.6 (Refs. 7, 13-16, and 18-24)		
Electron effective mass	0.1–0.2 m _o (Refs. 12 and 25)		
Optical dielectric	7 (Ref. 1), 5.2 (Ref. 11), 10.8 (Ref. 12)		
constant (ɛ)			
Infrared refractive index	2.56 (Ref. 26)		
$(at 400 - 8000 cm^{-1})$			
Young's modulus (GPa)	270-356 (Refs. 8, 27, and 28)		
Hardness (GPa)	21.1 ± 1.1 (Ref. 25)		
Poisson's ratio	0.188 ± 0.005 (Ref. 8), 0.20 ± 0.04 (Ref. 30)		
Thermal expansion coeff. $(10^{-6}/^{\circ}C)$	8.1 (Ref. 4), 8.68 (Ref. 23), 4 (Refs. 29 and 30)		
T_{melt} (°C)	2550 ± 50 (Ref. 23)		
Thermal	10–20 (Refs. 19 and 28)		
conductivity (W/m K)			
Oxidation resistance	Inert in air to temperatures of 600 °C (Ref. 23)		
Etchants	Inert in most acids and bases(Refs. 23 and 32)		
Seebeck	39 (Ref. 22), 86 (Refs. 18, 19, and 28)		
coefficient (μ V/K)			

^aSi, C, Zn, and Mg have produced only compensated material.

numerous electronic,^{47–49} optoelectronic,^{50–60} ferroelectric,⁶⁰ ferromagnetic semiconducting,^{61–65} piezoelectric,^{65–79} thermoelectric,^{18,19,28,79–82} and 2D semiconducting⁸³ applications. The high temperature thermodynamic stability⁹ and reported direct band gap of 2.1–2.4 eV (Ref. 1) has in particular made ScN an interesting potential replacement for InN in the fabrication of blue light-emitting diodes, lasers, and

TABLE II. Summary of lattice constant matching between ScN and various substrates utilized for heteroepitaxial growth (Refs. 33 and 34).

Substrate	Lattice constant (nm)	% Mismatch ScN (001)	
(001) ScN	0.450	0	
(001) MgO	0.421	6.4	
(001) Si	0.543	-20.6	
(001) 3C-SiC	0.436	3.2	
(001) c-AlN	0.438	2.7	
(001) c-GaN	0.452	-0.4	
(001) c-InN	0.498	-10.6	
Substrate Lattice constant (nm)		% Mismatch ScN (111)	
(111) ScN	0.314	0	
(111) Si	0.380	-22.3	
(0001) Al ₂ O ₃	0.458	-51.6	
(0001) 6H-SiC	0.308	1.9	
(0001) w-AlN	0.311	0.9	
(0001) w-GaN	0.319	-1.6	
(0001) w-InN	0.354	-12.8	

other III-N optoelectronic applications.^{50–54} However, a serious impediment to the use of ScN in many of these applications is the difference in crystal structure between ScN (NaCl) and group IIIA nitride semiconductors (wurtzite or zinc-blende). Prior investigations have shown a limited alloying window for ScN with GaN $(\sim 17\%)^{51,54-56}$ and AlN $(\sim 20\%)^{57,58}$ before the films become either amorphous or microcrystalline with the rock salt crystal structure.^{50,55}

Prior investigations of ScN epitaxy have focused primarily on hydride vapor phase epitaxy (HVPE),^{4,10,84,85} magnetron sputtering, $1\overline{8},24,\overline{86}$ or N_2 plasma activated molecular beam epitaxy (MBE)^{13,16,41,87,88} using substrates such as MgO (100), 16,19,24,87,88 Al₂O₃ (0001), 4,18 Si (111), 8,89 and Si (100).^{13,90} In this report, we investigate gas source MBE (GSMBE) of ScN on 3C-SiC and 2H-GaN surfaces using ammonia (NH₃) and thermally evaporated Sc in a III-N GSMBE system previously utilized to investigate AlN and GaN heteroepitaxy on 6H-SiC.^{91–93} SiC is a particularly interesting substrate for heteroepitaxial ScN growth due to both commercial availability and a reasonably close lattice matching to both ScN and III-NA semiconductors GaN and AlN (see Table II).^{33,34} The previously demonstrated use of ScN as a dislocation reducing buffer layer for GaN epitaxy on Si substrates^{35–43} offers the tantalizing possibility for using ScN as a more conductive (and lattice matched) buffer layer for GaN heteroepitaxy on SiC. The low resistivity and high temperature stability of ScN also makes it of interest as a potential Ohmic contact to SiC in both high temperature and high frequency device applications. It is important to note that, as shown in Table II, the lattice mismatch between ScN (111) and 3C-SiC (111) is only 3.5% and significantly better than that for other substrates previously investigated such as Al₂O₃ (0001), 13.9%; Si (001), 20.6%; and MgO (001), 7.3%.84,89,90

There have been only a few reported investigations of ScN or Ga_{1-x}Sc_xN NH₃-GSMBE.^{8,38,89,94} Most of these studies utilized oxide or Si substrates. Reports of ScN growth on SiC are (to the authors knowledge) limited to a single investigation using HVPE.⁸⁴ These prior investigations focused primarily on either the crystallinity, surface morphology, and mechanical properties of ScN;^{8,87,89} or the use of ScN as a buffer layer for GaN heteroepitaxy.³⁸ These studies have shown that, in general, an epitaxial relationship exists between the orientation of the substrate and the resulting ScN epilayer (i.e., $(111)_{ScN}/(111)_{Si}$, $(111)_{ScN}/(0001)_{A12O3}$ and (100)_{ScN}/(100)_{MgO}). However, ScN films grown heteroepitaxially on (111) and (0001) surfaces have typically exhibited a columnar texture with rough surfaces exposing (100) facets. On the other hand, ScN films grown on MgO (100) surfaces have been reported to exhibit comparatively atomic smooth surfaces¹⁷ that are presumably the result of the greater adatom mobility on ScN (100) surfaces.87,88,95,96

In order to understand and advance the state of the art for ScN heteroepitaxy, we have undertaken a detailed thermodynamic and experimental investigation of the growth conditions, growth mechanisms, and resulting films' properties and microstructure for ScN NH₃-GSMBE on 3C-SiC (111) and (100) and 2H-GaN (0001) surfaces. We specifically utilized the HSC thermochemistry software to first map out the thermodynamic stability window for ScN under NH₃-GSMBE growth conditions and to understand the reactivity and stability for Sc and ScN interfaces with SiC. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were utilized to experimentally investigate the stoichiometry and growth mechanism of the first several monolayers of ScN on 3C-SiC (111) surfaces. Techniques such as low energy electron diffraction (LEED), scanning electron microscopy (SEM), x-ray diffraction ω -2 θ rocking curve (XRC) and transmission electron microscopy (TEM) were used to investigate the surface structure, surface topography, and crystallinity of thicker ScN films grown on both 3C-SiC and 2H-GaN surfaces. Ultraviolet photoelectron spectroscopy (UPS), reflection electron energy loss spectroscopy (REELS), Hg probe capacitance-voltage (CV), four point probe and thermal probe measurements were additionally utilized to understand the electronic properties of these same films with and without Si, C or O doping. Preliminary attempts at the growth of $Ga_xSc_{1-x}N$ alloys are also described.

II. EXPERIMENT

A. ScN thermodynamics

To determine the initial process conditions for NH₃-GSMBE ScN growth, the HSC Chemistry software (version $(6.1, \text{Outotec})^{97}$ was utilized to determine the thermodynamic stability window for ScN under NH3-GSMBE growth conditions as a function of temperature and pressure. The HSC software utilizes the Gibbs free energy minimization method to find the most stable phases and phase compositions at a fixed mass balance, temperature, and pressure for a given initial starting composition. More specifically, HSC seeks to find the phase composition where the Gibbs free energy of the system is minimized. This method has been described in detail elsewhere98,99 and has been previously successfully utilized for modeling the growth of a variety of materials by chemical vapor deposition^{100,101} and atomic layer deposition.^{102,103} The pressure and temperature conditions considered covered a range common for both MBE and CVD growth of III-N compounds. All the known thermodynamic equilibrium species in the Sc-N-H system were considered including solids ScN and Sc and gases/vapors NH₃, N₂, H₂, H, N, NH, NH₂, N₂H₂, N₂H₄, N₃H, Sc, and Sc₂.

HSC Chemistry was additionally utilized to investigate the reactivity of Sc with SiC during initial ScN growth, and the thermodynamic stability of ScN/SiC interfaces. In this case, only solid state species such as Sc, ScN, SiC, C, Si₃N₄, Si, and Sc₅Si₃ were considered. For these calculations, a range of temperatures (0–1200 °C) were explored at a constant pressure of 760 Torr (1 atm).

B. ScN Growth

A GSMBE system designed and constructed specifically for the growth of ScN, AlN, and GaN thin films was utilized in these studies.^{104,105} The GSMBE was connected to an ultrahigh vacuum transfer line that allowed for *in-situ* LEED, AES, REELS, XPS, and UPS analysis of the ScN films.^{106–109} A base pressure of 10^{-10} Torr was achieved in the GSMBE system via a 400 l/s turbo pump and a 500 l/s ion pump. During nitride growth, the GSMBE system was pumped by the turbo pump only in order to prevent irreversible damage to the ion pump. Substrate temperatures of 1100 °C were easily achieved via a hot tungsten filament heater.

Source materials in the GSMBE system consisted of NH₃ (99.9995%), SiH₄ (99.999%), C₂H₄ (99.999%), Sc (99.99%), Ga (99.99999%), and Al (99.99999%). The NH₃ was further purified via an inline metalorganic resin purifier connected directly to a leak valve mounted on the GSMBE chamber. The SiH₄ and C_2H_4 gases were utilized for surface cleaning and ScN doping and were used as received without additional purification. The metals were evaporated from standard 25 cc Knudsen cells. Impurities in the scandium charge (including Al, Ca, Cr, Cu, Mn, Si, and Y) were each <30 parts per million (ppm) according to the manufacturer (Alfa-Aesar) and not detected during in-situ AES and XPS measurements of test Sc films evaporated onto 6H-SiC (0001) substrates. However, significant amounts of fluorine (~ 5 at. %) were initially detected by XPS in these test Sc films and attributed to the scandium charge.¹⁸ Fluorine was not detected by XPS in any of the subsequently grown ScN films.

Vicinal and on axis, 6H-SiC wafers (0001) ($N_d \approx 10^{18}$ / cm³) with a 1 μ m 3C-SiC epitaxial layer (N_d $\approx 10^{17}$ /cm³) were provided by Cree Inc. The unpolished sides of these wafers were coated with an opaque tungsten film via RF sputtering to increase the thermal heating efficiency of the SiC substrate, as the latter is transparent to the infrared radiation emitted by the tungsten filament heater. After sputter coating, the wafers were ultrasonicated in trichloroethylene, acetone, and methanol for 10 min each, and then dipped in 10:1 buffered HF for 10 min to remove the surface oxide.^{110,111} The wafers were subsequently degassed/annealed at 1050 °C in 10⁻⁹ Torr vacuum in the GSMBE system for 10–15 min to desorb the surface oxide.^{112,113} This surface displayed a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ reconstruction in LEED that has been previously shown to be slightly carbon rich relative to the $(\sqrt{3} \times \sqrt{3})$ R30° surface generated by annealing in Si or SiH₄.^{114–116} For the latter surface preparation, the surface reconstruction has been conclusively shown to consist of a Si adatom sitting in a T₄ site over a complete Si-C bilayer.^{117,118}

The 3C-SiC epilayers grown on Si (100) substrates were provided by Hoya Research Co. These wafers received a similar wet chemical solvent and HF clean prior to loading into vacuum and a high temperature anneal in SiH₄ that produced an oxygen free (3×2) reconstructed surface. The 3C-SiC (100)–(3×2) surface has been previously shown to be Si rich consisting of Si adatoms (1/3 monolayer) resting on top of a Si adlayer (2/3 monolayer) on the bulk truncated Si plane of 3C-SiC.¹¹⁹

The 2H-GaN (0001) surfaces were prepared *in-situ* by GSMBE on 6H-SiC (0001) substrates using a high temperature AlN buffer layer as previously described.¹²⁰ Prior to ScN growth, the 2H-GaN (0001) surface was annealed for 5 min in 10^{-5} Torr NH₃ at the growth temperature to remove

any background surface carbon or oxygen contamination from extended storage in the UHV transfer line. This procedure has been previously shown to reduce such surface contaminations to <1% monolayer and produce a suitably clean surface for heteroepitaxy.^{108,121}

Details concerning NH₃-GSMBE of ScN have been previously provided elsewhere.^{105,106} Briefly, growth of ScN was investigated on the 3C-SiC and 2H-GaN surfaces in 10^{-5} -10⁻⁴ Torr NH₃ at temperatures ranging from 800 to 1050 °C. The temperature range investigated was intentionally selected to probe the regions of ScN phase stability identified in the previously described thermodynamic analysis. As will be shown later, NH₃ was introduced first to avoid formation of Sc₅Si₃ before ScN growth. The sublimation temperature for the Sc Knudsen cell was set at 1250–1350 °C. Growth proceeded at a rate of $\sim 100 \text{ nm/h}$ and was terminated by shuttering the Sc Knudsen cell. The samples were cooled in flowing NH₃ until approximately 400 °C at which point the NH₃ valve was closed and the GSMBE system was pumped to base to facilitate transfer to the other connected UHV systems for further analysis

The XPS, and UPS measurements have been described previously and were performed in a separate vacuum chamber attached to the main UHV transfer line.¹⁰⁷ Briefly, all XPS spectra were collected using Al K α radiation (h ν = 1484.6 eV) in a 2 × 10⁻¹⁰ Torr UHV system. Calibration of the binding energy scale for all scans was achieved by periodically taking scans of the Au 4f_{7/2} and Cu 2p_{3/2} peaks from standards and correcting for any discrepancies with the known values (83.98 and 932.67 eV, respectively). A combined Gaussian– Lorentzian curve shape with a linear back-ground was found to best represent the data.

The LEED and AES/REELS optics were mounted on a six-way cross connected to the transfer line and pumped through the transfer line. A 3 keV, 1 mA beam was used in the AES analysis and 100–1000 eV beam in REELS. Each AES spectrum was collected in the undifferentiated mode and numerically differentiated. An 80 eV, 1 mA beam was used in the LEED optics.

SEM imaging was performed using a JEOL 6400FE operating at 5 kV, and conventional high resolution TEM was conducted using a Topcon EM-002B microscope operating at 200 kV.¹²² High-resolution x-ray rocking curve ω -2 θ were performed using a Philips X'Pert MRD diffractometer in the triple axis mode.¹²³ The electrical resistivity of the ScN films were measured using a Veeco FPP-5000 fourpoint probe system and the carrier concentration was estimated using capacitance–voltage measurements performed on a MDC CSM/2 Hg prober.¹²⁴ Secondary ion mass spectrometry (SIMS) was performed using a Cameca IMS-3F ion microscope system.^{125,126}

III. RESULTS AND DISCUSSION

A. ScN thermodynamics

To understand and select an initial set of NH₃-GSMBE growth conditions to explore, an MBE/CVD equilibrium diagram for ScN was computed using the HSC Chemistry



Fig. 1. (Color online) Calculated GSMBE-CVD ScN equilibrium phase diagram for $NH_3/Sc = 5000:1$.

software package for an NH₃/Sc ratio of 5000:1. The computed equilibrium diagram shown in Fig. 1 illustrates that under GSMBE conditions $(10^{-5}-10^{-4} \text{ Torr NH}_3)$, ScN is the equilibrium phase to ~900 °C. This phase is stable at higher temperatures, but is in equilibrium with a significant amount of Sc(v). At still higher temperatures, ScN decomposes completely into Sc(v) and N₂(g). Decreasing the NH₃/Sc ratio to 500:1 and 1:1 was observed to push the ScN/ScN + Sc(v) and ScN + Sc(v)/Sc(v) + N₂ boundaries to higher temperatures by 120 and 160 °C, respectively. Based on this preliminary analysis, a temperature window of 800–1050 °C was selected for initial exploration of ScN NH₃-GSMBE.

B. ScN growth initiation on 3C-SiC

As scandium is a very reactive metal with the strong possibility of interfacial silicide formation for Si based substrates, the stability of scandium with SiC was additionally investigated using the HSC software. The results of these calculations are shown in Fig. 2 for a starting composition of 1000 mol of 3C-SiC and 100 mol of metallic Sc. As can be seen, Sc was predicted to react completely with SiC to form Sc₅Si₃ and free carbon at low temperatures with some small amounts of metallic Sc remaining at higher temperatures (800 °C) typical for GSMBE and CVD.

To experimentally check for the possibility of scandium silicide formation during initiation of ScN growth on SiC, Sc



Fig. 2. (Color online) Calculated equilibrium phases for 100 mol Sc with 1000 mol 3C-SiC. Note: 3C-SiC phase excluded for clarity.



FIG. 3. (Color online) XPS spectra of Si2p core level from (a) Sc evaporated on 3C-SiC (111)/6H-SiC (0001) at 500 °C, and (b) ScN grown on 3C-SiC (111)-($\sqrt{3} \times \sqrt{3}$)R30° at 800 °C.

was evaporated on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surfaces at 500 °C. Figures 3(a) and 4(a) show XPS spectra of the Si 2p and C 1s core levels, respectively, after the deposition of several monolayers of Sc. Both figures show two clearly resolvable peaks that can be attributed to Si and C in two distinct chemical environments. The higher binding energy Si 2p and C 1s peaks at 101 and 283.2 eV are consistent with those of Si-C bonding, whereas the two lower binding energy peaks are attributed to ScSi_x formation and free carbon as predicted in the thermodynamic calculations shown in Fig. 2. We also note that the lower binding energy C 1s peak may be due to Sc₃C₄ formation not considered in the thermodynamic analysis due to lack of thermochemical data on this compound.^{127,128} Based on these results and concerns of creating a heteroepitaxy limiting ScSi_x/C interfacial layer, all ScN growth on SiC was initiated by first exposing the substrate to NH₃ and then quickly opening the Sc effusion cell. Prior studies of AlN heteroepitaxy on SiC⁹¹ have shown this will lead to some Si-N bonding at the ScN/SiC interface, but will likely not represent a serious impediment to heteroepitaxial growth.

C. Growth—ScN on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30°

In-situ XPS and AES of ~200 nm thick ScN films grown on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surfaces using 10⁻⁵ Torr



FIG. 5. (Color online) XPS of $Sc2p_{3/2,1/2}$ and N1s from (a) room temperature evaporated Sc, and (b) GSMBE ScN grown on 3C-SiC (111)/6H-SiC (0001).

NH₃ at temperatures of 800–1050 °C detected the presence of only Sc and N with a trace of oxygen (1%–2%). Other contaminants such as carbon or fluorine were not detected. The oxygen detected in XPS is believed to be located strictly at the surface and the result of Sc reaction with background moisture in the UHV transfer line. The reported heat of formation for Sc₂O₃ is highly negative (–1908 kJ/mol)⁹⁷ and hence there is a huge chemical driving force for reaction of some surface Sc with background H₂O. Secondary ion mass spectroscopy (SIMS) measurements to be described later found the oxygen in the bulk of the ScN films to be in the ppm range.

Figure 5 shows an XPS spectrum encompassing the N 1s and Sc $2p_{3/2,1/2}$ core levels for (a) a Sc film evaporated at room temperature, and (b) a ScN film grown at 1050 °C on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surfaces. As can be seen, the Sc $2p_{3/2,1/2}$ core levels in ScN are shifted to higher binding energy consistent with Sc being bonded to N as opposed to metallic Sc. The ScN XPS spectrum shown in Fig. 5(b) is also extremely similar to the one obtained by Porte for a 1:1 stoichiometric ScN film prepared by argon sputtering Sc onto a Ta foil in 3×10^{-7} Torr N₂.¹²⁹ The Sc $2p_{3/2,1/2}$ and N 1s core levels for the ScN film were well fitted using a single mixed Gauusian–Lorentzian peak and showed no evidence of a second metallic Sc peak. As shown in Fig. 6, the full



FIG. 4. (Color online) XPS spectra of C1s core level from (a) Sc evaporated on 3C-SiC (111)/6H-SiC (0001) at 500 °C, and (b) ScN grown on 3C-SiC (111)- $(\sqrt{3} \times \sqrt{3})$ R30° at 800 °C.



FIG. 6. (Color online) Sc $2p_{3/2}$ and N 1s FWHM as a function ScN GSMBE growth temperature.



Fig. 7. (Color online) UPS spectra of ScN grown on 3C-SiC (111)/6H-SiC (0001) at (a) 800, (b) 925, and (c) 1050 $^\circ\text{C}.$

width half maximum (FWHM) of the Sc 2p and N 1s core levels were observed to decrease with decreasing growth temperature. This suggests a more uniform bonding environment for Sc and N in films deposited at lower temperatures. However, the position of the Sc $2p_{3/2}$ core level relative to the N 1s was interestingly found to be constant at ~4.3 eV for films grown at 800–1050 °C.

The ratio of the integrated areas for the Sc $2p_{3/2}$ and N 1s core levels was found to increase slightly (~1%–5%) with decreasing growth temperature. However, using published XPS sensitivity factors for the Sc $2p_{3/2}$ and N 1s core levels,¹³⁰ respectively, the Sc/N ratio for all the films was determined to be 1.0 ± 0.05 . This was confirmed by separate *ex-situ* Rutherford backscattering (RBS) measurements performed at the University of Albany Dynamitron Accelerator Laboratory.¹³¹ Thus, any possible variation in ScN film stoichiometry with growth temperature was determined to be within the experimental accuracy of XPS and RBS.

The position of the ScN valence band maximum relative to the system Fermi level (VBM- E_F) was also observed to be a function of growth temperature. As illustrated in the UPS spectra shown in Fig. 7, VBM-E_F was observed to decrease from 1.4 eV for films grown at 1050 °C to 0.8 eV for films grown at 800 °C. The ScN UPS spectra shown in Fig. 7 are qualitatively similar to the ScN UPS spectra previously obtained by Porte for N2 sputter deposited ScN on polycrystalline Ta¹²⁹ and by Gall et al. for N₂ magnetron sputter deposited ScN on TiN/MgO (001).¹ All three sets of UPS spectra exhibit a double peak between the valence band maximum and ~ 6.5 eV binding energy that is associated with N 2p bands. However, VBM- E_F for the ScN films studies by Porte and Gall are both at ~ 2.0 eV below the Fermi level. Both do not exhibit a small peak at 7.2 eV that starts to develop in the 925 °C UPS spectrum of this study and is clearly prominent in the 800 °C UPS spectrum. As no such state is apparent in any of the theoretical valence band density of states published for ScN (001),^{1,3,129,132–134} we attribute this feature to an unknown surface state for the ScN (111) surface. Further evidence to confirm this feature as a surface state will be presented in a separate publication.¹⁰⁵

As thermal probe measurements indicated all of the ScN films in this study were n-type, the variation in VBM- E_F



FIG. 8. (Color online) REELS spectrum of ScN grown on 3C-SiC (111)/6H-SiC (0001) at 800 °C.

between different studies and the observed change with growth temperature could be due to a narrowing of the ScN band gap,¹³² upward surface band bending due to the creation of midgap surface states, or a change in the Fermi level in the bulk ScN film. For the former, the band-gap of the ScN films as a function of growth temperature was estimated using *in-situ* REELS. It has been previously shown that an extrapolation to the x-axis of the turn in energy loss below the main elastic scattering peak in REELS spectra provides an accurate estimate of the band-gap of a material.^{135,136} In this case, we determined a band-gap of 1.4 ± 0.2 eV for a ScN film grown at 800 °C (as shown in Fig. 8) and a bandgap of 1.6 ± 0.2 eV for a film grown at $1050 \degree$ C (not shown). These values are consistent with the ScN band-gap value of 1.3 ± 0.3 eV determined by Gall based on a compilation of different measurements for ScN films deposited by a variety of methods.¹ The value of 1.6 eV for the band-gap of the 1050 °C ScN film is also consistent with the value of 1.4 eV for VBM-E_F observed in UPS for a highly n-type film. The slight increase in band-gap with growth temperature is also possibly consistent with the density functional theory (DFT) calculations by Moreno-Armenta that have shown a widening of the ScN band-gap for nitrogen rich compositions.¹³² However, these slight changes in band-gap with growth temperature/composition do not explain the observed change in VBM-E_F with growth temperature.

To address the possibility of surface states and surface band bending, we note that relatively little is known about (111) oriented ScN surfaces. However, several theoretical and experimental investigations of ScN (001) surfaces have been made that may provide some insight. In this regard, DFT calculations by Takeuchi and Ulloa¹³³ and Stampfl *et al.*^{3,137} have both indicated that Sc rich surfaces are metallic while N rich ScN (001) surfaces are semiconducting with no surface states in the gap. Experimentally, these results have been confirmed by scanning tunneling spectroscopy (STS) measurements performed by Al-Brithen *et al.*¹⁷ where semiconducting behavior was observed for nitrogen rich (001) surfaces and metallic behavior for Sc rich (001) surfaces formed via RF N₂ MBE of ScN on MgO (001) substrates. For the N rich surface, these STS measurements indicated that Sc 3d derived surface states reside deep in the conduction band and N derived states in the valence band. A slight downward band bending of 0.1–0.3 eV was also observed for the N rich surface, which was attributed to lowering of the conduction band edge by a Coulomb field created by ionized subsurface donors. This downward band bending could explain the slightly larger values of VBM- $E_F \cong 2.0$ observed in the Porte and Gall UPS studies.^{1,129} These results also indicate that the decrease in VBM- E_F with decreasing growth temperature could be due to a change in surface stoichiometry from N to Sc rich.

To address the possibility of a change in bulk Fermi level position with growth temperature, we note that the resistivity of the GSMBE ScN films was observed to be a function of the growth temperature. Four point probe resistivity measurements for films grown at 1050 °C were found to be conductive with a resistivity of $\sim 0.01 \ \Omega$ cm. However, films grown at lower temperatures of 925 and 800°C were observed to be highly resistive and beyond the impedance of the four point probe (0.04 M Ω cm). The combined UPS and resistivity measurements, therefore, imply a decrease in effective carrier concentration with ScN growth temperature. This was confirmed via Hg probe capacitance-voltage measurements where films with a resistivity of $\sim 0.01 \Omega$ cm exhibited high carrier concentrations of $(N_D-N_A) = 10^{19}-10^{20}/cm^3$ whereas the most resistive films grown at 800 °C exhibited N_D-N_A carrier concentrations of $\approx 5 \times 10^{16}$ /cm³. It should be noted that we have previously observed Hg probe CV measurements to underestimate the carrier concentration in NH₃-GSMBE GaN relative to more detailed Hall mobility measurements where carrier concentrations were typically found to be an order of magnitude higher.¹²⁰

Ohgaki et al. have observed a similar decrease in carrier concentration with decreasing growth temperature for RF N₂ MBE ScN films grown on MgO (001) substrates.²¹ In that study, the n-type carrier concentration was observed to decrease from 8×10^{20} /cm³ for growth at 850 °C to 2×10^{19} / cm³ for films grown at 300 °C. This was attributed primarily to a change in native defect concentration with growth temperature. Smith et al. have also observed that the resistivity of RF N₂ MBE ScN can vary with the deposition stoichiometry with N rich conditions yielding films with a resistivity of $5.8 \times 10^{-4} \ \Omega$ cm and Sc rich conditions yielding more conductive films with a resistivity of $1 \times 10^{-4} \ \Omega \ \text{cm.}^{16}$ However, these resistivities and carrier concentrations are, respectively, substantially lower and higher than those for the films grown in this study. Previously reported resistivity and carrier concentrations for ScN range from 10^{-4} to $0.1 \,\Omega$ cm and 10^{18} to 10^{21} /cm³, respectively.^{10,13,16–21} We attribute the higher resistivity and lower carrier concentrations for the films in this study to reduced background oxygen concentrations relative to other films. High carrier concentrations have been previously attributed to background oxygen,^{15,18,19} and Oshima has recently demonstrated some of the highest mobility/lowest carrier concentration $(10^{18}/\text{cm}^3)$ ScN films via careful attention to sources of oxygen in HVPE grown ScN.⁸⁵ As we will show later, we find that unintentional oxygen doping during GSMBE growth of ScN at 800 °C can lead to films with resistivities of <0.01 Ω cm and carrier concentrations of >10²⁰/cm³. Although not the focus of this study, we believe the lower background oxygen contents achieved in this study are a result of the lower system base pressure and the use of a LN₂ cryo panel with a high pumping speed for background H₂O and O₂.

In-situ XPS analysis of thinner (2–3 nm) ScN films grown on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surfaces allowed both the chemical structure of the ScN/3C-SiC interface as well the ScN growth mechanism to be investigated. Figures 3(b) and 4(b) show XPS spectra of the Si 2p and C 1s core levels, respectively, for ScN grown on 3C-SiC at 800°C with an NH₃ pre-exposure. In contrast to Sc evaporated directly on 3C-SiC at 500°C, only single Si 2p and C 1s core levels from the SiC substrate were observed with no clear evidence for the formation of any silicide, silicon nitride, or free carbon interface layers.

The growth mechanism of the first several monolayers of ScN was also investigated by monitoring the attenuation of the Si 2p and C 1s core levels after the growth of several consecutive 0.1–2 nm thick ScN layers. As has been previously shown,¹²⁰ the attenuation of the substrate core levels should decrease exponentially for Frank van der Merwe (FM) 2D layer-by-layer growth according to the following relationship:

$$I_S/I_0 = \exp(-t/\lambda),\tag{1}$$

where *t* is the overlying film thickness, λ is the mean free path of the photoelectron being measured, I_0 is the initial intensity of the substrate core level, and I_S the substrate core level intensity with overlying film of thickness *t*. The mean free paths for the Si 2p and C 1s core levels in ScN were determined to be 1.9 and 2.1 nm, respectively, using the following relationship from Briggs and Seah:¹³⁰

$$\lambda = 0.41 \left(aE \right)^{1/2} + 538E^{-2},\tag{2}$$

where λ is in monolayers, *E* is the kinetic energy of the photoelectron, $a = (\rho M_W/N_A)^{1/3}$, ρ is the density of the film, M_W = molecular weight of the film, and N_A is Avogadro's number. As shown in Fig. 9, the attenuation of the Si 2p and C 1s core levels with increasing ScN thickness was well fitted by Eq. (1) using the calculated mean free paths and indicates that the growth of the first several nanometers of ScN on SiC occurs in a 2D layer-by-layer fashion. This is consistent with SEM examination of thicker (100–200 nm) ScN films where featureless surfaces were observed up to magnifications of 10 000×. Additionally, some films grown on offaxis 6H-SiC (0001) surfaces exhibited a steplike structure apparently mimicking the steps on the SiC substrate surface.

Hexagonal (1 × 1) LEED patterns were obtained at $E_p \approx$ 50 eV from all ScN films indicating growth of (111) oriented ScN with a ScN₍₁₁₁₎/3C-SiC₍₁₁₁₎/6H-SiC₍₀₀₀₁₎ epitaxial relationship. However, a large FWHM of 0.29° (1047 arc sec) was observed in ω -2 θ XRC measurements of ScN films grown at 800 °C. This is in agreement with transmission electron microscopy images of the same 800 °C ScN films which revealed a fine grained polycrystalline structure with



FIG. 9. (Color online) Attenuation of Si 2p and C 1s core levels (I/I_0) from the 3C-SiC (111)/6H-SiC (0001) substrate as a function of overlying ScN film thickness. Dashed line represents the theoretical I/I_0 for FM layer-by-layer growth.

the grains oriented at an angle of $\sim 15^{\circ}$ to the [0001] direction of the 6H-SiC substrate (see Fig. 10). These results are similar to those obtained by Edgar et al. for HVPE growth of ScN on 6H-SiC (0001) substrates.⁸⁴ In that study, the authors observed growth of (111) oriented ScN grains at temperatures of 800-900 °C. At higher temperatures of 1000 °C, a mixture of (100) and (111) orientations were observed. For NH₃-GSMBE ScN, Moram et al. have also observed the growth of (111) oriented ScN on Si (111).8,38,89 For optimized growth conditions at 850 °C, the FWHM of 0.51° obtained in ω -2 θ XRC measurements is higher but comparable to that obtained in this study. Interestingly, Moram intentionally pre-exposed the Si substrate to Sc to form a Sc silicide interfacial layer.⁹⁰ Pre-exposure to NH₃, as in this study, was reported to result in poorly oriented films.⁸⁹ Moram also observed the root mean square (RMS) roughness of the ScN epilayers grown on Si (111) increased with increasing ScN thickness and growth temperature.^{8,38} For the former, Moram observed the RMS roughness to increase from 2.5 nm at 50 nm thickness to 10-12 nm at >200 nm thickness.³⁸ This is somewhat consistent with our observation of layer-by-layer growth on 3C-SiC (111) for the first several nanometers of ScN followed by eventual surface roughening as a poly-crystalline surface morphology develops as observed in TEM (see Fig. 10).

The etch resistance for the ScN films grown at 800 °C on 3C-SiC (111) was investigated in a variety of different concentrated acids and bases via covering portions of the ScN film with melted black wax. In general, the ScN films were visually observed to be readily etched at room temperature after immersion for 2–30 min in concentrated acids such as HCl, HF, HNO₃, and H₂SO₄, but not etched (or very slow etched) in concentrated alkaline bases such as NaOH and KOH for the same amount of time. These results are consistent with early reports by Dismukes that ScN dissolves only in strong acids and molten NaOH.^{4,10} The latter results are also consistent with the defect selective etch study of Chaudhuri where no etching of ScN was observed by NaOH and KOH at temperatures below 200 °C.^{32,138}

D. Growth—ScN on 2H-GaN (0001)

Although not investigated in as great a detail, ScN growth on 2H-GaN (0001)–(1 × 1) surfaces exhibited many similarities to growth on the 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surface. ScN films grown at 800 °C on 2H-GaN (0001) exhibited similar stoichiometry to those grown on 3C-SiC (111) based on *in-situ* XPS and AES measurements and were also highly resistive based on four point probe measurements. The same films exhibited sharp hexagonal (1 × 1) LEED patterns indicative of (111) oriented ScN with a ScN(111)/GaN(0001) epitaxial relationship. As with growth on 3C-SiC (111), TEM micrographs showed that the ScN films grown on GaN were polycrystalline with the grains oriented at an angle to the (0001) surface normal (see Fig. 11).

While there have been several investigations of GaN on ScN buffer layers,^{35–43} there have been relatively few investigations of ScN growth on GaN. Perjeru *et al.* utilized plasma assisted physical vapor deposition to grow n-type



Fig. 10. TEM micrograph of ScN grown on 3C-SiC (111)-($\sqrt{3}\times\sqrt{3})R30^\circ$ surface at 800 $^\circ C.$



FIG. 11. TEM micrograph of ScN grown on GaN (0001) surface.

ScN on metalorganic chemical vapor deposited n-type GaN (0001) and characterized only the rectifying electrical properties of the heterojunction.^{44,45} In contrast, Hall *et al.* investigated RF N₂ MBE of ScN on (100) oriented cubic GaN formed via nitridation of a GaAs (100) surface.⁴² In this case, Hall observed that ScN grew with a twinned (111) orientation relative to the c-GaN (100) surface.

The adsorption, reaction, and nitridation of Sc deposited on GaN (0001) has been investigated in more detail both experimentally and theoretically. Experimentally, Kaplan investigated the evaporation of Sc onto metalorganic chemical vapor deposition (MOCVD) GaN (0001) surfaces at temperatures of 645-780°C.35 Using AES and XPS, Kaplan observed Sc to react with GaN to form a ScN interfacial layer that exhibited a facetted hexagonal (1×1) LEED pattern. The thickness of the ScN interfacial layer formed was 3-15 nm depending on the GaN surface temperature. In contrast, Moram investigated the high temperature $(1070 \,^{\circ}\text{C})$ nitridation of metallic Sc sputter deposited on MOCVD GaN (0001) at room temperature.^{37–40} XRD of the resulting ScN showed the films to be poly-crystalline with (111) orientation. These results are consistent with the (111) oriented ScN films grown directly on GaN (0001) in this study.

More recently, Lopez-Perez and Gonzalez-Hernandez have, respectively, conducted DFT studies of Sc adsorption on $(0001)^{139}$ and $(10\overline{1}0)^{140}$ surfaces of GaN. For the GaN $(0001)-(2 \times 2)$ surface, Lopez-Perez found that while the T₄ site is the energetically most favorable adsorption site, Sc adatoms prefer to incorporate into the GaN surface at Ga substitutional sites.¹³⁹ Similarly for the GaN $(11\overline{2}0)$ and $(10\overline{1}0)$ surfaces, Gonzalez-Hernandez found that Sc prefers to incorporate in Ga substitutional sites as well.¹⁴⁰ These results are consistent with the previously mentioned AES and XPS measurements of Sc/GaN interfaces by Kaplan,³⁵ and may partially explain the twinned (111) orientation observed by Hall⁴² for ScN growth on GaN (100) surfaces and the tilted orientation of the ScN grains in the films for this study.

E. Growth—ScN on 3C-SiC (001)– (3×2)

Based on the above results for ScN growth on (111)/ (0001) oriented SiC and GaN surfaces and the demonstrated improvements in crystallinity and surface roughness for ScN growth on (100) oriented versus (110) MgO and (0001) Al₂O₃ surfaces,⁸⁷ ScN growth on (001) oriented 3C-SiC was attempted to see if films with improved crystallinity could be achieved. Unfortunately, ScN growth on the 3C-SiC (001)- (3×2) surface exhibited contrasting behavior compared to the results observed for 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surfaces. While films grown on 3C-SiC (001)– (3×2) at 800-1050 °C were observed to have a similar Sc/N stoichiometry in XPS and AES to those grown on 3C-SiC (111), all of the films were found to be conductive with resistivities $<0.01 \Omega$ cm. The LEED patterns for the ScN films grown on 3C-SiC (001)–(3 \times 2) were generally diffuse and exhibited weak (1×1) patterns. SEM investigation of the surface morphology for films grown at 800-950 °C showed what appeared to be highly facetted ScN islands on top of a ScN film or SiC surface. Overall, the surface morphology for these films resembled those reported by Edgar for HVPE growth on 6H-SiC (0001) substrates.⁸⁴ However, for films grown at 1025 °C, a continuous film with no faceting was observed.

These results indicate dramatically different growth on $(111) - (\sqrt{3} \times \sqrt{3}) R 30^{\circ}$ mechanisms for ScN VS (100)– (3×2) oriented SiC surfaces. This result is perhaps not surprising given the prior reported differences in ScN growth on (100) vs (110) and (111)/(0001) MgO surfaces where smooth film surfaces were observed for growth on (100) orientations and rough surfaces were observed for (110) and (111)/(0001) orientations.⁸⁷ These differences have been primarily attributed to differences in the surface diffusion length for Sc adatoms on (001), (110), and (111)/(0001) surfaces.^{24,27,87} However, aside from simple differences in crystallographic orientation, there are also significant differences in surface composition for the (111)- $(\sqrt{3} \times \sqrt{3})$ R30° and (100)-(3 × 2) oriented 3C-SiC surfaces utilized in this study that need to be considered. As mentioned previously, the 3C-SiC (111)-($\sqrt{3} \times \sqrt{3}$)R30° surface prepared in this study is slightly carbon rich¹¹² whereas the 3C-SiC (100)-(3 \times 2) surface is silicon rich with a nearly full Si monolayer coverage over bulk terminated 3C-SiC (100). Given the previously mentioned high reactivity and thermodynamic driving force for Sc to form Sc₃Si₅ with SiC, the presence of an extra Si monolayer on 3C-SiC (100)-(3×2) in addition to the difference in surface structure and bond density could dramatically alter ScN growth on this surface.

Interestingly, Moram has previously observed significant differences in growth of ScN on Si (111) and (100) surfaces that were attributed to crystallographic differences in how an intentional ScSi1.7 interfacial layer formed on the two surfaces due to a Sc pre-exposure.⁹⁰ To test the influence of an additional Si adlayer on growth of ScN on 3C-SiC (111) surfaces, one ScN film was grown on the 3C-SiC (111)- (3×3) surface which also consists of a Si-Si bilayer.¹¹¹ In this case, three dimensional growth and ScN island formation was also observed. Similarly, pre-exposing the 3C-SiC (100)-(3 \times 2) surface to Sc rather than NH₃ resulted in a ScN film that exhibited no discernable LEED pattern. These results confirm the presence of the Si-Si adlayer as the likely origin for the differences in ScN growth observed on 3C-SiC (111) and (100) surfaces and provides high motivation for ScN growth on bulk terminated or carbon rich 3C-SiC (100) surfaces. (Note: this will be the focus of possible future research.)

F. ScN doping and alloying

In an attempt to further modulate the electrical properties of ScN, Si and C doping of ScN films grown on 3C-SiC (111) using SiH₄ and C₂H₄, respectively, was also investigated. Attempts at doping ScN with Si using a background partial pressure of 10^{-8} – 10^{-7} Torr SiH₄ did not noticeably affect the resistivity of ScN films grown at 800 °C. In contrast, the resistivity of ScN films grown using a background pressure of 10^{-8} – 10^{-7} Torr C₂H₄ showed a dramatic decrease in resistivity to $<0.01 \Omega$ cm and an increase in N_D- N_A to 10^{20} /cm³ in Hg probe CV measurements. These results initially suggested carbon to be an effective n-type dopant for ScN. However, subsequent SIMS analysis showed no incorporation of carbon into the ScN films, but instead showed the oxygen background had increased by 2-3 order of magnitudes. The increase in background oxygen in the ScN was likely a result of H₂O or O₂ impurities in the C₂H₄. These results, however, are in excellent agreement with those of Moram where oxygen was found to be an excellent n-type dopant for ScN.¹⁵ Most recently, Oshima et al. have demonstrated a marked reduction in free carrier concentrations for HVPE ScN via reducing background C, O, Si, and Cl contamination through elimination of sources of reactor hardware corrosion. These combined observations point to the high resistivity/low carrier concentrations reported earlier being a result of reduced background oxygen contamination relative to previous ScN MBE investigations.

To explore the ultimate goal of replacing In with Sc in III-N optoelectronic devices, growth of Ga_{1-x}Sc_xN alloys was also explored using a growth temperature of 800 °C. Initials attempts at combining the previously determined optimum GaN growth conditions¹²⁰ with those utilized for ScN growth resulted in a nominally Ga_{0.5}Sc_{0.5}N film as shown by the *ex-situ* AES spectrum in Fig. 12. This $Ga_{0.5}Sc_{0.5}N$ film grown on a 100 nm thick ScN (111) buffer layer previously grown in-situ on 3C-SiC (111) exhibited triangular facetted grains suggesting a cubic crystal structure. However, LEED measurements exhibited only a diffuse hexagonal (1×1) pattern. More Ga rich $Ga_xSc_{1-x}N$ alloys were also attempted on an in-situ grown GaN/AlN buffer layer grown on a 6H-SiC (0001) substrate via lowering the Sc Knudsen cell evaporation temperature to 1100-1275 °C. This resulted in $Ga_xSc_{1-x}N$ alloys where the Sc content was <5% or below the AES detection limit. These films exhibited smooth surfaces under SEM examination, but were also observed to have formed surface channel cracks on cooling from the deposition temperature that prohibited further electrical characterization. All of the $Ga_{1-x}Sc_xN$ alloys were observed to exhibit brilliant blue cathodoluminescence during AES а measurements.

Growth of low Sc content $Ga_xSc_{1-x}N$ alloys (x < 2%) via NH₃ GSMBE has been previously demonstrated by Moram⁵⁴ and Knoll^{94,141} using 500 nm thick GaN buffer layers deposited on (0001) Al₂O₃ substrates. These studies showed Sc was soluble in GaN up to these concentrations and that the alloys retained the GaN wurtzite structure with increased lattice constants. Theoretical studies have indicated a wide alloying window for a wurtzite $Ga_xSc_{1-x}N$ of up to 66% Sc.^{55,56} However, the RF N₂ MBE studies of Constantin *et al.* have experimentally found the critical Sc concentration to be lower at ~17% for growth on a 50 nm MOCVD GaN buffer layer on a (0001) Al₂O₃ substrate.^{51,52} At higher Sc concentrations, the $Ga_xSc_{1-x}N$ films were observed to exhibit a transitional structure until a Sc content of 54% was reached where the rock salt structure stabilizes.



FIG. 12. (Color online) *Ex-situ* AES spectrum of nominally Ga_{0.5}Sc_{0.5}N film grown on 100 nm ScN/3C-SiC (111).

These results are consistent with our observation of a possible cubic structure for a $Ga_{0.5}Sc_{0.5}N$ film.

G. Selection of optimum ScN and ScN alloy growth conditions

The above growth studies show that ScN films can be easily grown on 3C-SiC and 2H-GaN surfaces via NH3-GSMBE in the temperature range of 800-1050 °C. Experimentally, films grown at 800 °C where found to exhibit the lowest N 1s and Sc 2p XPS FWHM, highest resistivity, and lowest carrier concentration. To the authors knowledge, the ω -2 θ XRC FWHM of 0.29° for the ScN films grown on 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° at 800°C is also the lowest experimentally reported for ScN epilayers to date. Moram et al. have also explored ScN NH₃-GSMBE on Si (111) surfaces over a slightly lower temperature window of 600-1000 °C and similarly found 800 °C to be an optimal growth temperature based on a minima in the ω -2 θ XRC FWHM for their films.^{8,38,89} Interestingly, almost all prior investigations of ScN heteroepitaxial growth under MBE like conditions (N₂ sputtering, RF N₂ MBE, and NH₃-GSMBE) all seem to have universally arrived at 750-850 °C as an optimal growth temperature (see Table III). This similarity, despite a variety of different growth methods, substrates, and surface preparation conditions, points to a universal underlying fundamental mechanism.

Some possible insight into the universal growth temperature of 750–850 °C for ScN heteroepitaxy can be provided by our ScN thermodynamic stability calculations. These results indicate that growth at 750–850 °C under MBE conditions cleanly lies in the ScN equilibrium region whereas growth at higher temperatures occurs in a temperature regime where ScN is in equilibrium with a significant amount of Sc vapor. Growth in the ScN + Sc(v) regime could lead to the formation of a variety of Sc and N vacancy related point defects that may explain the higher resistivity for the ScN films in this study and the higher ω -2 θ XRC FWHM observed by Moram⁸⁹ for films grown at >900 °C. Interestingly, optimal HVPE ScN growth temperatures are slightly higher relative to the other ScN growth methods investigated (see Table III). This is fully consistent with the higher pressures utilized in this growth method and our ScN phase diagram which shows the pure ScN stability window to extend to higher temperatures at higher pressures.

However, we do note that there may be additional contributing factors in the selection of ScN growth temperature. As noted by Gall, a growth temperature of 750 °C for UHV N_2 sputter deposition of ScN on MgO was selected primarily to limit the interfacial reaction of ScN with MgO.¹ Also, Smith has pointed out the importance of surface adatom mobility in the growth of ScN.¹⁶ In addition to being substrate orientation dependent, surface diffusion is also exponentially dependent on surface temperature and this is likely why the highest possible growth temperatures in the ScN stability region have been selected for growth under MBE like conditions.

Another possible universal observation in the growth of ScN appears to be the correlation between background oxygen contamination and resistivity/carrier concentration. In this study, we have directly observed a sharp decrease in resistivity and increase in carrier concentration due to unintentional oxygen doping of our ScN films. Moram¹⁵ has previously noted similar effects in N₂ sputter deposited ScN and Oshima⁸⁵ has recently demonstrated a several order of magnitude reduction in carrier concentrations for HVPE deposited ScN films by reducing background sources of O and other contaminants. As the primary limiter for ScN in semiconducting applications is the high background carrier concentrations and the in-ability to achieve p-type material, these combined results clearly indicate that careful attention to sources of oxygen (and other background contaminants) must be taken into consideration. However, minimizing background oxygen contamination in ScN will be particularly challenging given the previously mentioned large negative heat of formation reported for Sc₂O₃ of -1908 kJ/ mol.⁹⁷

An additional consideration for the heteroepitaxial growth of ScN is the surface composition, structure and termination of the substrate. Prior studies by other authors have shown a clear dependence on substrate orientation [i.e., (100) vs (111)]. However, the results of this study have shown a clear

TABLE III. Summary of optimum ScN growth conditions (T_{grow}) for various ScN growth methods reported in the literature (HV = high vacuum, UHV = ultra HV, NS = not specified.)

Method	Substrate	$T_{ m grow}$ (°C)	N ₂ /NH ₃ pressure (Torr)	Reference
UHV N ₂ Sputter	MgO (100)	750	5×10^{-3}	1, 9, 24
HV N ₂ Sputter	Al ₂ O ₃ (0001)	800	1.5×10^{-3}	18
HV N ₂ Sputter	MgO (100)	850	2×10^{-3}	19
RF N ₂ MBE	MgO (100)	800	9×10^{-6}	16, 88
RF N2 MBE	MgO (100)	800	5×10^{-6}	21
RF N ₂ MBE	Si (100)	800	3×10^{-5}	90
NH ₃ -GSMBE	Si (111)	850	NS	8, 38, 89
NH ₃ -GSMBE	Si (111)	800	$10^{-5} - 10^{-4}$	This study
HVPE	Al ₂ O ₃ (0001)	850-930	NS	4, 10
HVPE	6H-SiC (0001)	800–900	0.7	84
HVPE	Al ₂ O ₃ (10–10)	1050	760	85

improvement in ω -2 θ XRC over previous results by growing or more highly lattice matched substrates, but radically different results when growing on C vs Si rich SiC surfaces. This can likely be attributed to the high reactivity of Sc and underscores the need for careful substrate surface preparation for achieving the highest possible quality growth of ScN.

Lastly, as 800 and 1050 °C have been determined to be our optimized growth temperatures for GaN and AlN, respectively,¹²⁰ ScN should be much easier to incorporate into these compounds than InN which is highly unstable at these temperatures under MBE.¹⁴² Previous attempts in this research to grow InN via NH₃-GSMBE at these temperatures were completely unsuccessful. In this study, we have successfully demonstrated the incorporation of 2%-5% Sc in GaN, and Constantin has demonstrated up to 17% Sc incorporation in GaN using RF N₂ MBE.^{51,52} Unfortunately, the difference in crystal structure between ScN and AlN/GaN will limit the range over which these compounds can be successfully combined to form equilibrium alloys.^{52,60} However, the results of Lee et al. have shown that single phase, NaCl structure $Al_xTi_{1-x}N$ with x as large as 0.8 can be fabricated via plasma enhanced chemical vapor deposition.¹⁴³ The observation by these investigators of metastable AlN particles with the NaCl structure is extremely encouraging with respect to perhaps achieving ScN-GaN-AlN devices with rock salt structure.

IV. SUMMARY AND CONCLUSIONS

ScN films have been successfully grown on 3C-SiC (111) and (100) and GaN (0001) surfaces by NH₃-GSMBE in the temperature range of 800-1050 °C. ScN growth on the carbon rich 3C-SiC (111)–($\sqrt{3} \times \sqrt{3}$)R30° surface was observed to initiate in a layer-by-layer fashion and exhibited smooth surfaces in SEM. Growth on the 3C-SiC (100)– (3×2) surfaces, however, exhibited rough surface topography. All ScN films grown on the various surfaces were stoichiometric, n-type, and polycrystalline. REELS measurements indicated the band-gap of the ScN films to be 1.5 ± 0.3 eV and the electrical properties of the films were observed to be sensitive to both the growth temperature and background oxygen impurities. Films grown at 800 °C were highly resistive with N_D - $N_A \cong 5 \times 10^{16}$ /cm³, whereas films grown at 1050 °C or unintentionally doped with oxygen were more conductive with resistivities of $<0.01 \Omega$ cm and $N_{\rm D}-N_{\rm A} \cong 10^{19}-10^{20}/{\rm cm}^3$.

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