

HVPE of scandium nitride on 6H–SiC(0001)

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Abstract

The epitaxy of scandium nitride deposited by hydride vapor phase epitaxy on 6H–SiC(0001) substrates is reported. The structure and composition of the deposited films were dependent on both the scandium metal source and substrate temperatures. At substrate temperatures between 800 and 900 °C, the ScN exhibited a single (111) orientation. At substrate temperatures of 1000 °C and above, the films were mixtures of (100) and (111) orientations. Aluminum was detected by EDAX in the ScN films when the scandium source temperature was greater than 900 °C, presumably due to the reaction between scandium and the alumina reactor tube. Chlorine was detected in the films, and its concentration increased as the scandium source temperature was decreased from 1000 to 800 °C.

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1. Introduction

The exceptional electrical, optical, electromechanical [1], and ferromagnetic [2] properties of transition metal nitride semiconductors and their alloys make this class of materials worthy of investigation for their potential applications in electronic and optoelectronic devices. Scandium nitride (ScN) is especially interesting, due to its low lattice constant mismatch with gallium nitride (0.1% in the (111) plane) [3]. Combinations of ScN and GaN which have been proposed or prepared include ScN buffer layers for GaN on Si substrates [4], ScN–GaN superlattices [5], ScN–GaN heterojunctions [6] and alloys [7–9]. Scandium nitride is also a good candidate as a substrate for GaN-based devices, as its bulk crystal growth by the sublimation–recondensation method is feasible [10]. Scandium nitride has a good thermal stability with a melting temperature above 2000 °C, and a low nitrogen vapor

pressure (in comparison to GaN and InN). Scandium is an element in the IIIB column of the periodic table, and normally has a valence of three, making ScN a group III nitride. Hence, the incorporation of trace amounts of scandium into GaN should not alter its electrical properties through doping.

Besides its good lattice constant match with GaN, scandium nitride has potentially useful optical and electrical properties: an indirect bandgap of 0.9 eV and an unusually strong direct bandgap of ~2.1 eV [11]; and a high electron mobility for high electron concentrations (twice as high as silicon at 10^{20} cm^{-3}) [12]. The normal crystal structure for ScN is rock salt with a lattice constant of 4.505 Å [3], but its metastable hexagonal form is predicted to have a very high piezoelectric coefficient [13]. A high solubility of manganese in ScN and a predicted high Curie temperature make ScN a good candidate for a ferromagnetic semiconductor [2].

Although ScN films have been prepared by a number of techniques including sputtering [6] and molecular beam epitaxy (MBE) [3,4,7–9], hydride vapor phase epitaxy (HVPE) is the most successful method for producing films several microns thick at high growth rates ($>1.0 \mu\text{m/h}$)

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[12,14]. In seminal studies, Dismukes et al. [12,14] thoroughly characterized the properties of ScN films deposited by HVPE. Scandium nitride films were prepared by first reacting HCl and other hydrogen halides (HBr and HI) with scandium to form a volatile compound, which was subsequently mixed with ammonia to form ScN. Films were deposited on *c*-plane (0001) and *r*-plane (1 $\bar{1}$ 02) sapphire substrates, and several other oxide substrates including magnesium oxide (MgO), spinel (MgAl₂O₄), and titania (TiO₂). Dismukes et al. [12] established that ScN films deposit with (111) and primarily (100) orientations on *c*-plane and *r*-plane sapphire, respectively, as determined by electron diffraction. The best quality films, those with a single crystal orientation and the highest electron mobility, were produced at a substrate temperature between 850 and 930 °C. The highest electron mobility obtained was 176 cm²/Vs for a ScN film with an electron concentration of 1.9×10^{20} cm⁻³. Scandium nitride films grown outside of this temperature range were polycrystalline with much lower electron mobilities [12].

The present study extends the work of Dismukes et al. [12,14] by further investigating the effects of process conditions on the structure and composition of ScN films produced by HVPE. Scandium nitride films were prepared by HVPE on 6H-SiC(0001) substrates, which has a smaller lattice constant mismatch compared to many other substrates, only -3.53% for *c*-plane 6H-SiC (0001). For comparison, the lattice constant mismatch is +13.9% on the *c*-plane sapphire, and 5.4% and 12.2% (in perpendicular directions) on *r*-plane sapphire, and is 7.3% for ScN on MgO (100) substrates. 6H-SiC is more thermally stable than sapphire or MgO, which might help to eliminate any tendency for reaction between the film and the substrate.

The process conditions examined in this study were the scandium metal source and the substrate temperatures. The orientations of the ScN films were characterized by X-ray diffraction. The morphology and thickness of the films were determined by optical and scanning electron microscopy. Energy dispersive absorption of X-rays (EDAX) was employed to test for the presence of impurities in the ScN films. These results are useful for identifying the specific effects of processing conditions on the properties of the ScN films and for optimizing the deposition process.

2. Background

The thermal stabilities of scandium metal, ScN, and chlorides of scandium makes the chemistry of ScN HVPE significantly different than that of GaN or AlN. Gallium and aluminum both form volatile chlorides (GaCl, GaCl₃, and AlCl₃) with boiling points (≤ 250 °C) significantly below the typical source or deposition temperatures for AlN or GaN HVPE (~ 1000 °C). These chlorides are gases at typical deposition temperatures with a low probability of condensing. In contrast, scandium trichloride (ScCl₃), one possible product formed by the reaction between HCl and

scandium, has a high melting temperature (967 °C) [15], and hence a lower volatility at typical source and deposition temperatures (800–1100 °C for ScN). Thus, for source or substrate temperatures below its melting point, ScCl₃ might condense.

Another significant difference is that scandium metal has a strong affinity for oxygen in contrast to gallium. Scandium is one of the few metals that will react with and reduce SiO₂, by forming silicon and scandium oxide [16]. Similarly, ScCl₃ reacts with quartz at elevated temperatures to form SiCl₄ and Sc₂Si₂O₇ [17].

Like aluminum but unlike gallium, scandium reacts with molecular nitrogen (N₂) to form the nitride. Gallium remains a liquid metal at typical source temperatures and does not form GaN when exposed to hot nitrogen. In contrast, scandium is a solid at typical source temperatures—its melting point is 1541 °C—and it readily nitridizes to form ScN at temperatures of 1000 °C [18]. Thus, to ensure that the source remained as scandium metal and did not form ScN during deposition, hydrogen was employed as the carrier gas over the Sc source in the present study.

3. Experimental procedure

Scandium nitride films were deposited in a horizontal HVPE reactor. The scandium source was the pure metal, with a metal-basis of 99.999 wt% scandium, according to the vendor. Nickel and copper were the major metal impurities; both were present at concentrations of 100 ppm. The concentrations of nonmetals (hydrogen, carbon, nitrogen, and oxygen) were not provided by the vendor, and were not measured.

Scandium metal was reacted with hydrogen chloride mixed in hydrogen to produce a volatile scandium chloride-hydrogen mixture in the source zone. This mixture was subsequently combined with ammonia and hydrogen just above the substrate to form ScN. Typical flows were 25 sccm HCl, 500 sccm NH₃, and 2900 sccm H₂. The pressure was held constant at 970 mbar. The films were deposited on both Si-face and C-face (0001) 6H-SiC substrates. Typically films were deposited for 1 h. The effect of temperature on the structure of the films was investigated by varying the substrate temperature from 800 to 1100 °C. In another series, three films were deposited at the same substrate temperature, 800 °C, but with three different source temperatures (800, 900, and 1000 °C), to investigate this effect on the film composition.

The out-of-plane orientations of the ScN films were determined by theta-two theta X-ray diffraction with copper K_α radiation. The average thicknesses of the layers were calculated from the mass change that occurred during deposition, taking the density of ScN to be 4.276 g/cm³. These were confirmed by measuring the films' thickness directly by examining the edges of cleaved cross-sections. The morphology of the films was characterized by optical and scanning electron microscopy. The compositions of the

films were analyzed by energy dispersive analysis of X-rays (EDAX).

4. Results

The reaction between the volatile scandium compound and the quartz reactor was confirmed in our initial studies of ScN deposition on sapphire: a high silicon concentration was detected in the ScN layers. Subsequently, the quartz source tube was replaced with an alumina tube to avoid direct contact between scandium metal and quartz. Alumina was viewed as more thermally stable and less likely to react with scandium.

A thick deposit of small ScN crystals formed on the outlet from the source. This spurious deposition reduced the amount of reactants reaching the substrate, and made it impossible to calculate the efficiency of the epitaxy. Deposition at the source outlet was not a problem with the epitaxy of GaN in the same reactor with the same reactor configuration. This suggests that the reaction between the volatile scandium chloride compounds and ammonia is more rapid and irreversible than in the analogous case of GaN.

4.1. Orientation of the ScN films on 6H-SiC(0001)

The orientation of the ScN films was dependent on the substrate temperature employed; a mixture of orientations was produced with deposition at a substrate temperature of 1000 °C or higher. A two-theta XRD pattern representative of samples prepared at high substrate temperatures is presented in Fig. 1. Diffraction peaks from the 6H-SiC substrate are seen at 35.74° and 75.72° for the (0006) and (00012) planes, respectively. For ScN films deposited at 1000 °C or higher, peaks from the (111), (200), and (222) planes were seen at 34.46°, 40.00°, and 72.65°. Thus ScN films deposited at high temperatures were a mixture of

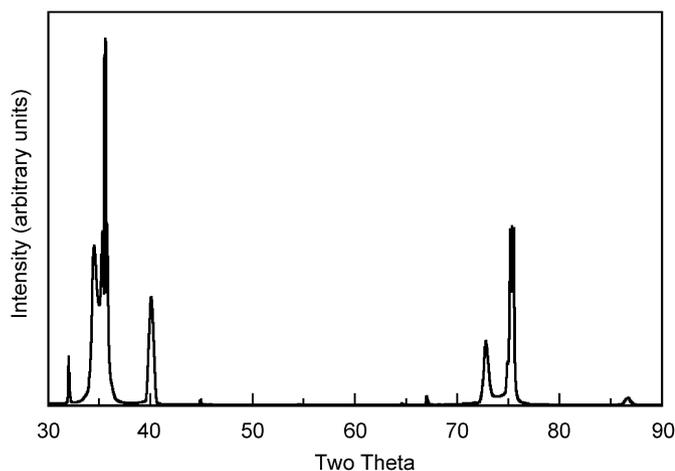


Fig. 1. X-ray diffraction pattern for a ScN/6H-SiC(0001) film deposited at scandium source temperature of 1000 °C and a substrate temperature of 1100 °C. The ScN layer exhibit a mixture of the (111) and (100) orientations.

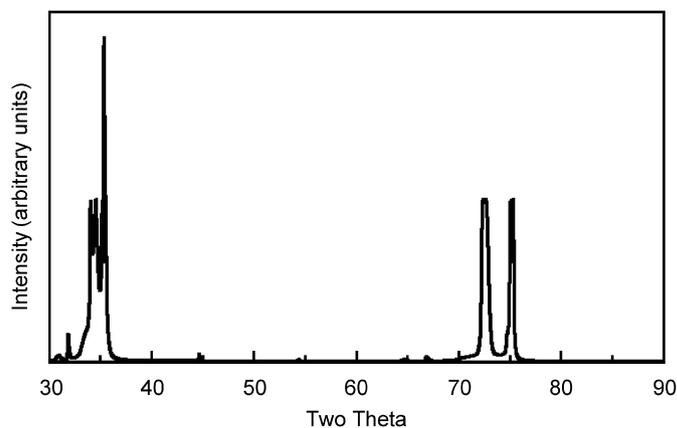


Fig. 2. XRD pattern for a ScN/6H-SiC(0001) film deposited using a scandium source temperature of 900 °C and a substrate temperature of 800 °C. In this case, the ScN deposits with only the (111) orientation, as indicated by the peaks at 34.5° and 72.65°.

(111) and (100) orientations. In contrast, ScN films deposited between 800 and 900 °C were a single orientation (Fig. 2). At the lower temperature, only the ScN (111) and (222) peaks were detected, indicating the films were (111) oriented.

4.2. Morphology

The texture of a series of ScN films deposited with a substrate temperature of 800 °C and source temperatures of 1000, 900, and 800 °C are shown in Fig. 3a–c. The thicknesses of these films were 3.0, 1.3 and 2.5 μm, respectively.

At a source temperature of 1000 °C, the deposit consisted of a continuous film with a high concentration of four-fold symmetry individual grains (Fig. 3a). The grains were preferentially deposited with a square base, inferring a (100) orientation parallel to the substrate surface. The facets on the grains appear to be (111) planes, based on their equilateral triangle shape and orientation relative to the square base of the grains. At a source temperature of 900 °C, a continuous film is formed, with a reduced concentration of individual grains (Fig. 3b). These grains were similar in shape to those forming at a source temperature of 1000 °C, but were smaller. Grain boundaries appeared to meander throughout the continuous film. At a source temperature of 800 °C, well-faceted triangular features of individual grains were apparent (Fig. 3c). The triangular shape of these grains suggests the formation of (111) surface parallel to the (0001) surface of the 6H-SiC. A few relatively large individual square deposits were also apparent on the surface of the film (Fig. 3c).

To gain a better perspective of the shape of deposits, the film deposited at a source temperature of 800 °C was examined at an inclined angle of 45° (Fig. 4). The individual islands of ScN form with (111) facets, as indicated by the shape of the sidewalls (Fig. 4a). While the top surfaces of the individual islands are smooth (Fig. 4a),

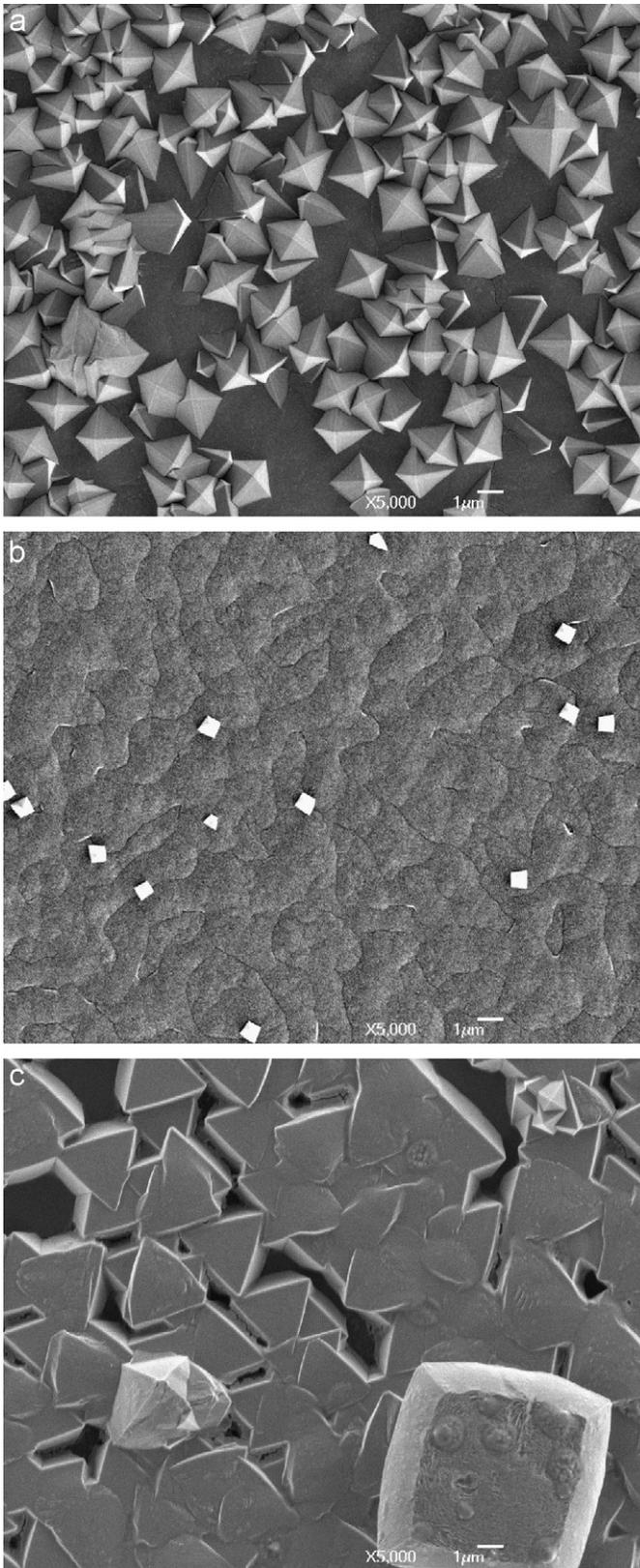


Fig. 3. Scanning electron micrographs of a ScN film deposited at a substrate temperature of 800 °C and a source temperature of (a) 1000 °C, (b) 900 °C, and (c) 800 °C (magnification 5000 \times).

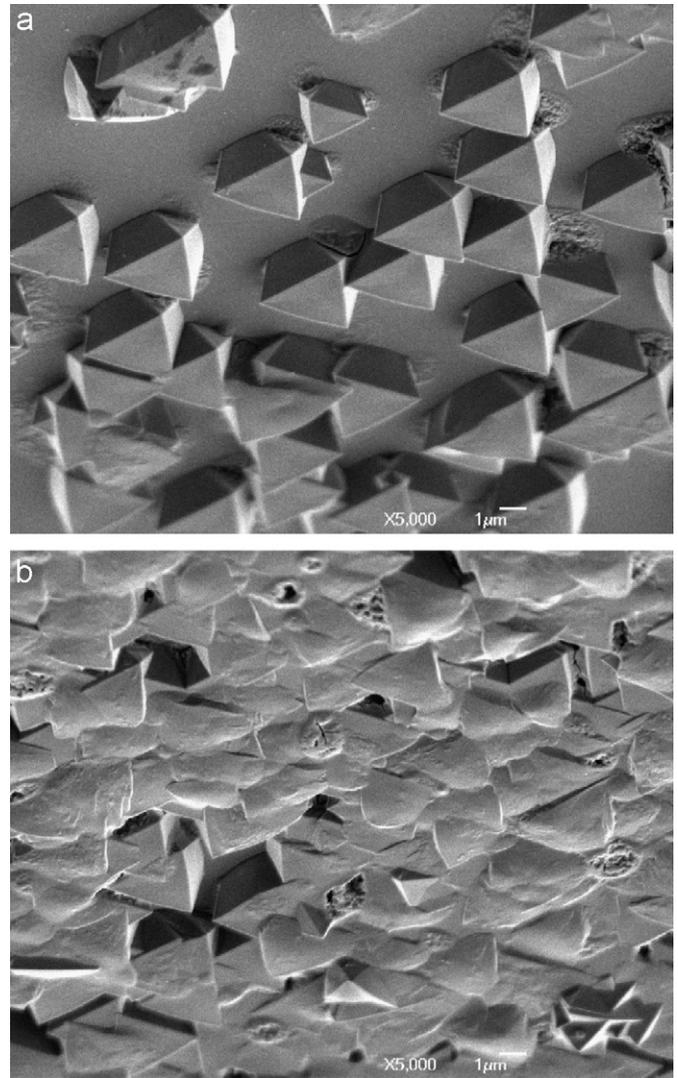


Fig. 4. SEM images of the ScN film on (0001) 6H-SiC deposited at a source temperature of 800 °C, incline 45°, (a) uncoalesced region, and (b) a nearly completely coalesced region.

the surface of the film becomes rougher after coalescence (Fig. 4b), a consequence of secondary nucleation.

4.3. Composition

Aluminum was the main impurity detected in all ScN sample deposited at combined substrate and source temperatures above 1000 °C. A typical Al concentration for a film deposited with both the source and substrate temperature greater or equal to 1000 °C was \sim 2 at%. The aluminum was uniformly distributed over the sample surface. Presumably, the Al originated from a reaction between the volatile scandium-chloride reactant and the alumina tube containing the scandium metal.

Three films were deposited at a substrate temperature of 800 °C and with decreasing source temperatures, to test whether reducing the source temperature would reduce the aluminum contamination in the ScN layer. The results are summarized in Table 1. Because the EDAX instrument was

Table 1
Compositions of three ScN films all deposited at a substrate temperature of 800 °C as measured by EDAX

Source temperature (°C)	Elements (at %)			
	N	Al	Cl	Sc
1000	54.7	1.5	1.9	41.9
900	55.6	1.3	0.6	42.5
800	55.5	0.5	2.7	41.4

not calibrated, the absolute values of the atomic percentages of elements are probably not accurate. Specifically, it is unlikely that the actual concentration of nitrogen in these samples exceed 50 at%. Nevertheless, the trends in the concentrations of impurities with process conditions should be valid, since all measurements were taken on similar samples under similar conditions.

The concentration of Al did indeed decrease as the source temperature was reduced, and was at the detection limits of EDAX for films prepared with a source temperature of 800 °C. However, for all of these films deposited with a substrate temperature of 800 °C, chlorine contamination was significant. No chlorine was detected in films with a substrate temperature of 1000 and 1100 °C, while the highest concentration of chlorine was detected in the film with both the source and substrate temperature of 800 °C. This suggests the chlorine concentration increases as the source and substrate temperatures are reduced. Dismukes et al. [12] reported similarly high chlorine concentration in their ScN films; values ranged from $1.8 \times 10^{20} \text{ cm}^{-3}$ (0.2 at%) to as high as $10^{22} \text{ atoms/cm}^3$ (~10 at%).

5. Discussion

The hydride vapor phase epitaxy of ScN films on 6H-SiC(0001) by HVPE is limited at high source temperatures (≥ 1000 °C) by the deposition of films with mixed orientations. The mixed orientations are probably a consequence of spontaneous gas phase nucleation. At a high temperature, a high concentration of volatile scandium and aluminum species are generated in the source zone. The reaction between the volatile source reactants and the ammonia-hydrogen mixture is rapid and irreversible. The diffusion rate of species at the substrate surface is relatively slow compared to the arrival rate of species. Consequently, this results in the deposition of films of mixed orientations.

At lower source temperatures, the concentration of reactants out of the source zone is lower, and therefore so is the degree of supersaturation. Less spontaneous nucleation occurs, so there is less interference with surface diffusion at the substrate. Consequently, the reactants can diffuse to the regions of lowest energy, corresponding to an epitaxial film with a single orientation.

Aluminum in the films is probably caused by a reaction between alumina and scandium compounds in the source zone. Reducing the source temperature suppresses this secondary reaction forming volatile aluminum compounds more strongly than the primary reaction between HCl and scandium metal. Thus, the Al concentration is reduced by lowering the source temperature.

The chlorine concentration in the ScN films increases as the substrate temperature is reduced. The vapor pressure of the main chloride of scandium, ScCl_3 , decreases by two orders of magnitude between 1000 and 800 °C [19]. Thus, chlorine incorporation in the ScN layer becomes much more likely as the substrate temperature is reduced.

6. Conclusions

6H-SiC carbide (0001) is a suitable substrate for the epitaxial growth of ScN(111) thin films. Epitaxy is limited to a substrate temperature of 900 °C; higher temperatures produce films with mixed (100) and (111) orientations. The morphology of films deposited at a high source temperature (1000 °C) and a low substrate temperature (800 °C) suggest the mixed orientations are caused by gas phase nucleation. A high scandium source temperature leads to the incorporation of aluminum in the ScN films due reactions between the scandium compounds and the alumina reactor tube. On the other hand, the incorporation of chlorine in the ScN films is increased as the substrate temperature is reduced. Thus, the best conditions for depositing epitaxial films of ScN by HVPE may involve a substrate temperature which is higher than the source temperature to achieve the goal of low Al and Cl concentrations simultaneously.

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