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Chemical Composition of AlN Thin Films Deposited at 523−723 K Using Dimethylethylamine Alane and Ammonia

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We have investigated a process for depositing AlN thin films at temperatures less than 800 K via surface reactions between specially chosen precursors. An Al precursor, dimethylethylamine alane (DMEAA, $(CH_3)_2C_2H_5N{:}AlH_3$) was used with ammonia (NH_3), and the reactants were delivered to the growth surface in separate steps using an atomic layer growth (ALG) process to promote film formation through a sequence of surface reactions. AlN thin films were deposited on Si(100), Si(111), Al_2O_3(00.1), and Al_2O_3(01.2) substrates at 523−723 K using a range of process flow conditions. Auger and X-ray photoelectron spectroscopy were employed to characterize the chemical composition of the films. These measurements detected carbon and oxygen contamination at the surface and smaller concentrations in the bulk. In the high-resolution X-ray photoelectron spectroscopy C(1s) data, binding energies for C−H and C−N species were identified but no C−Al species were present. In the N(1s) data, N−O species were not detected, but chemically bonded H was present in the films as NH_{3-x} ($x = 0-2$) species. The composition varied with process conditions, and the hydrogen content decreased in AlN films processed above 600 K.

Introduction

Aluminum nitride (AlN) is a refractory ceramic and a wide band-gap semiconductor with a high thermal conductivity which can be utilized in microelectronic packaging applications, high-power and high-temperature microelectronic devices, blue and UV photodetectors, and light-emitting diodes.[1,2] Conventional chemical vapor deposition (CVD) processes for epitaxial AlN growth require heating the substrate to temperatures greater than 1400 K. This is because high-quality epitaxy typically requires the growth temperature to be a large fraction of the melting point of the compound being grown or for very low growth rates to be employed. A notable challenge to fabricating devices that incorporate AlN films is the development of lower temperature processes for depositing high-quality films. Here we wish to emphasize that many applications do not require epitaxial growth. As an example, for the replacement of silicon dioxide with AlN as the gate dielectric in a MOSFET device, a thin amorphous layer would suffice. Our definition of high-quality refers to a film of high purity with a desired and controllable microstructure.

For many years, metalorganic chemical vapor deposition (MOCVD) processing was constrained by the limited availability of different types of metalorganic sources. Recently, the widespread use of MOCVD for processing advanced electronic materials has generated a steady increase in the commercial availability of a variety of precursor compounds, enhancing the versatility of MOCVD as a materials synthesis technique.[3,4] Surface chemistry studies have effectively revealed viable routes to AlN thin-film formation at lower temperatures via surface reactions between specially chosen precursors.[5−7]

Trialkylaluminum compounds, such as triethylaluminum (TEAl) and trimethylaluminum (TMAl), are the most commonly used metalorganic Al sources. These compounds have been commercially available for many years and have the advantage of being inexpensive. Manasevit first reported the growth of compound semiconductors by MOCVD using trialkyl sources and demonstrated epitaxial AlN growth using TMAl and ammonia [NH_3] at 1400 K.[8] Many studies of AlN growth by MOCVD utilized this precursor combination, typically with process temperatures greater than 1200 K. High temperatures are required for efficient decomposition of the precursor to elemental species and for thermally activated diffusion and other kinetic mechanisms that are responsible for crystalline film forma-

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tion. Trialkylaluminum compounds are characterized by the presence of Al−C bonds, and at lower processing temperatures, the thermally activated dissociation of this bond is limited, leading to undesirable carbon contamination.[9]

As an alternative to trialkylaluminum compounds, researchers have investigated processes using single-source precursors for growth of nitrides at lower temperatures. These molecular sources contain covalently bonded aluminum and nitrogen; the Al−N containing species are delivered to the surface with a fixed stoichiometric ratio and the kinetic barriers to forming a metal−nitrogen bond are partially circumvented. Unfortunately, the relatively low vapor pressures associated with these large molecules present a difficulty in delivering a sufficient partial pressure to the reactor. Also, the molecules often contain an Al−C bond that must be broken to achieve complete dissociation to AlN. Various groups have demonstrated AlN growth by CVD using sources of this nature such as diethylaluminum azide and tris(dimethylaluminum) amide.[10,11] Ho et al. reported that films deposited at 723−1173 K with diethylaluminum azide were amorphous and AlN deposited from separate precursors, TEAl and NH_3, had comparatively better crystallinity.[12] Interrante and co-workers studied tris(dimethylaluminum) amide as a single-source precursor and deposited polycrystalline AlN with good stoichiometry at temperatures down to 773 K.[11] Hexakis(dimethylamido)dialuminum has also been used as an AlN precursor but experiments showed that significant carbon contamination was present in the films.[13,14] With only hydrogen as a byproduct and a low decomposition temperature, aluminum hydride or alane (AlH_3) would be a superior Al source molecule. Unfortunately, at ambient conditions pure AlH_3 is a polymeric solid with no appreciable vapor pressure.[15] Lewis acid−base adducts of AlH_3 bound to amine groups have relatively high vapor pressures and provide a way to transport the AlH_3 molecule to the deposition surface. The absence of an Al−C bond in these molecules results in less carbon contamination, and they dissociate readily at temperatures as low as 373 K.[16] For this work we chose dimethylethylamine alane (DMEAA; $(CH_3)_2C_2H_5N{:}AlH_3$), which is a liquid with a vapor pressure of 1.5 Torr at 293 K.[17] DMEAA has been used to deposit high-quality thin films of Al,[18,19] AlAs,[20] and $Al_xGa_{1-x}As$.[21]

The potential of alane adducts as MOCVD precursors for lower temperature growth stems from the enhanced reactivity due to the relatively weak Al−N bond. Dubois and co-workers studied the surface reaction chemistry of trimethylamine alane (TMAA) on Al, Si, and oxidized Al surfaces and reported that the sticking probability of TMAA was low at 80−280 K but increased at temperatures greater than 320 K, producing steady-state Al film growth.[22] Gladfelter et al. also studied Al deposition using TMAA in a low-pressure CVD process and found that the precursor pyrolyzed at temperatures as low as 373 K to produce high-quality Al films on Si(100) substrates.[23] Bertolet et al. first reported formation of AlN at temperatures as low as 400 K using TMAA and NH_3.[6] In terms of processing, the low decomposition temperature and high reactivity of this type of precursor can produce undesirable effects such as enhanced gas-phase reactions and associated particle formation, reactant depletion, and nonuniform deposition on the substrate.[21,24,25] To process compound semiconductor films using alane adducts with other reactants, techniques that minimize interaction of the reactants in the gas phase need to be utilized. One approach is to use metalorganic molecular beam epitaxy (MOMBE) or low-pressure MOCVD, where the gas-phase interactions are limited at reduced pressures. Another alternative is atomic layer growth (ALG), where the source gases are flowed into the reactor in separate, sequential steps.[16,21,26−28] Ohtsuka et al. reported ALG of AlAs on GaAs(100) using TMAA and AsH_3 in a pulsed jet epitaxy system where films deposited at temperatures as low as 423 K showed good crystallinity with narrow X-ray diffraction peaks.[27] Fujii and co-workers also deposited AlAs using ALG with TMAA and an amino−As source.[29] The source gases were alternately flowed into a UHV chamber, and at 623 K they observed 1 monolayer/cycle and 2 mono-

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layer/cycle self-limited growth on GaAs(100) substrates. Abernathy and co-workers have utilized MOMBE to deposit AlN films using TMAA as the Al source and a N_2 plasma as the nitrogen source.[30]

Our experiments were done in a commercial MOCVD reactor using 3 in. Si wafers and smaller Al_2O_3 substrates. An ALG process was developed where AlN was deposited through a sequence of adsorption and reaction steps between DMEAA and NH_3 molecules at the substrate surface. This research extends previous surface reaction studies, which sought to reveal viable routes to low-temperature growth via specific reactants and surface reaction mechanisms, by implementing this strategy into a larger-scale process. In this article we report the results of chemical composition analysis of the AlN films deposited at 523−723 K using DMEAA and NH_3 in an ALG process and discuss the implication of these findings in terms of developing an understanding of the mechanism of low-temperature AlN film formation.

Experimental Procedure

Thin-film deposition was done in a Crystal Specialties Inc. (CSI) 425 horizontal-style MOCVD reactor. Purified hydrogen (H_2) was used as the carrier gas for the process. The DMEAA was contained in a standard stainless steel vertical-style cylinder, and the temperature was controlled by immersion in a temperature bath. Purified H_2 was bubbled through the cylinder to transport the DMEAA to the reactor. The NH_3 was housed in a gas cylinder and fed undiluted into the system gas cabinet through stainless steel lines. The reactant lines and H_2 flush lines fed into a stainless steel radial gas mixing manifold. The manifold was equipped with three-way switching valves to direct gas flow to the reactor or out through the exhaust manifold, enabling abrupt switching of the flow composition without changing the overall flow rate. The wafer was positioned approximately 30 cm from the gas manifold outlet nozzle. The system was equipped with a single-stage mechanical pump with a pumping speed of 0.013 m^3/s and a base pressure of 6.7×10^{-2} Pa (5×10^{-4} Torr). To operate at low pressure (3.3−13 kPa or 25−100 Torr) the exhaust path was directed through the main pump, and the reactor pressure was controlled using a butterfly valve controller positioned at the pump inlet which interfaces with the Baratron gauge. After exiting the reactor system, the exhaust flow was incinerated in a fume hood. The system base pressure was 0.8 Pa (6×10^{-3} Torr) as measured using a Bendix thermocouple vacuum gauge. The substrates were mounted on a silicon carbide (SiC) coated graphite susceptor that was heated by rf induction using a Westinghouse 7.5 kW rf generator. The temperature was measured using a chromel−alumel (K-type) thermocouple inserted into a quartz tube in contact with the bottom of the susceptor. The thermocouple was monitored by a Eurotherm Model 820 controller that interfaced with the rf generator to control the temperature. The temperature was in turn calibrated using an optical pyrometer that was calibrated from the melting point of pure metals (Al, Zn) placed on the susceptor.

DMEAA was purchased from Air Products (Allentown, PA) and used without further purification. The bubbler cylinder was stored at 280 K during idle periods and held at 293 K during processing. Ultrapure, nitride grade NH_3, purchased from Airco (Murray Hill, NJ), was used as the nitrogen source gas.

Single-crystal Si(100), Si(111), Al_2O_3(00.1), and Al_2O_3(01.2) wafers were used as substrates for the thin-film growth. Prior to processing, all substrates were cleaned by a standard degreasing procedure using trichloroethane, acetone, and methanol, followed by a rinse in deionized H_2O. The wafers were soaked in each liquid for 5 min and blow-dried with filtered N_2. The Si wafers were oxide etched in 10% (by volume) aqueous HF solution, rinsed in deionized H_2O, and air-dried immediately before being loaded into the reactor. Prior to film growth, the substrates were heated to 1073 K under a H_2 flow for 10 min, after which the substrate temperature was lowered to the process temperature and allowed to stabilize before beginning the reactant flow sequence.

The DMEAA and NH_3 were sequentially flowed into the reactor with flush steps of pure H_2 between each reactant flow step. Process sequences with DMEAA and NH_3 flow steps of 2, 4, and 8 s were used. Between reactant flow the chamber was flushed for 5 s with H_2. The process sequences are notated by the time duration of each flow step, e.g., the 8−5−4−5 process sequence corresponded to 8 s of DMEAA flow and 4 s of NH_3 flow with 5 s flow of pure H_2 between each reactant flow step. The total flow and pressure in the reactor was kept constant during each step of the process sequence. Samples were processed at reactor pressures of 3.3×10^3 and 6.6×10^3 Pa (25 and 50 Torr) with a total flow ranging from 2400 to 6000 sccm. At these conditions the gas velocity at the upstream edge of the wafer sled varied between 6 and 50 cm/s. During the reactant steps, the partial pressures of the DMEAA and NH_3 were 0.65−3.28 Pa (4.9−24.6 $\times 10^{-3}$ Torr) and 0.33−1.67 kPa (2.5−12.5 Torr), respectively. The reactant partial pressures were varied by adjusting the total flow rate and the total reactor pressure. The ratio of the NH_3 to DMEAA partial pressures (V/III) was 510. During processing the DMEAA bubbler was held at atmospheric pressure and 293 K, and ultrapure H_2 was flowed through the bubbler at a rate of 300 sccm. Undiluted NH_3 was flowed into the carrier gas stream at a rate of 300 sccm. Following processing the samples were cooled to room temperature under a H_2 flow and then removed from the reactor and transported to a separate UHV analysis system for the X-ray photoelectron (XPS) and Auger electron spectroscopy (AES) measurements.

XPS data were collected using a Surface Science Instruments (SSI) X-Probe ESCA system (Mt. View, CA). An aluminum $K\alpha_{1,2}$ monochromatized X-ray source was used to initiate photoemission. The energy of the emitted electrons was measured with a hemispherical energy analyzer at pass energies of 25 eV for the high-resolution spectra and 150 eV for the low-resolution broad scans. An electron flood gun set at 5 eV was used to minimize surface charging of the samples. The pressure in the analysis chamber during data acquisition was 1.3×10^{-7} Pa (1×10^{-9} Torr). Standard ESCA data analysis software was used to calculate the elemental compositions from the peak areas and to curve fit the high-resolution spectra. AES data were collected using a Perkin-Elmer (Eden Prairie, MN) PHI Model 560 ESCA system with a 3 kV, 1.5 mA electron beam. The pressure in the analysis chamber during data acquisition was 1.3×10^{-6} Pa (1×10^{-8} Torr). Sputter profile data were obtained from AES measurements taken while sputtering the surface with an Ar^+ source.

Results

Low-resolution XPS data were collected over a range of 0−1000 eV to determine the chemical composition near the surface of the film. Figure 1 shows a compositional survey scan of an AlN thin film on Si(100) processed at 673 K and 6.7 kPa (50 Torr) with a 4−5−4−5 process sequence. Peaks associated with Al, N, C, and O were observed in the spectrum. This spectrum was typical of XPS broad scans collected for AlN films in this study.

Depth profile analysis by AES of the AlN films indicated that the oxygen and carbon were concentrated at the surface of the film. Figure 2 shows AES spectra collected from AlN on Al_2O_3(00.1) processed at 613 K

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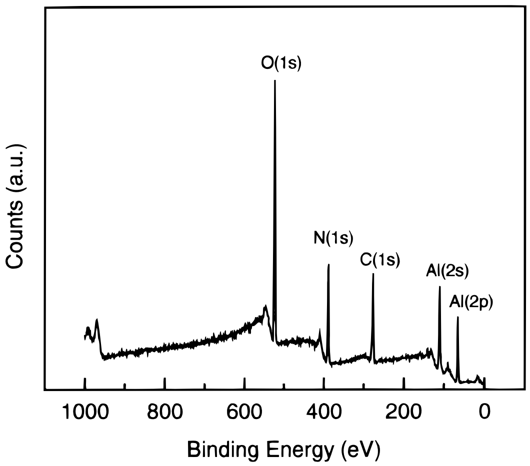

Figure 1. XPS survey scan of AlN on Si(100) deposited at 673 K and 50 Torr using a 4−5−4−5 atomic layer growth process. The carbon and oxygen species were associated with adventitious hydrocarbon and an oxidized AlN surface that resulted from exposure to air after the film was grown.

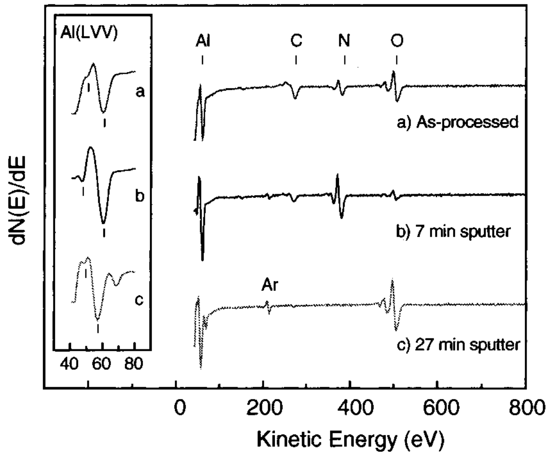

Figure 2. AES spectra collected while sputtering a sample of AlN on Al_2O_3(00.1). The inset shows the Al(LVV) signature revealing line shapes collected from the (a) as-processed sample, (b) from the bulk of the film after 7 min, and (c) from the underlying substrate after 27 min of sputtering. The regions were identified as (a) oxidized AlN, (b) AlN, and (c) Al_2O_3.

and 101 kPa (760 Torr) using a 4−2−2−2 sequence. The AlN film thickness was measured by ellipsometry to be 70 nm. The individual spectra were collected at time intervals during sputtering of the surface with an Ar^+ beam. In the initial measurement, taken on the as-processed sample, Al(LVV), N(KLL), O(KLL), and C(KLL) peaks were detected. Sputtering for 1 min resulted in a marked decrease in the detected carbon and oxygen. After the surface was sputtered for 7 min, the carbon and oxygen signals decreased to a small fraction of their initial intensity, and the aluminum and nitrogen signals increased slightly, indicating removal of surface oxygen and carbon species and detection of bulk AlN. Argon, embedded during the sputtering process, was also detected. After sputtering for 27 min, nitrogen was no longer detected and only aluminum and oxygen signals were present, signifying removal of the AlN film and detection of the underlying Al_2O_3 substrate.

Changes in the Al(LVV) signature as a function of depth are a good indication of the composition profile. The inset shows an expanded view of the Al(LVV) region collected at three different stages in the sputtering process. The data collected from the sample after extended sputtering (c) matched the Al(LVV) signature for Al_2O_3.[31−33] The line shape and relative positions of minima at 57 and 49 eV matched published data. Comparisons of AES line shapes for elemental Al with oxidized Al have suggested that these features are associated with interatomic transitions involving Al and O levels. The positions of the minima in our data were shifted by approximately 3 eV from reported measurements, but our data were not energy shifted to correct for charging effects, which may explain the discrepancy. The line shape of signal detected from the bulk of the film (b) matched the line shape for AlN.[31−34] In particular, the relative positions of the features at 60.5 and 47.5 eV are characteristic of AlN and associated with transitions from Al and N levels.[33,31] The data collected prior to sputtering (a) showed a spectrum with features at energies which could be associated with both Al_2O_3 (49.5 eV) and AlN (60.5 eV), which was indicative of an oxidized AlN surface. In summary, line-shape analysis of the Al(LVV) feature revealed an oxidized layer at the surface and AlN in the bulk of the film. After several minutes of sputtering, some oxygen and carbon were still detected, but it could not be determined whether the residual amounts were from sputtering artifacts (knock-on) or were impurities deposited during film growth.

Higher resolution XPS data were collected for the Al(2p), N(1s), C(1s), and O(1s) energy regions. An energy correction shift, determined from the C(1s) data and discussed below, was applied to the N(1s), O(1s), and Al(2p) spectra collected in the same measurement series. The peak energy values reported here were energy-corrected values.

Examples of high-resolution XPS spectra are shown in Figure 3. The C(1s) spectrum shown in Figure 3 was collected from AlN on Si(100) processed at 673 K using a 4−5−4−5 process sequence. The C(1s) spectra of the AlN films typically showed three spectral features. A dominant peak lower binding energy feature (peak a) was assigned to adventitious hydrocarbon species. Its energy was used to determine an energy correction factor; the data were uniformly shifted to place this feature at 285 eV.[35] The presence of a strong adventitious carbon signal in the C(1s) data was consistent with the AES analysis which showed that the detected carbon was concentrated at the surface and likely originated from exposure to air. A shoulder at 286.4 ± 0.3 eV (peak b) was also present in the C(1s) data. This binding energy corresponds to C−N species which probably originated from residual amine groups at the surface. Liu detected a peak at 286.1 eV following molecular adsorption of TMAA which was associated with carbon bound to nitrogen in amine species.[7] It is also possible that the signal derived from the detection of chemisorbed hydrocarbon species at nitrogen sites on the surface. In either case, the signal intensity at 286.4 eV

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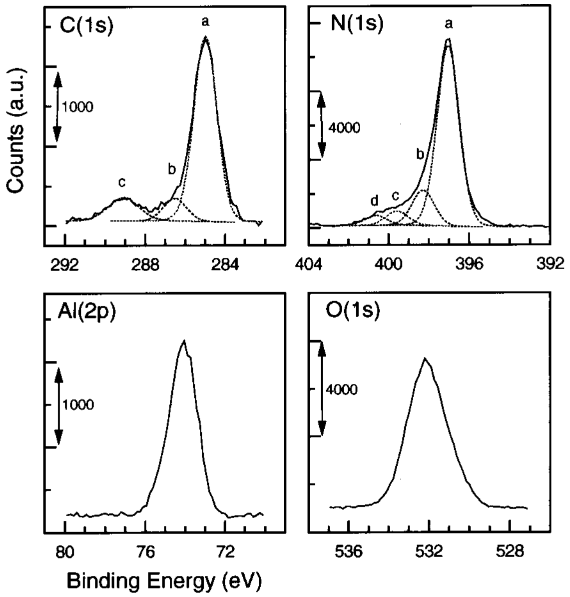

Figure 3. XPS high-resolution C(1s), Al(2p), and O(1s) data collected from AlN deposited on Si(100) at 673 K and 50 Torr with a 4−5−4−5 process. The N(1s) data were collected from AlN on Si(100) processed at 613 K and 25 Torr with the same process sequence. The N(1s) spectrum contained a dominant feature at 396.8 eV associated with AlN and the higher energy peaks at 398.0−400.5 eV associated with NH_{3-x} ($x = 0-2$) species.

associated with C−N bonding was a fraction of the signal associated with the surface contamination, suggesting that the DMEAA amine ligands left the surface intact. A broad peak at 289.1 ± 0.2 eV (peak c), associated with oxidized carbon−nitrogen species, was also observed in the C(1s) data and attributed to surface species generated during exposure to air. The binding energy range of 289.3−289.7 eV has been identified with carbamate species (O−C−N) in other studies.[36] A binding energy of 289 eV was also associated with surface contamination in experiments of AlN oxidation where C(1s) peaks were observed at 288.5−289.3 eV from presputtered samples of Al_2O_3, $Al(OH)_3$, AlOOH, and Al.[37] In summary, residual carbon species were detected at the surface of the AlN films, including adventitious hydrocarbon and C−N species. The C−N species could have originated from undesorbed amine groups left from the final process steps or from hydrocarbon contamination at nitrogen sites on the surface. No binding energies below 285 eV, indicative of Al−C species, were detected in our AlN films, indicating that the amine groups did not dissociate into carbon-containing radicals which would then incorporate at Al sites forming Al−C bonds. Except for changes in overall intensity, the C(1s) spectral signature was not strongly effected by the process parameters.

The Al(2p) spectra for AlN films deposited by this process typically showed a broad peak centered at approximately 74 eV with a fwhm of 2 eV. This binding energy was characteristic of AlN,[38,39] although the Al(2p) binding energies for AlN and Al_2O_3 differ by less than 0.5 eV. The Al(2p) region contains spin−orbit split components which broadened the peaks and complicated accurate curve fitting of the data into features associated with specific Al species. No lower binding energy features associated with metallic Al (72.7 eV) were detected. The O(1s) spectra for the AlN films typically contained a broad peak centered at approximately 532 eV with a fwhm of ~3 eV. The peak was slightly asymmetric, but no distinct features were resolved. The peak position and width matched well to O(1s) spectra of pure AlN powders exposed to air.[37] The O(1s) binding energy was shifted higher by 1.5 eV from the reported value for pure Al_2O_3.[39]

The N(1s) data in Figure 3 were collected from a sample of AlN deposited on Si(100) at 613 K and 25 Torr using a 4−5−4−5 process. The data show features typically observed in the N(1s) spectra from AlN films. The signal is dominated by a peak centered at 396.8 eV (peak a), associated with the N(1s) binding energy for AlN.[38] A shoulder at 397.8 eV (peak b) was also present. Curve fitting revealed additional features at 399.5 (peak c) and 400.7 eV(peak d) at the higher energy side of the spectrum. The higher energy peaks at 400.7, 399.5, and 397.8 eV match the energies for NH_{3-x} ($x = 0-2$) species.[40,41] The N(1s) binding energy is sensitive to the chemical environment of the nitrogen atom and can be used to identify the type of nitrogen species; the N(1s) binding energy increases as the number of hydrogen atoms bound to the nitrogen increases.[40−42] The reaction to form AlN is thermally driven, and partially dissociated NH_3 species were a product of the reaction between the Al source and NH_3 at lower temperatures.

The effect of processing parameters on the reactions leading to thin-film formation was explored by examining the chemical composition of films deposited at various conditions. Figure 4 shows N(1s) data collected from AlN films processed at 523−723 K using a 4−5−4−5 process at 25 Torr. The relative intensities of N(1s) peaks were strongly dependent on the AlN processing temperature where spectral features associated with NH_{3-x} species ($x = 0-2$) were more intense for AlN processed at lower temperatures. In films processed at 523 K, approximately 45% of the detected nitrogen was associated with NH_{3-x} species and 55% with AlN. In samples processed above 600 K a significantly greater percentage of the detected nitrogen was associated with AlN (~80%).

The microstructure of the films, film uniformity, and other growth parameters as a function of the growth temperature and the type of substrate have been reported previously.[26]

Discussion

The concentrations of carbon and oxygen species at the near surface of the as-processed AlN films prevented

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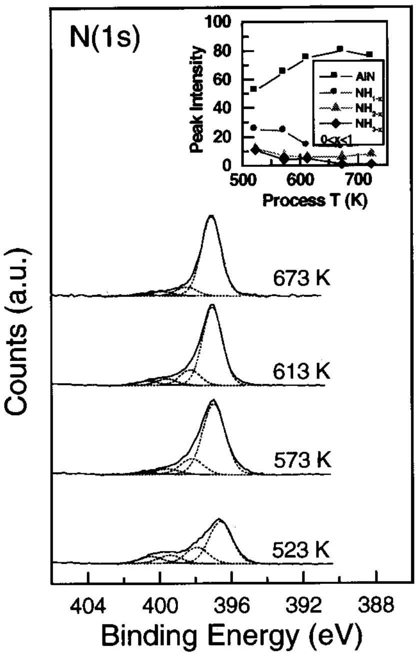

Figure 4. N(1s) spectra of AlN on Si(100) processed at 523−673 K. The concentration of NH_x species was less in samples processed at the higher temperatures, indicating a more complete reaction to AlN.

accurate determination of the bulk composition. Analysis of the surface following sputtering demonstrated that the oxygen and carbon species were concentrated at the surface with a stoichiometric composition in the bulk. Results of X-ray diffractometry and Rutherford backscattering spectroscopy measurements from the AlN samples also indicated that the films were stoichiometric AlN. Diffraction peak positions were characteristic of oriented AlN with an unstrained wurzite structure.[26] Rutherford backscattering spectroscopy (RBS) data recorded for AlN deposited on Si(100) at 673 K showed equal concentrations of aluminum and nitrogen with 5 atomic % oxygen and 10 atomic % hydrogen in the bulk of the film, but no carbon was detected.

The N(1s) binding energies observed in the data were associated with AlN and NH_x species incorporated into the films. The N(1s) spectra of AlN processed by ALG showed a dominant AlN peak at 396.8 ± 0.2 eV which has been identified by several studies as AlN.[38,43] Surface reaction experiments have also correlated N(1s) binding energies in the range of 398−401 eV with NH_x species.[40−43] Mayer et al. studied the nucleation of AlN from surface reactions between TMAl and NH_3 where the presence of a broad spectral feature in the N(1s) spectrum at ∼400 eV was directly correlated with the chemisorption and reaction of NH_3.[43] Studies of NH_3 decomposition on Si showed a systematic variation in the N(1s) energy with hydrogen content where the energies for NH_x species were as follows: NH, 398.0 eV; NH_2, 398.6 eV; physisorbed NH_3, 400.1 eV.[40,41] The binding energies of the three lower intensity components observed in our data match these values. Peaks were not observed at energies greater than 401 eV which corresponds to the N(1s) energy range for nitrogen in heavily oxidized AlN or aluminum oxynitride.[37,44]

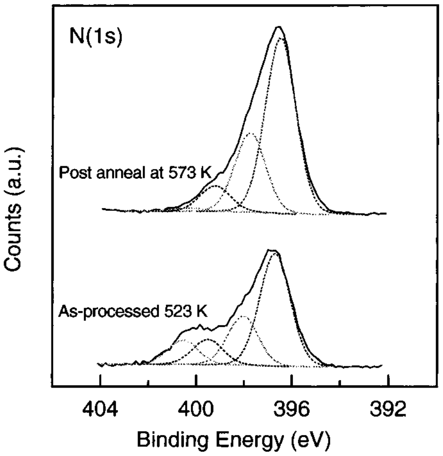

Figure 5. N(1s) spectrum for an as-processed sample, deposited at 523 K and 25 Torr, and after heating to 573 K in UHV. The postgrowth heating resulted in a quantitative shift of the higher energy intensity to lower energies indicating removal or conversion of residual NH_3 species.

The presence of higher energy peaks in the N(1s) spectrum signifies the incomplete reaction of NH_3 in the process. These findings were consistent with the results of other researchers. Several groups have observed the presence of residual NH_x species with reactions at lower temperatures (<600 K) following the decomposition of Al metalorganic compounds with NH_3 to form AlN.[6,7,43,45] As mentioned above, Mayer et al. examined the low-temperature formation of AlN from the coadsorption and pyrolysis of TMAl and NH_3 on Si(100) and observed two distinct components, a nitride peak at 397.4 eV and a component at 400.0 eV, in the N(1s) spectrum at 300 K.[43] Annealing this surface at 700 K resulted in a quantitative conversion of most of the intensity from the higher energy component to the lower energy nitride feature, signifying an AlN-forming reaction. Bertolet et al. obtained similar results from experiments where the α-Al_2O_3 surface was sequentially exposed to TMAA and NH_3.[6] With this process, AlN formed at temperatures as low as 400 K but with limited efficiency, and annealing to 1200 K resulted in greater AlN formation but with chemisorbed NH_2 remaining on the surface.[6]

For AlN samples processed at lower temperatures, a greater amount of the detected nitrogen was associated with NH_{3-x} ($x = 0-2$) species than was observed at higher processing temperatures. To further examine this effect, AlN films were processed at 523 K and transported to the UHV XPS chamber for characterization where data were collected from the sample, as-processed and after heating to 573 K in the UHV environment. Figure 5 shows the N(1s) spectrum for the as-processed AlN, deposited at 523 K, and the spectrum collected after annealing the sample at 573 K for 180 min. Heating resulted in a significant drop in the intensity of the NH_3 feature (400.5 eV). Analysis of the normalized peak intensities before and after the heating process showed a quantitative shift of the higher energy intensity to lower energies. This result probably indicates a reaction of NH_3 to NH_2 and AlN. However,

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the measurement was made on the surface of a relatively thick AlN film, and the same shift in intensity would result from NH_3 desorbing from this surface. In either case, this result further clarified that a temperature boundary existed, below which the reaction to form AlN was incomplete, resulting in residual NH_3 and other NH_x species in the films.

Importantly, our studies showed that metallic Al was not incorporated into the films as a reaction product. Experiments of Al film growth using alane adduct precursors have shown growth rates in excess of 1 μm/min, signifying rapid decomposition of the source molecules to elemental Al at temperatures as low as 373 K.[23] Decomposition of the DMEAA at very high rates in the ALG process would have led to formation of a relatively thick Al layer, whereby nitridation to AlN by the subsequent NH_3 step would be restricted by the energy barriers imposed by solid-state diffusion within the Al film. The ability to deposit crystalline AlN by this process hinged on generating controlled surface reactions such that the DMEAA molecules adsorbed and decomposed to a limited extent. Other researchers have observed that the decomposition rate of TMAA at a given temperature was sensitive to the substrate and differed significantly on Si, Al, and oxidized Al surfaces; the decomposition of TMAA on Si and oxidized Al was kinetically complex and more highly activated than the steady-state growth of Al on an Al surface.[22] By analogy for the present case, the formation of a nitride surface after the first deposition sequence should lead to a less reactive surface for DMEAA decomposition relative to decomposition on a metallic Al surface. In addition, simple equilibrium arguments suggest that the hydrogen used as the carrier gas actively participates in the gas−surface interactions by suppressing the decomposition of DMEAA. Therefore, the sequential delivery of the reactants as discussed above provides a mechanism to deposit stoichiometric AlN films through the ordered reaction steps.

Summary

XPS and AES have been used to characterize the chemical composition of AlN deposited using an ALG process. AES sputter depth profiling revealed carbon and oxygen contamination at the surface with much smaller concentrations in the bulk. Nitrogen−hydrogen species were detected in the films by XPS and identified by their N(1s) binding energy. We observed that the reaction of NH_3 was incomplete at temperatures below ~550 K resulting in unreacted NH_x species. In AlN films processed above 600 K, the NH_x concentration was lower and the majority of detected nitrogen was associated with pure AlN.

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