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Organometallic Azides as Precursors for Aluminum Nitride Thin Films

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A new route to thin films of metal nitrides employing organometallic azides as the source of nitrogen is described. Depositions of AlN on several substrates at temperatures as low as 400 °C are reported by using dialkylaluminum azides. The depositions were conducted by using two separate reactors. The first was a diffusion-pumped, all-glass horizontal reactor that generated samples used for thickness measurements, microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. The second system allowed experiments to be conducted in an antechamber appended directly to an X-ray photoelectron spectrometer (XPS). The XPS data indicated that the formation of AlN had occurred and suggests that in the case of the diethylaluminum azide some unreacted azide precursor remained on the surface. Comparisons are made to a related amido precursor $[Et_2AlNH_2]_3$.

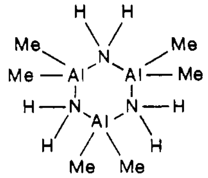
Introduction

Aluminum nitride has the wurtzite crystal structure and several physical properties that make it especially interesting, both as a bulk material and as a thin film. As a large bandgap (6.2 eV) group III–V compound,[1] which is hard (between corundum and diamond), resistant to chemical attack, and high melting (2400 °C),[2] it has useful properties for coatings, especially for optical or optoelectronic devices. Its piezoelectric nature makes it important in the fabrication of surface acoustic wave devices. There is interest in exploiting its high thermal conductivity for use in applications for packaging of electronic microcircuits.[3]

Organometallic aluminum compounds have been used to generate thin films of AlN in various chemical vapor deposition (CVD) systems. The first such report[4] involved the reaction of $AlMe_3$ with NH_3 (eq 1) at 1200 °C on

$$Al(CH_3)_3 + NH_3 \rightarrow AlN + 3CH_4 \qquad (1)$$

crystalline substrates such as Al_2O_3 and Si. Although the film grew epitaxially, the high temperatures involved are undesirable for many applications. Two recent reports describe efforts at lowering the temperature of the deposition. In the study by Gaskill and co-workers, hydrazine (N_2H_4) was used as the nitrogen source in place of ammonia.[5] Lower deposition temperatures were anticipated through the use of a source of nitrogen that is less stable and, therefore, more reactive than NH_3. The result was that thin films of polycrystalline AlN could be deposited at significantly lower temperatures (725 °C). Interrante and co-workers examined a different approach that involved utilization of a precursor comprised of Al and N.[6,7] Their strategy involved the isolation and characterization of intermediates from the alkylaluminum/NH_3 reaction (eq 1) for a variety of different alkyls. The most volatile of the isolated intermediate compounds was crystalline $[(CH_3)_2Al(NH_2)]_3$, found to exist as the six-membered ring in a chair conformation:[6]



The major advantages of including both the nitrogen and aluminum in a single precursor are 2-fold. First, by fixing the Al:N ratio in the precursor, one may gain control of the stoichiometry of the film. Second, the use of a single reagent leads to simplification of reactor design, which is also likely to improve the integrity of the reaction chamber.

We have initiated a study of the deposition of thin films of AlN using new precursors designed to react under even milder conditions. In this report, we will summarize the first use of molecular azides as precursors to metal nitrides. A preliminary report of these observations has appeared.[8]

Experimental Section

General Instrumentation. IR spectra were recorded on a Mattson Cygnus 25 spectrometer equipped with a HgCdTe detector. ^1H NMR spectra were recorded on an IBM AC-200 or an IBM AC-300 spectrometer. All mass spectra were obtained by using a VG 7070 E-HF spectrometer. Chemical ionization was performed with CH_4 as the reagent gas. GC/MS experiments employed a Hewlett-Packard Model 5890A GC interfaced to the above-mentioned mass spectrometer. X-ray diffraction studies were conducted by using a Seimens D500 diffractometer with monochromatic (graphite) Cu Kα radiation. Film thicknesses were measured by ellipsometry (Gaertner Model L117) and/or by stylus profilimetry (Tencor Alphastep). Scanning electron micrographs were taken with a JEOL 840 II. Elemental analyses were performed by Galbraith Laboratories. For samples prepared in the survey reactor (see below), the AlN thin films were analyzed by using a Perkin-Elmer Corp./Physical Electronics Division Model 5400 X-ray photoelectron spectrometer. Because of the tendency for AlN samples to undergo surface oxidation upon exposure to oxygen, these analyses were performed by using the XPS depth-profiling mode. Samples were sputtered to steady-state bulk composition and then immediately analyzed at a 90° emission angle. A pass energy of 189 eV and a 0.6-mm^2 analysis area were employed, with integration of the multiplexed Al(2p), N(1s), C(1s), and O(1s) photoelectron bands followed by normalization with the appropriate sensitivity factors to yield the reported atomic

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(1) Yim, W. M.; Stofko, E. J.; Zanzucchi, P. J.; Pankove, J. I.; Ettenberg, M.; Gilbert, S. L. *J. Appl. Phys.* **1973**, *44*, 292.

(2) *Handbook of Chemistry and Physics*, 51st ed.; Weast, R. C., Ed.; The Chemical Rubber Co.: Cleveland, 1970.

(3) Baker, R. T.; Bolt, J. D.; Chowdhry, U.; Klabunde, U.; Reddy, G. S.; Roe, D. C.; Staley, R. H.; Tebbe, F. N.; Vega, A. J. *Mater. Res. Soc. Symp. Proc.*, in press.

(4) Manasevit, H. M.; Erdmann, F. M.; Simpson, W. I. *J. Electrochem. Soc.* **1971**, *118*, 1864.

(5) Gaskill, D. K.; Bottka, N.; Lin, M. C. *J. Cryst. Growth* **1986**, *77*, 418.

(6) Interrante, L. V.; Carpenter, Jr., L.; Whitmarsh, C.; Lee, W.; Garbaukas, M.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 359.

(7) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.*, in press.

(8) Schulze, R. K.; Mantell, D. R.; Gladfelter, W. L.; Evans, J. F. *J. Vac. Sci. Technol.* **1988**, *A6*, 2162.

concentrations. The base pressure of this system was (2–4) × 10^{-10} Torr and, as such, gave results that indicated lower oxygen content than those from the appendage reactor attached to a second instrument, a Perkin-Elmer Corp./Physical Electronics Division Model 555 electron spectrometer. Because the second apparatus requires the sample to be deposited on a substrate affixed to the rapid introduction rod, the base pressure of the system is typically 1 order of magnitude higher. This leads to higher apparent bulk oxygen content for films grown in the appendage reactor due to the highly reactive surface generated when AlN is sputter-cleaned. As for the 5400, film compositions are determined by integrating Al(2p), N(1s), C(1s), and O(1s) photoelectron bands with normalization using the atomic sensitivity factors supplied by the manufacturer. Higher resolution (25-eV pass energy) data were acquired with this instrument to record standard spectra for the condensed and adsorbed precursors for comparison to AlN. A Mg Kα X-ray source was used for excitation and was operated at 300 W for both electron spectrometers. Ion sputtering (4 or 5 keV Ar^+) was carried out after analysis of the "as-deposited" thin-film samples to compare the surface composition of the film to that of the bulk. Spectra of the precursor materials were obtained by dosing these materials onto a sample of sputter-cleaned gold foil cooled to 77 K in the latter instrument (Model 555).

Synthesis and Characterization of Precursors. All manipulations were carried out under a purified N_2 atmosphere by using standard Schlenk techniques. Benzene was dried by shaking with H_2SO_4, saturated $NaHCO_3$, saturated NaCl, Na_2SO_4, and CaH_2 and then distilled from sodium metal. $[(CH_3)_2AlCl]_2$, $[(C_2H_5)_2AlCl]_2$, and NaN_3 (Aldrich Chemical Co., Inc.) were used as received. $[R_2AlN_3]_3$ (R = Me, Et) were prepared by halide substitution of $[R_2AlCl]_2$ by N_3^- via a NaN_3/benzene suspension.[9] Filtration of NaCl and excess NaN_3, followed by removal of solvent gave $[R_2AlN_3]_3$ in high yield. purification of $[Me_2AlN_3]_3$ was achieved by vacuum sublimation onto a cold finger (ice–water bath) at ca. 3 mTorr from a vessel held at 25–35 °C. $[Et_2AlN_3]_3$ was purified by vacuum distillation at ca. 3 mTorr by using a short-path distillation column. The vessel containing the material to be purified was held at 90–95 °C, and the head temperature was 65–69 °C for the fraction collected at the indicated pressure.

The precursor molecules were characterized by ^1H NMR, IR XPS, and elemental analysis. $[Me_2AlN_3]_3$: Anal. Calcd: C, 24.25; H, 6.10; N, 42.41. Found: C, 23.71; H, 6.07; N, 41.65. ^1H NMR (C_6D_6) δ −0.55. $[Et_2AlN_3]_3$: Anal. Calcd: C, 37.79; H, 7.93; N, 33.05. Found: C, 37.41; H, 7.69; N, 33.22. ^1H NMR (C_6D_6) δ 1.171 (t, 3 H, J = 8.23 Hz), 0.163 (q, 2 H, J = 8.20 Hz).

Azides of any type should be treated as potentially explosive materials. Reflux of $[Et_2AlN_3]_3$ has been carried out under vacuum (ca. 1 Torr) at temperatures as high as 120 °C without incident. We have neither seen reports of explosions nor experienced such difficulties while working with the dialkylaluminum azides. Storage of these materials under purified nitrogen for several months has not resulted in decomposition.

$[Et_2AlNH_2]_3$ was prepared by the method of Interrante.[6]

Reactor Configuration and Procedures Employed for Thin-Film Deposition and Characterization. The survey reactor employed in low-pressure thin-film depositions was an all-glass system equipped with an oil diffusion pump capable of base pressures of 3 × 10^{-5} Torr. Si⟨100⟩ wafer substrates were degreased/etched by immersion in each of the following baths for 10 min each: tetrachloroethylene, EtOH, deionized H_2O, dilute HF, deionized H_2O. They were then placed in a horizontal quartz tube appended to the main vacuum line. The substrates and tube were evacuated to base pressure and heated with a Lindberg tube furnace 18–24 h prior to deposition. The precursor source vessels were loaded in a drybox and maintained at constant temperature during depositions with a HAAKE A81 circulating bath. The thin films obtained from this survey reactor were characterized by IR and XPS spectroscopies, X-ray diffraction (XRD), and SEM. Film thickness and refractive indexes were evaluated by stylus profilometry and ellipsometry.

In the case of the appendage reactor, thin-film depositions of aluminum nitride were carried out in the six-way cross which is a component part of the rapid introduction system of the ultrahigh vacuum electron spectrometer (Figure 1). The body of the reactor is isolated from the ultrahigh vacuum analysis chamber by a gate valve. The precursor dosing line was attached to the top port of the cross and a pumping line, separated from the reactor by a butterfly valve, was attached to the bottom port. A sample introduction rod equipped with four electrical feedthroughs was used to mount the substrate/heater/thermocouple assembly. A viewport and a VCR feed-through flange, with a capacitance manometer and a gas dosing line, occupied other ports on the six-way cross.

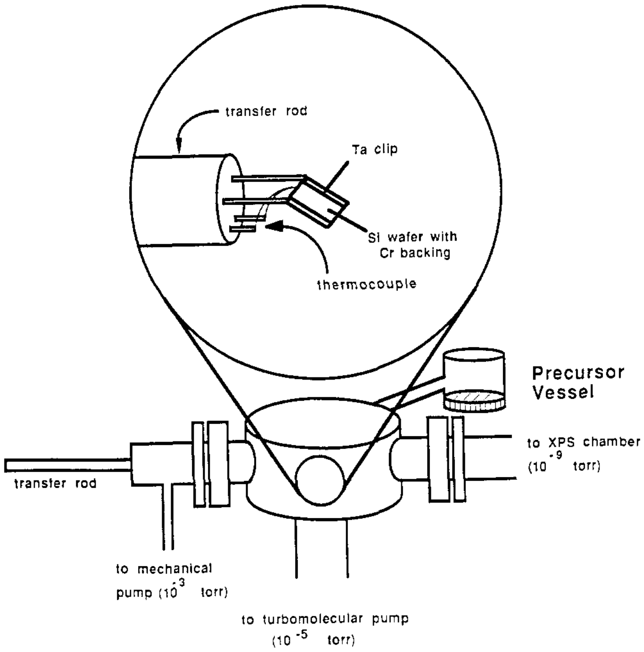

Figure 1. Schematic diagram of the reactor appended to the ultrahigh vacuum surface analysis system. Inset shows the manner in which the substrate/thermocouple assembly was attached. The stage had two tantalum support clips, electrically isolated from one another by an insulating ceramic. The stage was directly attached to the rapid sample introduction rod by barrel connectors. The temperature of the sample was monitored with a type K thermocouple making contact to the front of the wafer and held by a third tantalum clip.

The organometallic precursors were introduced through a dosing line fitted with a shutoff value and a metering value in series, both equipped with VCR fittings. Two different types of precursor storage vessels were used in the depositions of AlN thin films. The earlier design was all glass and incorporated viton O-ring sealed components. This design was abandoned in favor of an all-metal design that used VCR and Conflat flanges exclusively. In both cases, the precursor storage vessels included shutoff valves so that they could be removed from the dosing line without contamination. As with the survey reactor, provision was made to control the temperature of the source vessel and delivery lines to provide sufficient vapor pressure of precursor.

Thin-film depositions in the appendage reactor were carried out on substrates of clean Si⟨100⟩ wafers with a thin film (ca. 1500 Å) of chromium vapor deposited on the back of the wafer. The samples were heated resistively to the necessary reaction temperature (400–500 °C) by passing current directly through the chromium as depicted in the inset of Figure 1. Readings of the temperature of the wafer were made with the current supply momentarily disconnected from the sample.

Depositions were carried out by introducing a sample to the reactor and pumping it to its base pressure. Impurity gases were then removed from the precursor storage vessel by several freeze/pump/thaw cycles. The sample and stage were next heated to 300 °C for 20–30 min to allow for outgassing. At the same time, with all dosing valves closed, the precursor vessel and dosing line were heated to 40–65 °C. The sample was brought to the desired deposition temperature, and the dosing line was opened to the reactor beginning the deposition. A low rate of gas flow was

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[9] Price, M. I.; Weiss, K. J. *J. Organomet. Chem.* **1966**, *5*, 584.

maintained in the reactor by throttling the valve to the pumping line. Deposition pressures were typically (4–6) × 10^{-4} Torr. The rate of deposition was crudely monitored by observing the color changes due to the development of interference fringes through the reactor viewport. A typical deposition was carried out for 1–2 interference fringe cycles (45 min–1 h), yielding films several thousands of angstroms thick.

Identification and Quantification of Gaseous Products. The residual hydrocarbon gases evolved during depositions in the survey reactor were trapped in a liquid nitrogen cooled vessel, which was warmed to room temperature and backfilled with N_2. Analysis of the mixture was performed only after lengthy equilibration of the resulting gas mixture. Calibrations were performed by trapping known quantities of the authentic gases with the same apparatus. Each of the components of the trapped gas mixtures was identified by GC/MS. Low molecular weight gaseous products (C_2 fraction) were analyzed by using a Hewlett-Packard Model 5890A gas chromatograph equipped with a Hewlett-Packard Model 3393A integrator, a 6 ft × $^1/_8$ in. stainless steel column packed with 80/100 mesh Carbosphere (Alltech Associates, Inc.) and a thermal conductivity detector. Butane and butene concentrations were measured with a 30 m × 0.53 mm open tubular column (NON-PAKD RSL-160, Alltech Associates, Inc.). The concentration of C_4 products is reported as a fraction relative to the total C_2 products. Favorable mass balance was observed in all cases for the diethylaluminum precursors.

Results

Thin Films Deposited. Two reactors were used in the present study: (1) a survey reactor in which gas-phase precursor was introduced into a heated quartz tube that held the substrates and (2) a reactor appended to the surface analytical system that employed resistive heating of the substrate only. The first system allowed for the convenient screening of precursors and for the trapping of gas-phase products as described below. The second system afforded a means of depositing a thin film under improved vacuum conditions and for the introduction of thin-film samples into the ultrahigh vacuum analysis chamber without exposure to atmospheric contaminants. This system also allowed for the XPS characterization of the condensed precursors to be made since these air-sensitive materials could be directly deposited onto a liquid nitrogen cooled surface by using the same apparatus. In both systems, reduced pressures of neat precursor (no carrier gas) were used for the majority of the experiments reported here. A single experiment employing H_2 carrier gas (1 Torr) was carried out for the $[Et_2AlN_3]_3$ precursor and gave solid and gaseous products that were indistinguishable from those from the neat runs, although the deposition rate may have been influenced by the presence of H_2.

Pyrolysis of $[R_2AlN_3]_3$ (R = Me, Et) at 400–600 °C resulted in deposition of uniform films of AlN on Si⟨100⟩ substrates. Both precursors react completely within the hot region of the reactor to form thin films of comparable composition. The films were analyzed by a variety of techniques, including IR, XPS, and XRD. All results were consistent with the AlN formulation. The films were generally amorphous as deposited. However, annealing of powdered deposits at 700 °C significantly increased the crystallinity of this material, allowing reflections assigned to AlN to become clearly visible. Microscopic examination up to a magnification of 55 000 revealed no features indicative of the formation of grains or crystallites. In certain cases in which very high deposition rates were observed due to high delivery vessel temperature, crazing of the AlN films along crystal axes of the Si substrate could be observed by optical microscopy. Occasionally this was accompanied by loss of adhesion to the substrate. Infrared spectra of the smooth films exhibit a rather broad feature at 680 ± 20 cm^{-1}, consistent with other reports of the Al–N stretching mode for AlN.[10]

Table I. XPS Data for Condensed (Unreacted) Precursor Films

	binding energies, eV[a]		
precursor	Al(2p)	N(1s)	Δ[b]
$[Me_2AlN_3]_3$	75.0	400.8	325.8
		401.4	326.4
		405.3	330.3
$[Et_2AlN_3]_3$	74.1	399.3	325.2
		400.8	326.7
		404.2	330.1
$[Et_2AlNH_2]_3$	74.4	399.2	324.8
		402.8	328.4[c]

[a] Absolute binding energies have been corrected to C(1s) at 284.6 eV. [b] We also report the difference, Δ, between the Al(2p) and N(1s) peaks due to uncertainties that may arise from the charge correction procedure. As such, more meaningful comparisons between N(1s) chemical shifts can be made for the azides. [c] This higher binding energy feature is ca. 10% of the total intensity and arises from an unknown source. It may be an artifact of the manner in which the unreacted precursor films are formed in that water is often co-condensed with the precursor in the antechamber.

The XPS data for precursors and films deposited in the two reactors are summarized in Tables I–III. For the condensed precursors (Table I) the high-resolution N(1s) spectra of the two azides give similar values for the binding energy shifts associated with the nitrogen in the three different chemical environments. The similarity for these spectra suggest a minimal perturbation to the electronic structure as the alkyl substituent is changed from methyl to ethyl. The highest binding energy N(1s) peak is assigned to the nitrogen atom in the center of the azide group due to this nitrogen having the lowest anticipated electron density relative to the terminal nitrogen atoms. Of the other two peaks we are hesitant to assign which one is attributable to the nitrogen atom bonded to the metal in the absence of any electronic structure calculations. The usual intuition that one applies in such cases is complicated by the multiplicity of available resonance structures that the azide group may adopt. Figure 2 shows the N(1s) region for the dimethylaluminum azide, where the relative intensities for the three contributions are found to be approximately equal from the curve fitting. There is an additional feature found at 403.2 eV with ca. 6% of the total band intensity which is unassigned and presumed to be an impurity.

Tables II and III give the data for AlN films deposited by using the various precursors in different reactors and analyzed both "as-deposited" and after brief sputtering to reflect the bulk composition of the films. For the "as-deposited" films prepared in the appendage reactor, there is strong evidence for the diethylaluminum azide precursor strongly adsorbing on the surface in a partially reacted state as previously noted.[8] This presumed intermediate was readily eliminated by subsequent heating in ultrahigh vacuum, or by sputtering. By contrast, no such surface species were found for either the more volatile methyl analogue or the amido precursor.

The thickness and refractive indexes of the films were measured by stylus profilometry and ellipsometry. A rate of deposition for $[Et_2AlN_3]_3$ of 760 Å/h was measured for depositions of 2–10 h with precursor and furnace temperatures of 40 and 500 °C, respectively. The refractive index of the films varied from 1.93 to 2.10 and averaged

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[10] Xinjiao, L.; Zechuan, X.; Ziyou, H.; Huazhe, C.; Wuda, S.; Zongcai, C.; Feng, Z.; Enguang, W. *Thin Solid Films* **1986**, *139*, 261.

Table II. XPS Data for Thin Films Deposited in Appendage Reactor

			binding energies, eV[b]			film comp,[c] %			
precursor	T_{subs}, °C	sample conditions[a]	Al(2p)	N(1s)	Δ[d]	Al	N	C	O
$[Me_2AlN_3]_3$	500	A	73.0	395.9	322.9	31–32	21–34	12–22	14–35
		B	74.5	397.8	323.3	35–47	29–37	7–10	8–29
$[Et_2AlN_3]_3$	500	A	74.0	397.2	323.2	30–34	40–45	15–23	2–10
		B	73.8	397.0	323.2	43–45	42–45	5–12	4–8
$[Et_2AlNH_2]_3$	550	A	75.6	398.6	323.0	36–38	22–26	2–9	30–31
		B	75.6	398.3	322.7	38–40	24–25	2–3	34–35

[a] A = as-deposited; B = after sputtering into the bulk of film. [b] Absolute binding energies have been corrected to C(1s) at 284.6 eV. [c] Ranges of compositional values (at. %) shown for several samples. [d] We also report the difference, Δ, between the Al(2p) and N(1s) peaks due to uncertainties that may arise from the charge correction procedure. As such, more meaningful comparisons of chemical shifts can be made.

Table III. XPS Data for Thin Films Deposited in Survey Reactor

			binding energies, eV[b]			film comp, %			
precursor	T_{subs}, °C	sample conditions[a]	Al(2p)	N(1s)	Δ[c]	Al	N	C	O
$[Me_2AlN_3]_3$	500	A	73.3	398.7	325.4	27	11	15	47
		B	75.9	399.1	323.2	43	44	11	2
$[Et_2AlN_3]_3$	500	A	73.4	396.7	323.3	21	8	19	52
		B	73.1	396.3	323.2	43	45	10	2
$[Et_2AlNH_2]_3$	550	A	73.2	396.2	323.0	18	6	50	26
		B	75.6	396.5	323.0	44	41	7	8

[a] A = as-deposited; B = after sputtering into the bulk of film. [b] Absolute binding energies have been corrected to C(1s) at 284.6 eV. [c] We also report the difference, Δ, between the Al(2p) and N(1s) peaks due to uncertainties that may arise from the charge correction procedure. As such, more meaningful comparisons of chemical shifts can be made.

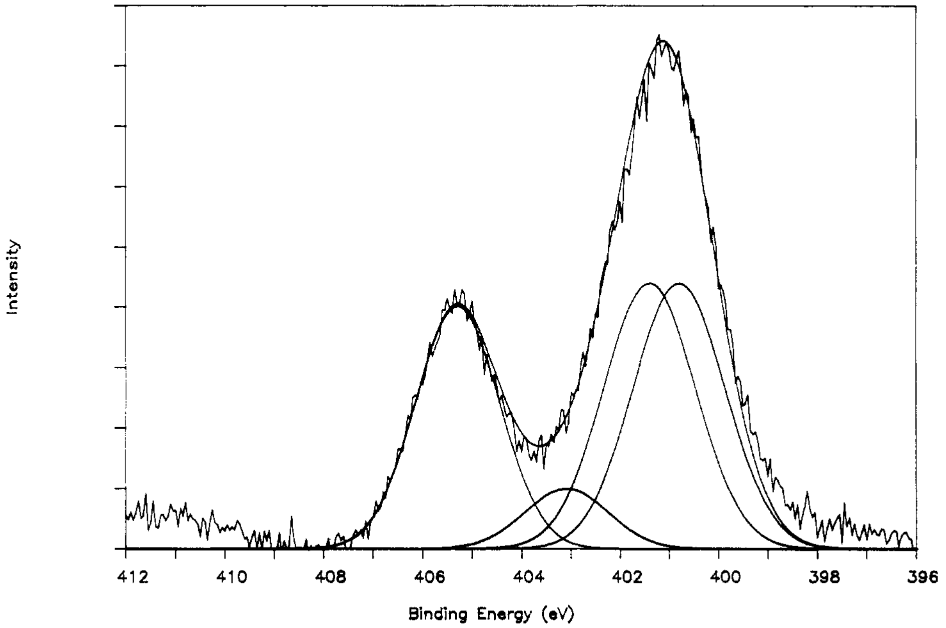


Figure 2. High-resolution XPS spectrum of the N(1s) region for condensed $[Me_2AlN_3]_3$. See text for assignments and discussion.

2.0. The relationship between these values and the film composition and structure are not obvious at this time, but the range of values is consistent with those reported elsewhere.[13]

Gas-Phase Products. The analysis of residual gases released from $[Et_2AlN_3]_3$ (precursor = 40 °C, furnace = 500 °C) reproducibly showed 70% ethylene, 30% ethane, and a very small amount of butane and butenes (C_4/C_2 = 0.03). On the basis of the mass of precursor consumed during the deposition and the total pressure of C_2H_4 and C_2H_6 trapped, 86% of the precursor ethyl groups are accounted for in this analysis. If one considers the small amount of C_4 products observed, the recovery rate is increased to 89%. Similar gas analyses are observed when the furnace temperature is increased to 650 °C (C_2H_4 = 76%, C_2H_6 = 24%, C_4/C_2 = 0.02, 95% recovery) or when the deposition is conducted under 1 Torr of H_2 carrier gas (C_2H_4 = 65%, C_2H_6 = 35%, C_4/C_2 = 0.01). For comparison, analysis of the gaseous products from CVD using Interrante's precursor,[6] $[Et_2AlNH_2]_3$, under similar deposition conditions, indicates the formation of ethane is significantly favored over ethylene (C_2H_4 = 25%, C_2H_6 = 75%, C_4/C_2 = 0.02, 81% recovery). When the same experiment was performed by using $[Me_2AlN_3]_3$, only 6% of the carbon availed by the precursor was recovered (C_2H_4 = 27%, C_2H_6 = 57%, C_2H_2 = 16%, no C_4 products observed). The carbon that is lost is presumed to be CH_4, which is not efficiently trapped at the liquid nitrogen temperatures employed here.

Discussion

We begin the discussion with a few comments regarding the design of the precursor. We have attempted to design a molecule incorporating the strategies of both Interrante[6,7] (aluminum and nitrogen in a single precursor structure) and Gaskill[5] (more reactive nitrogen source). The choice of the nitrogen source was based on the established high reactivity of azide compounds. Organic,[14] main-group,[14] and transition-metal azides[15] are all known to readily lose N_2 upon thermal or photochemical activation. As can be seen in reactions 2–4 (ref 16–18, respectively), the state of the nitrene (or nitrido ligand) depends on the starting azide.

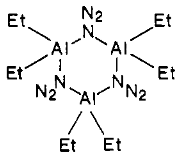
$$\mathrm{MeN_3} \xrightarrow{720\ ^\circ\mathrm{C}} \mathrm{CH_3{-}N + N_2 \rightarrow H_2C{=}NH}\ \text{(ref 16)} \qquad (2)$$

$$\mathrm{(Me)_3GeN_3} \xrightarrow{830\ ^\circ\mathrm{C}} \mathrm{GeNH + N_2} + \text{hydrocarbons (ref 17)} \qquad (3)$$

$$mer\text{-}\mathrm{Re(PMe_2Ph)_3Cl_3 + N_3^-} \xrightarrow{\mathrm{rt}} mer\text{-}\mathrm{Re(PMe_2Ph)_3Cl_2(N) + N_2 + Cl^-}\ \text{(ref 18)} \qquad (4)$$

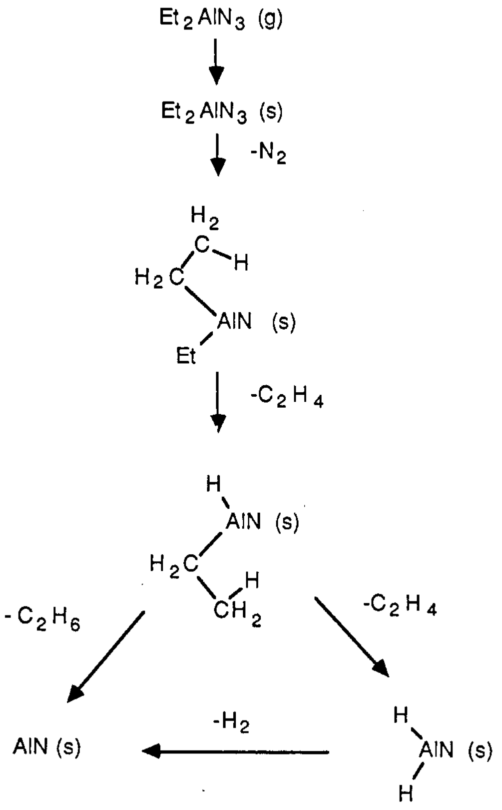
An equally important aspect of the design involves the consideration of a facile mechanism for the cleavage of the aluminum–carbon bonds. Note that alkyl substituents were first considered because of the requisite volatility that they impart to the organometallic compound, a requirement that reduced our choices in the case of aluminum azides to the simplest of alkyl substituents. $[\mathrm{Et_2AlN_3}]_3$ received most of our attention, as the presence of β-hydrogens offered a potential pathway for the Al–C cleavage through β-hydrogen elimination.[19]

The trimeric formulation of the diethylaluminum azide as shown here is based on the solution studies of Dehnicke and co-workers:[20]



Although no evidence for the existence of other oligomers (or of the monomer) has been described for the azides, recent reports suggest the structurally related amide, $[\mathrm{Et_2AlNH_2}]_3$, equilibrates with a dimeric form.[3] The fluid solution studies of $[\mathrm{R_2AlNH_2}]_3$ allow speculation regarding the nature of the reactive fragment responsible for AlN deposition from trimeric precursors of this type. The structure of $[\mathrm{R_2AlN_3}]_n$ in the gas phase is unknown at this time, but chemical ionization mass spectra obtained from $[\mathrm{Et_2AlN_3}]_3$ exhibit signals for both the dimeric and trimeric aggregates of the $\mathrm{Et_2AlN_3}$ unit, indicating that the proposed structure in solution is maintained by a portion of the precursor during gas-phase transport. Room-temperature ^{1}H NMR spectroscopy of $[\mathrm{Et_2AlN_3}]_3$ shows one ethyl pattern, giving no evidence of structures of differing nuclearity. Furthermore, if the gas-phase dissociation of $[\mathrm{R_2AlN_3}]_3$ does occur, it is reversible; infrared spectra obtained before and after gas-phase transport are identical. Further studies designed to elucidate the precise gas-phase structures of $[\mathrm{R_2AlN_3}]_n$ are currently in progress.

Scheme I



Stoichiometric investigations have been undertaken to formulate a hypothesis for the mechanism of AlN deposition from the dialkylaluminum azides. For the $[\mathrm{Et_2AlN_3}]_3$ precursor, the stoichiometry has been determined by analysis of the hydrocarbon gases trapped during AlN deposition. Using these data and normalizing to account for all of the carbon present in the precursor structures suggest for $[\mathrm{Et_2AlN_3}]_3$

$$[\mathrm{Et_2AlN_3}]_3 \xrightarrow{500\ ^\circ\mathrm{C}} \mathrm{3AlN + 3N_2 + 4.2C_2H_4 + 1.8C_2H_6 + 1.2H_2} \qquad (5)$$

and, similarly, for $[\mathrm{Et_2AlNH_2}]_3$

$$[\mathrm{Et_2AlNH_2}]_3 \xrightarrow{500\ ^\circ\mathrm{C}} \mathrm{3AlN + 1.4C_2H_4 + 4.6C_2H_6 + 1.4\ H_2} \qquad (6)$$

The relatively small variations in the gas analyses for $[\mathrm{Et_2AlN_3}]_3$ as the deposition temperature is altered or as H_2 is added as a carrier suggest that no substantial changes in mechanism are occurring. On the other hand the dramatic change in gaseous product distribution as the nature of the nitrogen-bearing functionality is changed from azide (ethane/ethylene = 0.43) to amido (ethane/ethylene = 3.00) suggests different pathways may be involved in the thermally activated decomposition of these two chemically dissimilar precursors. Presumably, the availability of the weakly acidic hydrogens of the NH_2 group allows facile protonolysis of the Al–C bond.[21]

The analysis of the products of the $[\mathrm{Et_2AlN_3}]_3$ reaction favors an Al–alkyl β-hydrogen elimination reaction over homolytic Al–alkyl bond cleavage. Homolytic bond cleavage would form ethyl radicals that could couple or disproportionate to yield C_4H_{10} and C_2H_4/C_2H_6, respec-

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tively. The gas-phase reactivity of ethyl radicals has been studied thoroughly by Lalonde and Price.[22] This study concluded that radical coupling (to form C_4H_{10}) is preferred over disproportionation by a factor of ~10. The results obtained from $[Et_2AlN_3]_3$ show the formation of C_4 products is *not* preferred under the experimental conditions employed ($C_4/C_2 = 0.03$); therefore, liberation of ethyl radicals into the gas phase is not the predominant mechanism of Al–C bond cleavage. Furthermore, the as-deposited N(1s) high-resolution XPS spectra provides evidence of a partially decomposed precursor or intermediate on the AlN thin films for the case of $[Et_2AlN_3]_3$. An alternative to homolytic Al–C bond cleavage, which is more consistent with the observed gaseous product distributions, is a β-hydrogen elimination reaction that would form an aluminum hydride intermediate species, and yield a molecule of ethylene, as shown in Scheme I. This intermediate might then undergo a second β-hydrogen elimination reaction with concomitant loss of H_2 or eliminate a molecule of C_2H_6 to ultimately yield AlN. No C_4 products are predicted in this scheme, though some amount of homolytic Al–C bond cleavage might be anticipated under the pyrolysis conditions of 500 °C. The sequence of fragmentation for each precursor is being investigated through temperature-programmed reaction studies to understand more thoroughly the mechanisms of thin-film formation.

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From Molecules to Thin Solid Films: Vibrational Characterization of Evaporated Organic Films

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The use of surface-enhanced Raman scattering (SERS) and resonance Raman scattering (SERRS) for vibrational characterization of physisorbed molecules at submonolayer coverage is emphasized and illustrated with the example of vanadyl phthalocyanine (VOPc). SERS and SERRS produced by three different surfaces with physisorbed VOPc are compared with the corresponding unenhanced spectra of VOPc aggregates obtained by evaporation. Silver and gold island films, with plasmon absorptions well separated in the visible region, and a SERS-active surface of Ag-coated Sn spheres that presents enhancing properties for most of the visible region of the spectrum were used. Thin solid films of VOPc were gradually grown onto the SERS-active surface of Ag-coated Sn spheres from thicknesses of 1 to 65 nm. The intensity of the SERS signal decreased with increasing film thickness, and the depolarized SERS spectra were replaced by a typical polarized spectra of the thin-film samples deposited onto alkali halide or glass substrate. Solid-state splittings of some vibrational frequencies were confirmed by their absence in the molecular (SERS) spectra.

Introduction

The vibrational characterization of a molecular system in its ground electronic state involves the identification of $3N - 6$ (or $3N - 5$ for a linear molecule) fundamental vibrational modes. For spectroscopic applications it is required that each fundamental be assigned to an irreducible representation of the molecular point group and correlated with one or more internal coordinate(s) (change in a bond length or bond angle). Since molecular association and aggregation introduce large perturbations of the vibrational energy levels, the vibrational analysis is normally carried out in the gas phase or dilute solution and matrices. SERS offers an additional method to carry out the vibrational characterization of physisorbed molecules at submonolayer coverage on a SERS-active surface. The method is of particular importance in the case of macromolecules, polymers, and biomolecules. In the case of chemisorption the vibrational analysis leads to the vibrational characterization of the surface complex. In the present work the molecular spectra of VOPc evaporated at submonolayer coverage onto Ag and Au island films and Ag-coated Sn spheres are presented and compared with the corresponding Raman spectra of thick films (thickness of 100 and 200 nm). The approach could help to define perturbations in the vibrational energy levels due to aggregation.

Experimental Section

Metal island films were prepared by slow vacuum evaporation (0.1 nm/s) of the metal onto glass slides kept at 200 °C, and the thickness was monitored with a quartz crystal oscillator. With control of the temperature of the substrate, metal island films were grown with a more homogeneous distribution of particle shapes. The plasmon absorption of the 10-nm Ag film was broad and centered at 490 nm; the corresponding plasmon absorption

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