A low cost, high efficiency TMA-replacement for the deposition of high-quality aluminum nitride by atomic layer deposition

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Abstract

A heteroleptic amidoalane precursor is presented as a viable candidate to replace trimethylaluminum (TMA) for atomic layer deposition of aluminum nitride (AlN). Ammonia (NH_3) plasma was used as a co-reagent to produce AlN films, which were crystalline when deposited at temperatures of 200 °C and above. The films produced were uniform and near stoichiometric with an Al:N ratio of 1.04. By designing a simple, low cost precursor ($AlH_2(NMe_2)$) with only metal-nitrogen and metal-hydrogen bonds, carbon and oxygen impurities in resultant AlN films were reduced to <1% and <2%, respectively. Compared to TMA, this precursor can improve film quality and reduce material cost by up to 2 orders of magnitude.

Introduction

Aluminum nitride (AlN) is an important wide bandgap (6.2 eV) semiconductor which has applications as a dielectric layer and in light-emitting diodes.[1] Due to increasingly small and non-trivial device morphologies, atomic layer deposition (ALD) is a valuable thin film deposition technique to employ for next generation microelectronic devices. ALD is a subset of chemical vapour deposition (CVD), but distinctly only employs surface-limited and self-terminating chemical reactions that allow precise thickness control down to the Ångström level.

Trimethylaluminum (TMA) is a commonly used precursor to deposit aluminum oxide (Al_2O_3) and AlN, but it has a significant drawback: many processes report carbon impurities in deposited films on the order of 3-6%;[2–4] these carbon impurities originate from the direct metal-carbon bonds present in this precursor.[3] Although TMA is readily available and well-studied, it does not deposit films with acceptably low impurities; this is an aspect of thin film deposition that can be improved through precursor design.

The basis behind this research emphasizes the importance of ligand-metal bonding in a precursor. Specifically, the inclusion of metal-nitrogen bonds and the elimination of metal-carbon bonds is an intuitive way to deposit 13-nitride films with low C contamination. We initially used TMA as a template to design an analogue, replacing all methyl grounds with amide ligands; tris(dimethylamido)aluminum(III) was used to deposit Al_2O_3 by ALD with C contamination of less than 1%.[5] The evolved precursor design presented herein came from an effort to minimize oxygen incorporation during film growth. Using ligand design to our advantage, a hydride ligand was employed to produce $AlH_2(NMe_2)$ (**1**). We hypothesized that this precursor could provide reducing surface conditions to allow the growing AlN film to resist oxidation during film growth. ALD processes in general can aim to employ precursors not only that are volatile and that contain target atoms, but that are designed to do so in the most effective and efficient way possible. The introduction and use of compound **1** in this work demonstrates the importance of smart precursor design to optimize ALD processes and results.

Experimental

Compound **1** was synthesized in a N_2-filled glovebox using an adapted literature procedure.[6] Dimethylammonium chloride (Me_2NH_2Cl) was dried under vacuum and ether was dried over 4 Å sieves prior to use. Lithium aluminum hydride ($LiAlH_4$) (4.20 g, 109 mmol) was added to a 250 mL round-bottomed flask with ~75 mL of ether and stirred with a magnetic stir bar. Me_2NH_2Cl (8.60 g, 105 mmol) was cooled (–35 °C), then added scoop-wise to the $LiAlH_4$ suspension. The mixture bubbled vigorously upon sequential additions and the resultant solution stirred overnight. The solution was filtered through a medium fritted filter and the volume was reduced under vacuum to produce a white solid (6.25 g, 81% unpurified yield).

Thermogravimetric analysis (TGA) experiments were performed using a TGA Q500 tool in an N_2 filled glovebox. The sample Pt pan was loaded with ~10 mg of precursor and the furnace was heated at a rate of 10 °C/min to 500 °C.

ALD experiments were performed on a hot-wall Picosun R-200 tool with a Litmas remote plasma source. The operating pressure was maintained at 4 mbar under a continuous flow of N_2 (99.999%), which was also used as a purge gas. NH_3 plasma as the co-reagent was pulsed for 12 s at a power of 2800 W. AlN films were deposited on 2.5 cm x 2.5 cm Si coupons.

PANalytical EMPYREAN MRD XRD with a Cu-anode X-ray tube and 5-axis (x-y-z-v-u) sample stage operating at 45 kV and 40 mA was used in grazing-incidence X-ray diffraction (GIXRD) mode with 0.5° incident angle to analyze film crystallinity. Stress and strain were estimated using GIXRD data for diffraction peaks; values of $\sin^2 \psi$ and ε were obtained using X'Pert Stress software. Kratos AXIS Ultra DLD X-ray photoelectron spectroscopy (XPS) equipped with an Ar sputtering source (0.5 keV) was used to analyze film composition. CasaXPS was used to analyze XPS data. High-resolution scans were fitted by Gaussian-Laurentius functions and Shirley background. Scanning electron microscopy (SEM) images were collected using a LEO 1550 tool operating at 10 kV in coordination with energy-dispersive X-ray spectroscopy (EDS) for compositional analysis.

Results and discussion

The synthesis of **1** employs lithium aluminum hydride ($LiAlH_4$) and dimethylammonium chloride (Me_2NH_2Cl), two very inexpensive and readily available starting materials. The reaction proceeds with the evolution of hydrogen gas and the precipitation of lithium chloride, both of which act as thermodynamic driving forces for the reaction to go to completion:

$$LiAlH_4 + Me_2NH_2Cl \rightarrow AlH_2(NMe_2) + 2\ H_2 + LiCl$$

The high crude yield and low cost of reactants, as well as the straightforward one-pot, single step synthesis makes compound **1** an accessible and inexpensive ALD precursor.

The TGA ramp experiment for **1** (Figure 1) demonstrates that it is a volatile and thermally stable precursor. The volatilization curve shows an exponential mass loss with no visible signs of decomposition and no residual mass. Its 1 Torr temperature was calculated to be 40 °C using mass loss derivative data.[7]

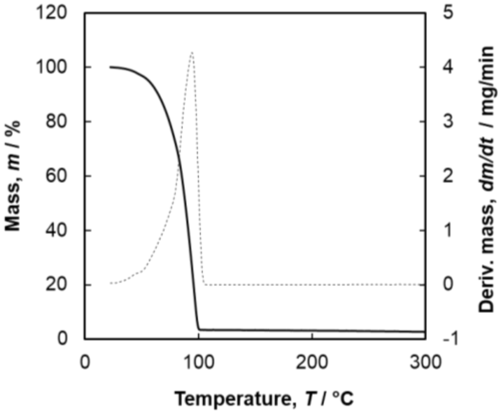

Figure 1: TGA ramp of compound **1**.

The saturation curve for **1** in ALD experiments to produce AlN is presented in Figure 2a. Saturative growth is observed after 8 s of exposure of **1** at temperatures of 150 and 200 °C with a growth per cycle (GPC) of approximately 4 Å. This GPC is notably higher than previous AlN ALD reports and lies just outside the lattice parameters for hexagonal AlN,[8] considering measurement error. Experiments run at 100 °C do not exhibit saturative ALD behaviour, which can be attributed to precursor condensation at the surface.

SEM micrographs (Figure 2c-d) show that ALD-grown AlN films are uniform and dense. Experiments performed at 100 °C (Figure 2a), however, show droplets present on the surface, which confirms that precursor condenses on the substrate at lower deposition temperatures. EDS measurements of AlN deposited at 200 °C demonstrated an Al:N ratio of 1.04, indicating near stoichiometric AlN.

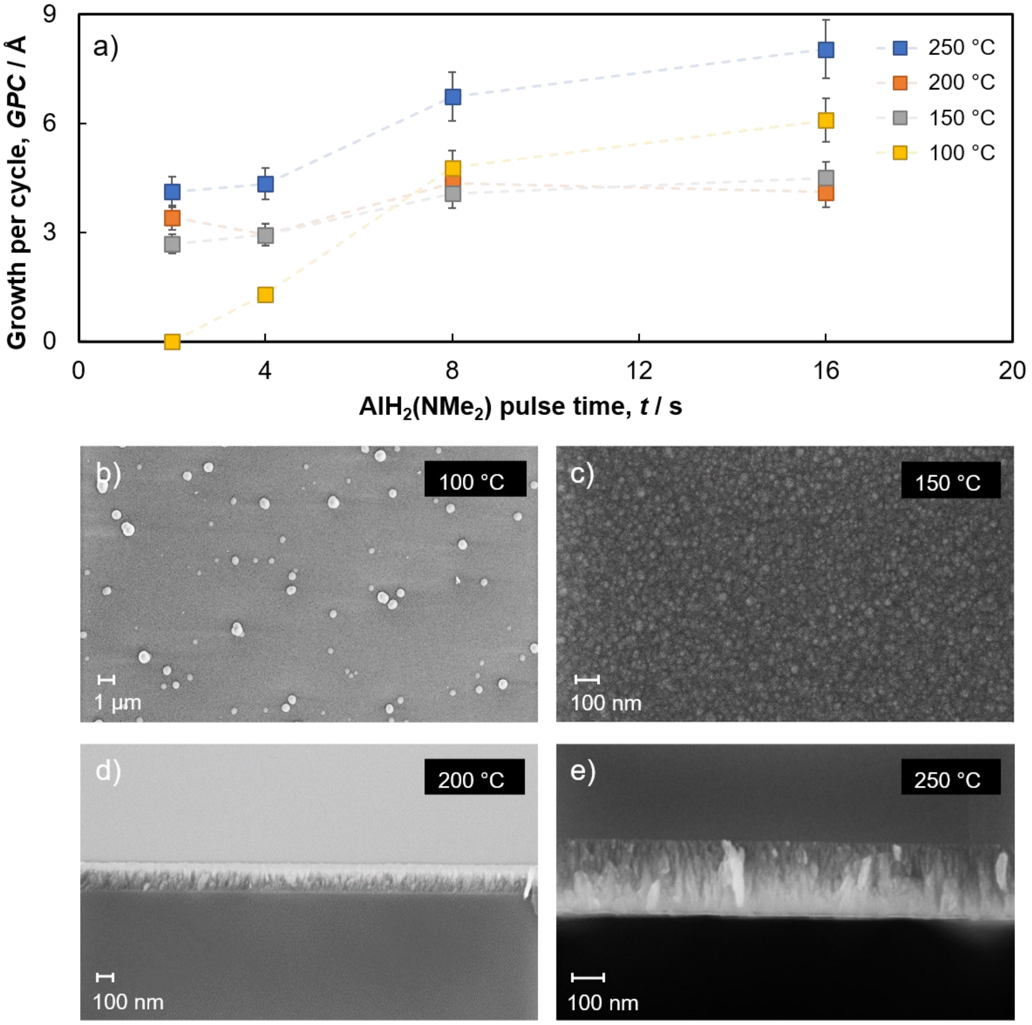

Figure 2: a) Saturation curve for **1** in ALD process with NH_3 plasma, and SEM micrographs of AlN films deposited at b) 100 °C, c) 150 °C, d) 200 °C, and e) 250 °C.

Figure 3a shows GIXRD data for AlN films deposited between 100 °C and 250 °C after 500 cycles of deposition. Films deposited at 200 and 250 °C showed the strongest peaks corresponding to crystalline hexagonal AlN; both the (100) and (002) peaks were observed. These peaks were also visible for the samples deposited at 150 °C, but with lower intensity. Crystallinity of these AlN films was seen to increase both with increased deposition temperature and number of cycles; low temperature depositions (100 °C) do not appear to be crystalline, and crystallinity of AlN films grown was not observed after only 200 deposition cycles, even at higher deposition temperatures. When AlN was deposited on SiC (shown in the left inset of Figure 3a), films were not epitaxial, though their crystallinity improved, and a very strong (103) peak was observed.

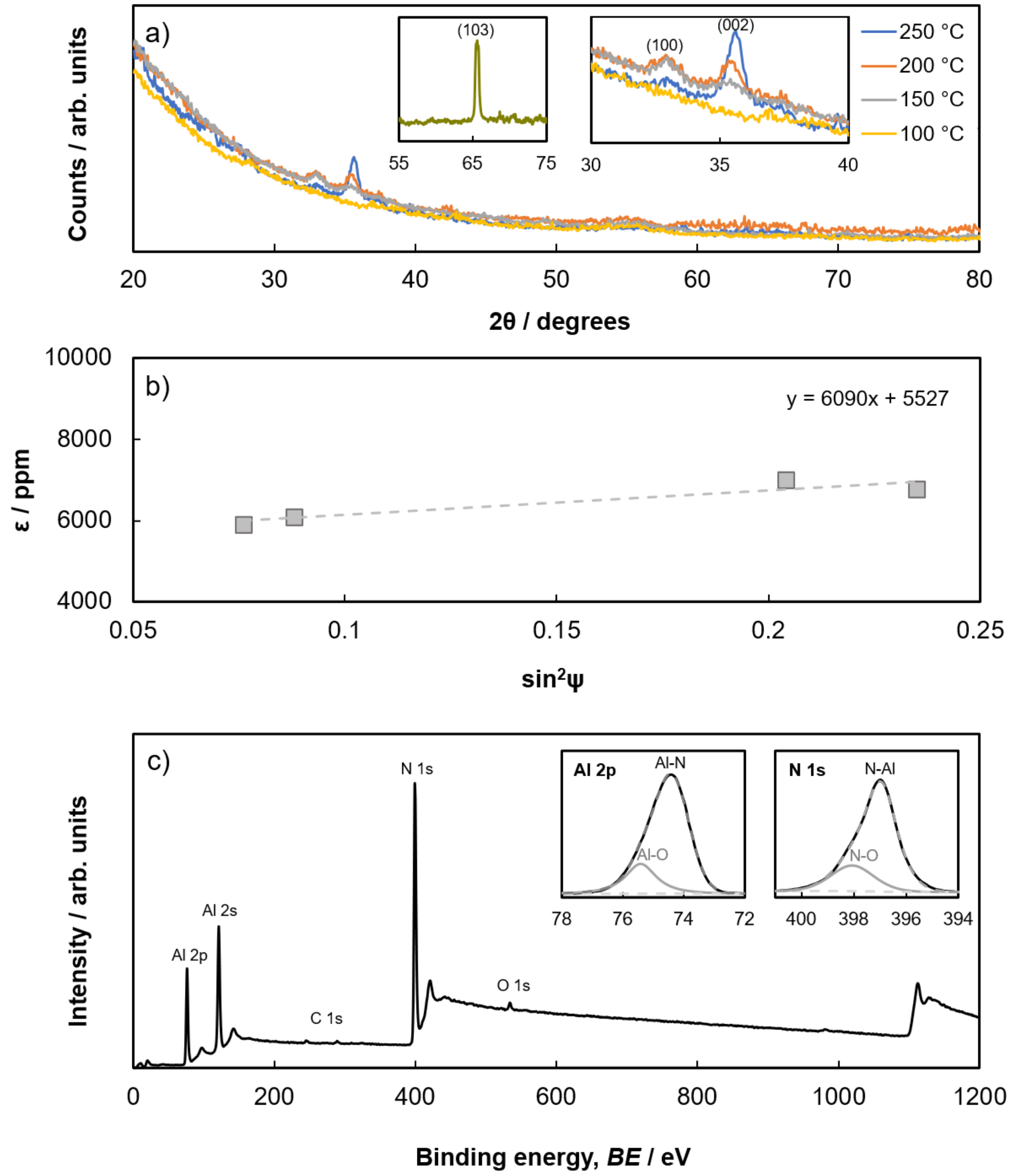

Figure 3: a) GIXRD plot of deposited AlN films (left inset for AlN deposited on SiC), b) $\sin^2\psi$ vs. ε plot to calculate film strain, c) XPS survey scan of AlN film deposited at 200 °C and inset high-resolution scans for Al and N.

Film composition was studied by XPS (Figure 3c) after sputtering to clean incidental contamination from the surface. High-resolution peaks were fitted for Al 2p at 74.7 and 75.5 eV as representing Al–N and Al–O bonds, respectively, while the N 1s spectrum was fitted for N–Al and N–O bonds at 397.9 and 399.4 eV. Importantly, for AlN deposited at 200 °C (Al:N ratio of 1.04), we observed impurity levels of carbon and oxygen at 0.7 and 1.7%, respectively. This indicates that metal-nitrogen and metal-hydride bonds designed into the precursor successfully respectively reduced carbon and oxygen contamination in AlN films. This is especially noteworthy when other processes using TMA and NH_3 plasma have employed plasma pulse lengths of 40 seconds [9–12] in order to reduce impurities in AlN films.

Finally, the stress and strain of the AlN films were estimated using GIXRD data from an $\varepsilon - \sin^2 \psi$ plot using a previously reported method,[13] shown in Figure 3b. The positive slope of 6090 ppm indicates a tensile strain of 0.61%. Tensile stress was calculated as a range between 1.50 and 1.67 GPa.[8,13] It is expected for tensile strain and stress to exist in these AlN films due to their large lattice mismatch compared to the Si substrate. Upcoming work will focus on mobility and charge carrier measurements for AlN depositions on semi-insulating SiC (SI-SiC).

Conclusions

This work emphasizes the importance of developing alternative precursors to TMA for Al-based ALD. The new ALD precursor $AlH_2(NMe_2)$ (**1**) produces excellent AlN films in a process with NH_3 plasma with measured carbon impurities significantly lower than many processes reported using TMA.

Using a TMA framework is an excellent way to design and synthesize alternative precursors better suited to AlN deposition by ALD. $AlH_2(NMe_2)$ (**1**) is easy to synthesize on a lab scale (tens of grams) in less than two hours at a materials cost of $1.26 (CAD) per gram without any requirements for further purification. On an “industry” scale (on the order of kilograms), this precursor could be synthesized for $0.67 per gram based on given catalog prices for starting materials. This is significant in comparison to the cost of TMA, which is available for purchase (25 g in a bubbler) from Sigma Aldrich at a cost of $2440, equivalent to $62 per gram. Though this comparison strictly highlights the materials cost difference between these two precursors, it emphasizes the fact that employing **1** as an ALD precursor compared to TMA can be significantly more accessible on the basis of upfront materials cost, ease and safety of synthesis and use, as well as the demonstrated high quality of films produced. Compound **1** is a non-pyrophoric solid, and could therefore be far easier to handle than TMA on large, industrial scales. It is especially important to consider the GPC of AlN achieved using **1**, which is three to four times higher than that when using TMA.

A simple shift away from TMA towards **1** in this experiment has shown that, if we design smart precursors, the quality of ALD-grown films and their subsequent applications can be improved; we should synthesize precursors to our advantage, and using **1** to deposit pure AlN is a demonstration of how well this can work.

Conflicts of Interest

There are no conflicts to declare.

Acknowledgements

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