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Tris(dialkylamino)aluminums: Syntheses, characterization, volatility comparison and atomic layer deposition of alumina thin films

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Abstract

The syntheses and characterization of both tris(diethylamino)aluminum and tris(diisopropylamino)aluminum are presented in this letter. Characterization includes vapor pressure measurements and comparison of the two non-pyrophoric precursors showing them to be viable alternatives to trimethylaluminum. Ultimately, tris(diisopropyl)aluminum was successful in the atomic layer deposition of alumina thin films. © 2007 Elsevier B.V. All rights reserved.

1. Introduction

The search for SiO_2 high κ replacements (κ is the dielectric constant) continues to receive considerable attention as complementary metal-oxide semiconductor (CMOS) technology shrinks [1–5]. Advancements in this area, pertaining to materials chemistry, test the requirements of ultra-thin film processing of insulating binary or higher order oxides, devoid of impurity atoms (*e.g.* halides) [1]. The numerous attributes of these layers (thinness, conformal coverage, compatibility with terminated silicon surfaces, abrupt interfaces, thermal processing, *etc.*) necessitate both new material developments as well as novel deposition techniques. Concerning the former, various Group III oxides are currently being explored, from Al_2O_3 to its heavier congeners Ln_2O_3 (lanthanide^{3+} ions). For the latter one promising growth method is atomic layer deposition (ALD) whose layer-by-layer, self-terminating mechanisms ideally offer exquisite control over thin film thickness, interfaces, stoichiometry, and surface roughness to mention only a few possible advantages [6,7].

ALD (and chemical vapor deposition, CVD) may also benefit from new chemical precursor design. Although the desired properties of ALD precursors remain debatable [7], each source must be volatile and show appropriate reactivity at the growth surface. Furthermore, liquid or gaseous sources offer certain industrial and academic advantages. For example, liquids often exhibit weaker intermolecular forces than solids, suggesting higher volatility, and always provide constant surface areas minimizing changes in vapor flux over time and are easier to handle and transfer. Although numerous alumina source molecules have been evaluated, $Al_2(CH_3)_6$ (and select hydrides) is the most common starting material [3–5,8,9]. However, as a hypergolic gas it is not without drawbacks — most important industrially are its dangerous, explosive properties. Thus, novel aluminum sources of similar volatility, decreased ambient atmosphere reactivity, and applicability to ALD or CVD are desirable.

To assess potential alternatives to trimethylaluminum (TMA) we began investigating homoleptic Al^{3+} aminos as ALD precursors [10–12]. Previously, this general class of molecules received only modest attention from the thin film community, mostly for the growth of nitrides (or oxides) from solid, crystalline sources [13,14]. This led us to the development of

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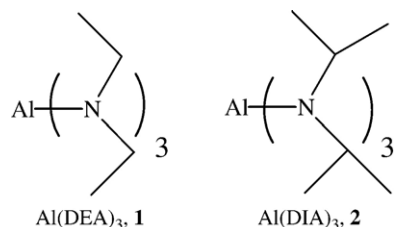
Fig. 1. Structures of tris(diethylamino)aluminum and tris(diisopropyl) aluminum.

ultrapure tris(diethylamino)aluminum (Al(DEA)$_3$, **1**), a liquid, and solid tris(diisopropylamino)aluminum (Al(DIA)$_3$, **2**) and tris (bis(trimethylsilyl)amino)aluminum (Al(TMSA)$_3$) (Fig. 1). These materials were hypothesized to show appropriate reactivity for ALD and oxide growth and 1.) their steric bulk should trigger the self-terminating paths and 2.) thermodynamics favor formation of an Al–O bond over the Al–N bond [15]. In addition, **1** and **2** show appreciable volatility (*vide infra*) – comparable to that of Al$_2$(CH$_3$)$_6$ – and were successfully implemented in the growth of amorphous alumina using H$_2$O as a coreactant.

2. Experimental

All manipulations were carried out using standard Schlenk techniques. Lithium aluminum hydride (95%, LiAlH$_4$), aluminum chloride (99.99%, AlCl$_3$), diethylamine (redistilled, 99.5%), and diisopropylamine (redistilled, 99.95%) were purchased from Aldrich and used as received. AlH$_3$·N(CH$_3$)$_3$ was purchased from Gelest and used as received. Benzene and tetrahydrofuran (THF) were dried and distilled from sodium prior to use. Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN, USA) and ^{1}H NMR was recorded at 400 MHz. The ALD chamber has been previously described [16].

2.1. Synthesis of tris(diethylamino)aluminum (Al(DEA)$_3$, **1**)

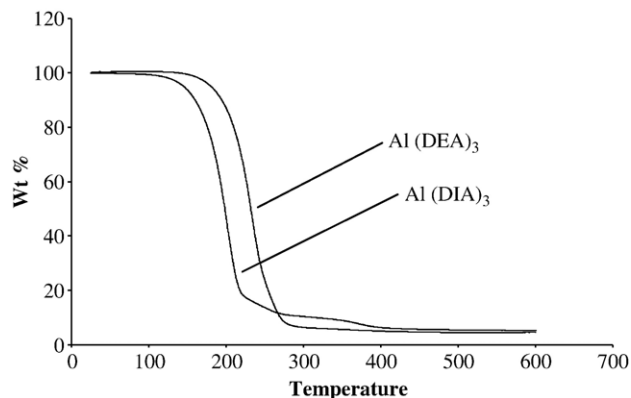A 250 mL, 2-neck, round bottom flask charged with a stir bar and LiAlH$_4$ (2.0 g, 0.053 mol) was sealed with a reflux
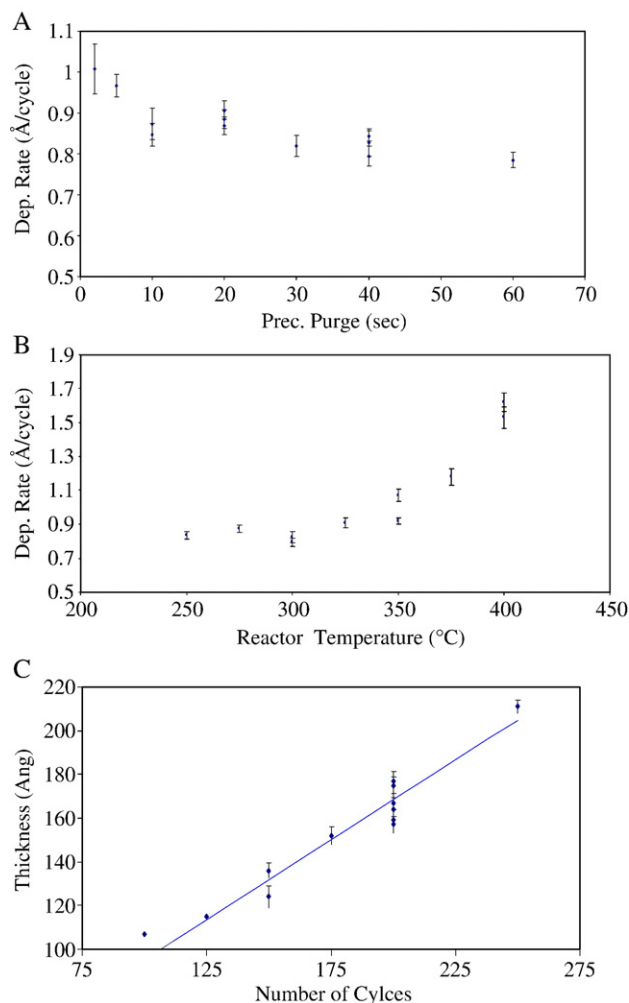

Fig. 3. ALD growth parameters for Al(DIA)$_3$. Precursor purge time (A), substrate temperature (B), and growth rate *versus* the number of cycles with linear fit (C).

condenser and a 100 mL addition funnel. Sequentially, the vessel was removed from the glove box, interfaced to a N$_2$-containing Schlenk line and 60 mL of THF was introduced *via* syringe. Diethylamine (22 mL, 0.21 mol) was then added dropwise (1 drop/s) while stirring at ambient temperature.

Fig. 2. Thermogravimetric analysis of Al(DEA)$_3$ and Al(DIA)$_3$ at atmospheric pressure and 50 cc/min He purge gas at a 10 °C/min heating rate.
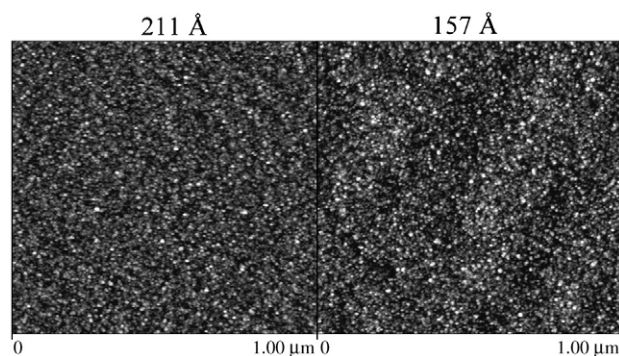

Fig. 4. Atomic force micrographs of two Al$_2$O$_3$ films of 211 Å and 157 Å thicknesses both having RMS roughnesses of 5 Å.

Following complete evolution of H₂ (∼30 min), AlCl₃ (2.4 g, 0.018 mol) in 26 mL of THF was added dropwise (2 drops/s) and the mixture heated at reflux for 1 h. Upon cooling to room temperature, the THF was removed *via* azeotrope distillation with benzene (125 mL) and the mixture concentrated to ∼50 mL. The reaction was filtered through a fine porosity fritted funnel and dried *in vacuo* (25 °C, 0.15 Torr) resulting in an orange oil. Pure Al(DEA)₃ was isolated as a colorless oil *via* vacuum distillation (150 °C, 10^{-4} Torr). Yield 60% (7.7 g); ^{1}H NMR (δ, C₆D₆) 1.15 (m, 3H); 1.38 (m, 3H), 3.1 (m, 2H), 3.35 (m, 2H); Elem. Anal. Found: C 59.52, H 12.18; Calcd. C 59.22, H 12.42.

2.2. Synthesis of tris(diisopropylamino)aluminum (Al(DIA)₃, **2**)

63 mL (8.8 eq, 0.45 mol) of diisopropylamine was slowly added (2 drops/s) to a cooled (liquid N₂) 250 mL flask containing 4.5 g AlH₃·N(CH₃)₃ (0.051 mol). H₂ evolution was immediately apparent. After amine addition the flask warmed to ambient temperature (2 h) and subsequently heated at reflux overnight. Excess amine was removed *in vacuo* and the crude product sublimed at 85 °C and 10^{-4} Torr to yield colorless crystals (6.9 g, 42%). ^{1}H NMR (δ, C₆D₆) 1.3 (d, 6H), 3.4 (sept., 1H); Elem. Anal. Found: C 65.84, H 12.82; Calcd. C 66.01, H 12.92.

3. Results and discussion

The synthetic methods utilized to arrive at these novel alumina precursors have one commonality — *to minimize halide content and cost* [10–12]. The preparation of Al(DEA)₃ uses inexpensive LiAlH₄ as the aluminum source whereas Al(DIA)₃ employs the alane, AlH₃·NMe₃. The purpose of these routes was to ultimately reduce contamination and charge carriers in the derived dielectric layer [1]. From the atmospheric pressure thermogravimetric analysis (TGA, Fig. 2) both precursors evaporate with onset temperatures of 200 °C and 150 °C for **1** and **2**, respectively. Although counterintuitive since **1** is a liquid, it is believed to exist as a dimer in this phase but evaporates as the monomer requiring more energy to break its dimeric structure [10,15,17]. This is unlike **2** which exists as a monomer, in both the solid and vapor phase [12]. The TGA data also supports nearly complete evaporation with little residue at ambient pressure and a 50 cc N₂ flow. Al(DEA)₃ leaves less than 4% residue while under identical conditions Al(DIA)₃ has an initially higher residual of ∼10%. This suggests that **2** is more susceptible to atmospheric contamination rather than decomposition, since the percentage varied amongst runs and approaches zero at reduced pressures.

To evaluate the vapor pressure of these new precursors *versus* the industry standard trimethylaluminum (Al₂(CH₃)₆) measurements were undertaken and fit to a modified Clausius–Clapeyron equation (supplemental information). From these data TMA is significantly more volatile than both Al(DEA)₃ and Al(DIA)₃, however Al(DIA)₃ is one to two orders of magnitude more volatile than Al(DEA)₃ in the high (>70 °C) and low temperature (<70 °C) regimes, respectively. At higher temperatures these values become less disparate but do not cross; thus **2** is always more volatile than **1**. Surprisingly both TMA and Al(DEA)₃ are liquids and dinuclear, making them structurally and chemically similar. From this observation we postulate that the greater vapor pressure of Al(DIA)₃ over Al(DEA)₃ is due to its mononuclear character. Although it is typical for liquids to exhibit weaker intermolecular forces, in this case it is a compromise between similar dispersive forces, molecular weight, and the energy required to break dimeric Al(DEA)₃.

All films were deposited on cleaned Si(100) coupons in a previously described hot-walled ALD reactor [16]. Initially films were grown to optimize suitable delivery conditions for the ALD growth regime using **2** at a constant precursor source temperature of 70 °C (where the vapor pressures of Al(DEA)₃ and Al(DEA)₃ become least disparate). This resulted in a usable parameter of 3, 2 s "plugs" of compound **2**. These "plugs" consist of the precursor vessel being slightly pressurized with carrier gas (N₂, 240 mTorr from 100 mTorr) and then the metal-organic being evacuated into the growth chamber at 100 mTorr. To verify precursor purge time and self limiting growth film, thickness was monitored as a function of seconds, and after 20 s found to be stable and linear (Fig. 3A).

Two additional contributing factors that were investigated were substrate temperature and oxidizer purge time. First it was found that growth became nonlinear beyond 325 °C at which point Al₂O₃ thickness per cycles increased, presumably due to decomposition at the silicon substrate (Fig. 3B). The second factor was oxidizer delivery, for **2** a 50 ms pulse (carrier gas passed through a water bubbler cooled in an ice bath) followed by a 30 s purge yielded optimal conditions and growth. These H₂O values are nearly identical to those found for **1** [16]. Using these conditions the thickness *versus* number of cycles was linear from 100 Å to 220 Å with an incubation period of 13 Å before growth stabilized at 0.73 Å/cycle (Fig. 3C). Granted these data points do not include thicknesses below 100 Å because reliable values in this regime are hard to obtain in our system.

The amorphous films were characterized by PXRD and AFM. All attempts to find diffraction peaks failed, even on thicker films, yielding us to conclude they are amorphous despite the complications associated with thinner films and diffraction. The AFM images (Fig. 4) of two thin films having thicknesses of 211 Å and 157 Å both have RMS identical roughnesses of 5 Å, over a 1 μm² area, at an abrupt atmospheric interface.

4. Summary

This letter presents the synthesis and characterization of two, non-pyrophoric alternatives for the industry standard TMA — Al(DEA)₃ and Al(DIA)₃. The compounds were designed to minimize halide content and were synthesized from aluminum hydrides instead of chlorides or heavier halides. The latter was used in the ALD growth of alumina on Si(100) whose conditions are explicitly given for a previously described hot-walled reactor. The derived films were amorphous by PXRD and have abrupt, uniform surfaces with RMS roughnesses of 5 Å.

Acknowledgments

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