

Volatile Amidoalane Compounds for Chemical Vapor Deposition of Aluminum

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Received May 7, 1998

Revised Manuscript Received July 20, 1998

Aluminum is one of the most important metals for interconnects in microelectronic devices. Chemical vapor deposition (CVD) of aluminum has been investigated for its capability of conformal step coverage and selective growth to overcome the limitations that conventional physical vapor deposition techniques encounter in processing ultralarge scale integration (ULSI) devices.

Triisobutylaluminum (TIBA) has received the most attention among alkyl aluminum compounds as CVD precursors because of its ability to deposit high-purity aluminum films.^{1–6} However, TIBA has a tendency to decompose to the less volatile diisobutylaluminum hydride in the gas phase⁷ and produces aluminum films of poor reflective properties.² Dimethylaluminum hydride (DMAH) has been reported to be a substantial improvement over TIBA or other alkyl aluminums,⁸ but a later study showed that the levels of carbon contamination in the Al_xGa_{1-x}As layers deposited from DMAH were identical to those obtained from trimethylaluminum.⁹

Donor–acceptor complexes of alane, such as trihydrido(trialkylamine)aluminum complexes, have been reported to be used for aluminum plating since late 1960s¹⁰ and have recently attracted much attention as precursors for aluminum CVD.¹¹ They are less air-sensitive than the trialkylaluminums. Since there are no aluminum–carbon bonds in these compounds, carbon incorporation in the deposited films is minimized. A major problem for these complexes, however, is their low thermal stability. Trimethylamine alane (TMAA) has been used as a precursor for CVD of aluminum and demonstrated high growth rates and low growth temperatures. Despite its high stability compared to other amine alane complexes, TMAA deposits Al films via

both surface and gas-phase reactions.¹¹ Another disadvantage of TMAA as a practical CVD precursor is that it is a solid with relatively high melting point. Dimethylethylamine alane (DMEAA) has been reported as a stable liquid precursor.¹² However, the thermal stability of DMEAA is not satisfactory for it to be a practical CVD precursor. It dissociates to produce free amine, alane, and aluminum during storage and vaporization processes. Aluminum particles have been observed in the gas phase during the CVD process using DMEAA.¹³

In the present work, we report H₂Al{N(Et)C₂H₄NMe₂} (1, DMEEDA) as a new stable liquid precursor for the CVD of aluminum. The bidentate ligand, N(Et)C₂H₄NMe₂, is coordinated to aluminum through its amine and amido ends intramolecularly to give rise to a coordinatively saturated aluminum complex, DMEEDA. As a result, it is less sensitive to water and oxygen than tertiary amine alanes. Due to its enhanced thermal stability, the gas-phase reactions can be minimized during the deposition process.

DMEEDA was synthesized by the reaction of lithium aluminumhydride with *N,N*-dimethyl-*N*-ethylethylenediamine hydrogen chloride in pentane solvent as shown in eq 1.¹⁴



DMEEDA was obtained as a volatile liquid with boiling point at 39–41 °C/0.3 Torr. The vaporization behavior at elevated temperatures was monitored up to 220 °C by gas-phase infrared spectroscopy using a Perkin-Elmer 1600 Series FT-IR spectrometer. The IR spectra showed no indication of free amine liberated during the heating process. This indicates that DMEEDA is thermally stable enough to maintain its molecular integrity in the gas phase at elevated temperatures. The IR spectrum of DMEEDA shows Al–H vibrations at 1771 and 1676 cm⁻¹. The compound is not pyrophoric and can be stored in a glass container at room temperature. The ¹H NMR spectra of both free *N,N*-dimethyl-*N*-ethylethylenediamine and DMEEDA were recorded in C₆D₆ on a Varian U400. The peaks of the ethyl group of DMEEDA appear at δ 1.15 (3H, triplet) and 2.99 (2H, quartet), respectively, while those of free amine appear at δ 1.01 (3H, triplet) and 2.30 (2H, quartet), respectively. The downfield shift of the ethyl group of DMEEDA, especially of the CH₂, indicates the coordination of the amine to the aluminum. That the broad N–H peak of free amine disappeared in the spectrum of DMEEDA supports the amido bond formation. The peaks of the methyl and ethylene groups of DMEEDA appear at δ 2.09 (6H, singlet), 2.90 (2H, triplet), and 2.43 (2H, triplet), respectively. The broad Al–H peak appears occasionally at around δ 3.1. The chemical shifts of the

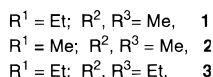
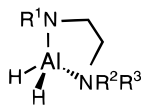
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above vary slightly, depending on the concentration of DMEEDA in benzene solvent.

We also synthesized $\text{H}_2\text{Al}\{\text{N}(\text{Me})\text{C}_2\text{H}_4\text{NMe}_2\}$ (**2**, TRMEDA) and $\text{H}_2\text{Al}\{\text{N}(\text{Et})\text{C}_2\text{H}_4\text{NEt}_2\}$ (**3**, TREEDA) by replacing *N,N*-dimethyl-*N*-ethylethylenediamine hydrogen chloride with *N,N,N*-triethylethylenediamine hydrogen chloride and *N,N,N*-triethylethylenediamine hydrogen chloride, respectively, in reaction 1. Both TRMEDA and TREEDA were obtained as thermally stable volatile solids with melting points of 70 and 70–75 °C, respectively. TRMEDA was purified by sublimation at 40–45 °C/0.08 Torr and TREEDA by vacuum distillation at 70–75 °C/0.3 Torr. Gas-phase IR spectra of these compounds at elevated temperatures showed no indication of free amine liberated as observed for DMEEDA.



CVD experiments were carried out using these amidoalane precursors in a glass reactor with a bubbler-type precursor vessel. No reducing agent such as H₂ was used for the film deposition experiments. The precursors were injected into the reactor with argon as a carrier gas at room temperature. Film depositions were conducted on Si and TiN sputtered on Si (TiN/Ti/BPSG/Si) substrates at temperatures of 80–300 °C. Si substrates were used as received without wet chemical cleaning process to avoid the Si–H formation on the surface. The entire CVD chamber was evacuated to a background pressure of 10^{−6} Torr and maintained at 0.1–10 Torr during the deposition reaction. However, the reaction pressure does not appear to be critical to the deposition of aluminum films since aluminum films were deposited at pressures lower than 10^{−4} Torr including ultrahigh vacuum conditions.¹⁵ A typical deposition rate was 400 Å/min at 120 °C.

All the three precursors, DMEEDA, TRMEDA, and TREEDA, produced pure aluminum films on the substrates used. Adhesion of films to the substrates was good. XPS as well as Auger spectra showed no impurities such as carbon or nitrogen in the deposited films. Figure 1 shows a cross-sectional SEM image of an aluminum film deposited using DMEEDA as a precursor on a patterned TiN substrate at 120 °C. The deposited film shows good step coverage on a via with a diameter of 0.35 μm and an aspect ratio of 3.5. The inset shows a top view of the via highlighting a remarkably smooth aluminum surface.

Interestingly, the Si substrates required higher temperatures for the deposition of aluminum films than TiN. The deposition behaviors on Si are rather complicated to interpret since the surface of Si is likely to have OH groups besides the native oxide. However, when the experiment was carried out using DMEEDA on thermally grown SiO₂ substrates, no deposition of

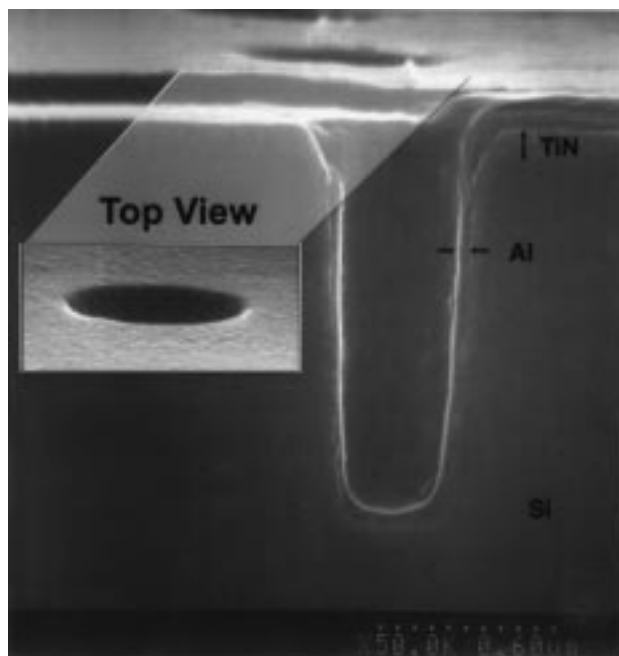


Figure 1. A cross-sectional SEM of an aluminum film deposited at 120 °C using DMEEDA as a precursor on a patterned TiN/Si wafer with vias with a diameter of 0.35 μm and aspect ratio of 3.5. The inset shows the smooth surface of the aluminum film.

Al was observed at temperatures as high as 250 °C, while deposition was observed on TiN even at 70 °C. This implies that the precursor could deposit Al selectively on electrically conductive surfaces versus dielectric surfaces without any loss of selectivity even at 250 °C. The high selectivity exhibited by DMEEDA is much superior to that of dimethylethylamine alane, which starts losing the selectivity at 140 °C and becomes unselective at 180 °C.¹⁶ Although further study is necessary to elucidate the mechanistic details of the decomposition of the precursor, it is not unreasonable to assume that the overall reaction would involve the reductive elimination of amine and hydrogen from the precursor molecule. Free electrons on the surface¹⁷ could play an important role for the reductive elimination processes. This may explain why the deposition of aluminum using the amidoalane precursors is favored on electrically conductive substrates. The remarkably low deposition temperatures exhibited by the present precursors support the surface catalysis process as well. The ability of these amidoalane complexes to deposit aluminum films at low temperatures is especially important for processing multi-metal-layer ICs to avoid thermally induced interdiffusion of layer materials at interfaces.

For an aluminum compound to be useful as a CVD precursor, it is essential that the coordinated ligand is bound to aluminum strongly enough so that the compound may be vaporized without thermal decomposition and yet weakly enough so that it may deposit aluminum at elevated temperatures. The amidoalane complexes in this study use diamine ligands, which contain both tertiary and secondary amine ends in the molecule, to

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form intramolecularly and coordinatively saturated alane complexes. The secondary amine end of the diamine reacts with aluminum trihydride to form an amido bond by eliminating a hydrogen molecule. The tertiary end forms a donor-acceptor bond and fills the fourth coordination site of the aluminum metal. As a result, the alane complexes exhibited high thermal stability. The fact that no decomposition of the complexes was observed by the gas-phase IR spectra at temperatures higher than 200 °C cannot be overlooked. The extremely high thermal stability of the amido alane complexes enables them to deposit aluminum by surface reactions only and to distinguish the metallic surfaces from the nonmetallic surfaces, which is important for the selective deposition of aluminum. DMEEDA selectively deposited Al on Si versus H-passivated Si surfaces at 200 °C under ultrahigh vacuum conditions.¹⁵ To the contrary, the presence of hydrides on HF-treated Si surfaces are reported to be critical to the deposition of Al from dimethylaluminum hydride.¹⁷ The remarkably

high selectivity observed for DMEEDA originates from its high thermal stability in conjunction with the catalytic effect of the electrically conductive substrates.

DMEEDA is a very attractive candidate for a practical precursor for the chemical vapor deposition of aluminum since it has the following advantages: (1) It is a volatile liquid at room temperature with high thermal stability. (2) It allows selective deposition of Al on electrically conducting surfaces with a wide process window. (3) It deposits high-purity Al at low deposition temperatures by surface reactions only. (4) The deposited Al films show extremely smooth surface morphology and good step coverage.

Acknowledgment. This research was supported by the Beckman Institute for Advanced Science and Technology. We would like to thank Dr. Sang-In Lee of Samsung Electronics Co., Ltd., for helpful discussions.

CM9803354