Chemical Vapor Deposition Precursor Chemistry. 5. The Photolytic Laser Deposition of Aluminum Thin Films By Chemical Vapor Deposition

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1. Introduction

A great deal of research has been devoted to the formation of both conformal and patterned solid state materials [1-2]. Much of this intense activity has been driven by the great importance of these materials to a wide variety of current technologically relevant applications. Particularly promising among these applications of aluminum containing thin films are their uses in the areas of microelectronics and metallized polymers. Since the bulk resistivity of pure aluminum (2.74 $\mu\Omega \text{cm}^{-1}$) is comparable to that of copper (1.70 $\mu\Omega \text{cm}^{-1}$) and silver (1.61 $\mu\Omega \text{cm}^{-1}$), it has become one of the most common metals employed in microelectronics device fabrication. Especially valuable are patterned aluminum-containing depositions on semiconductor substrates for use in high electron mobility transistors (HEMT), pseudomorphic and heterostructural devices, heterojunction bipolar transistors (HBT), ultra high-speed microelectronic devices, and optoelectronic devices [3]. In addition, the aluminum metallization of plastics and polymers has numerous applications including the creation of gas diffusion barriers on otherwise porous substrates, providing very high optical reflectance properties to thin films and allowing the fabrication of ultra lightweight devices.

Of particular interest in microelectronics fabrication has been the development of methods which would allow for the direct writing of metal thin films on substrates for circuit repair, rapid customization of integrated circuits and formation of suitable device interconnects [4-8]. Such applications typically require clean interfaces and very sharp feature profiles along with very high compositional purities and densities of the deposited material (void-free). Chemical vapor deposition processes, particularly photoassisted methods, appear to be among the most suitable for these critically demanding microelectronic data in the plot was caused by the electronic noise.
present during data measurement. The nonlinearity observed above 2 μm film thickness in the nitrogen laser growth data is consistent with preferential crystalline growth and increased surface roughness that is often observed in thick crystalline films deposited by other technique. The observed growth rates on the gold substrates were similar to those achieved in the pyrolysis of TMAA on copper surfaces [15]. While it is difficult to directly compare growth rates among the many literature reports due to uncertainties in the pressures of the precursor employed and the power density of the illumination during the deposition, it appears that the aluminum deposited in this work is consistent with previous growth rates on other substrates using TMAA [2, 13].

The formation of volatile species during the deposition of aluminum from TMAA was investigated by quadrupole mass spectrometry (QMS) of the reactant gas stream. Typical QMS plots for depositions involving the photolysis of TMAA using argon ion and pulsed nitrogen laser irradiations are shown in Figure 2. The highest intensity post-deposition mass fragments were observed at m/z 58, 43 and 42 amu. These fragments correspond to [NC₃H₈]+, [NC₂H₇]+ and [NC₂H₅]+, respectively, which arise from the dissociation and subsequent fragmentation of the trimethylamine ligand from the starting TMAA complex. These results indicate that both the visible and ultraviolet photolysis of TMAA proceeds through the initial loss of the trimethyl amine unit to generate alane in situ. The overwhelming dominance of the fragment at mass 58 from [NC₃H₈] instead of mass 59 for the free trimethylamine suggests that ligand loss is also accompanied by the facile liberation of hydrogen. Since atomic hydrogen production is very unlikely, the resulting gas-phase aluminum species may actually be a subhydride of alane (AlHₓ where x < 3) in order to allow H₂ production to occur. These observations are fully consistent with the decomposition pathways proposed previously for TMAA by both pyrolytic and photolytic pathways as summarized in Scheme 1.

The mechanism reported previously for the pyrolytic deposition of aluminum from the bis(trimethylamine) alane adduct, AlH₃·(NMe₃)₂, proposed that the initial steps

\[
\text{AlH}_3(N\text{Me}_3)_2 \rightarrow \text{AlH}_3(N\text{Me}_3) + N\text{Me}_3
\]

\[
\text{AlH}_3(N\text{Me}_3) \rightarrow \text{AlH}_3 + N\text{Me}_3
\]

\[
\text{AlH}_3 + 2\text{Al}_{(l)} \rightarrow 3\text{AlH}_{(l)}
\]

\[
\text{AlH}_{(l)} \rightarrow \text{Al} + \frac{1}{2}\text{H}_2
\]

Scheme 1. Decomposition processes in TMAA.

Figure 1. Plot of the thickness of the deposited aluminum thin films from trimethylamine alane (TMAA) on gold substrates as a function of irradiation time; (A) 514 nm argon ion laser, and (B) 337 nm pulsed nitrogen laser.

Figure 2. Quadrupole mass spectral plots of the post-deposition reactant stream following the irradiation of condensed trimethylamine alane (-196°C) on gold substrates. (A) 514 nm argon ion laser, and (B) 337 nm pulsed nitrogen laser irradiation.
involve the dissociation of the two trimethylamino groups from the alane [13, 29]. These studies also indicated that the dissociation of trimethylamine ligands from AlH$_3$·(NMe$_3$)$_2$ precedes hydrogen loss [30]. After the thermal ligand dissociation steps, the alane is proposed to adsorb onto the aluminum surface to produce AlH$_{16}$ species. The final step is the loss of hydrogen from the aluminum growth surface. Thermal hydrogen desorption studies from aluminum surfaces have shown that H$_2$ desorbs around 60°C [29, 31]. Pyrolytic thin film formation was not observed, however, from AlH$_3$·(NMe$_3$)$_2$ until 100°C and no film formation was observed at room temperature [13]. It was therefore impossible to decide unambiguously between the initial ligand dissociation step or the final hydrogen desorption step as the rate limiting step of the process. The photolytic mechanism, as supported by the QMS and quantum chemical calculations (vide infra) studies reported here, is believed to occur by a very similar mechanism to the pyrolytic process. The m/z 1 amu peaks observed in Figure 2 result from desorbed hydrogen and from a known QMS artifact.

The aluminum-nitrogen bond in trimethylamine is rather weak and the dissociation energy of trimethylamine from TMAA has been estimated to be approximately 26 kcal mol$^{-1}$ in the gas phase [21]. Semi-empirical quantum chemical calculations, such as those using the modified neglect of differential overlap (MNDO) method, have been shown to provide valuable insights into the selection and reaction chemistry of potential CVD precursor molecules [27, 32]. Recently, MNDO calculations for a variety of Al(CH$_3$)$_{3n}$H$_{1-n}$ compounds (where n = 0 to 3) have been used to rationalize the selection of an aluminum source gas for selective aluminum CVD [32]. In our work, MNDO calculations of TMAA provided further support that photolysis of this precursor should result principally in ligand dissociation processes. The LUMO orbital for TMAA, shown in Figures 3 and 4, is primarily an aluminum-nitrogen antibonding interaction while the HOMO orbital, shown in Figure 3, is a degenerate set of primarily aluminum-hydrogen bonding interactions.

In the photolysis experiments involving the lower energy laser light (514 nm argon ion laser), significantly less hydrogen loss from the photo-generated free trimethylamine ligand was observed. QMS peaks at 59 [N(CH$_3$)$_3$] and 43 [N(CH$_3$)(CH$_2$)] m/z were found in the argon ion laser irradiation experiments which were not observed in the nitrogen laser photolysis reactions. This result was anticipated since the argon ion laser photon energy is much closer to the trimethylamine dissociation threshold energy of 26 kcal mol$^{-1}$ than the much higher energy pulsed nitrogen laser. In addition, the QMS observed for the argon ion laser irradiation experiments showed a peak for the parent alane, AlH$_3$, at 30 m/z which was not observed in the nitrogen laser irradiation experi-

![HOMO (-10.33 eV)](image1)

![LUMO (+1.05 eV)](image2)

Figure 3. MNDO contour plots for the HOMO and LUMO orbitals calculated for a minimized energy geometry for trimethylamine alane (TMAA) (the orientation of the molecule is shown in the small stick diagram).
ments. The peak for alane is presumably not observed in the higher energy irradiation because of facile hydrogen loss from the alane in the photolysis step in addition to hydrogen loss from the triethylamine ligand. These observations are also consistent with the larger amount of hydrogen observed in the QMS from the nitrogen laser irradiation. The effect of the lower photon energy photolysis can also be seen in the growth rate data since the higher energy irradiation gave higher growth rates and cleaner rate profiles.

X-ray emission spectroscopic (XES) data were measured for the aluminum films prepared from TMAA on a variety of substrates. All the spectra clearly showed the intense signals from aluminum at 1.487 keV ($K_{\alpha 1}$) and those signals which arose from the substrate [Teflon (PTFE), GaAs (110), and Si (111)] or from slight surface contamination from atmospheric exposure or from the SEM. Typical XES plots for the deposited aluminum films are shown in Figure 5. Silicon $K_{\alpha}$ X-rays (1.740 keV) are a common artifact of the particular XES/SEM system employed in this work.

An aluminum film deposited on Teflon (PTFE) from TMAA was analyzed using Laser Microprobe Mass Analysis (LAMMA). Besides a small amount of surface contamination from atmospheric exposure, only aluminum was detected in the bulk sample. The microstructures of the aluminum films were investigated by using scanning electron microscopy (SEM).
Typical micrographs of the aluminum thin films photolytically deposited from TMAA are shown in Figure 6. Films deposited on semiconductor substrates, such as Si (111) and GaAs (110), showed preferential growth and faceting corresponding to the formation of aluminum crystallites. The grain sizes in these films were relatively uniform with an average size of 0.5 \( \mu \). This value compares with the average crystallite size of 0.15 \( \mu \) for the CVD aluminum films previously reported by Gladfelter [13]. The polycrystalline nature of these mirror-like films is evident from Figure 6. Similar aluminum crystallites have been observed in previous photolytic depositions by Baum et al. from TMAA on SiO\(_2\) substrates [13]. Aluminum films deposited from TMAA on metallic substrates, however, did not show any observable crystallite formation. One possible explanation is that the initial nucleation sites may form more rapidly on the semiconductor substrates leading to crystallite formation. No evidence

Figure 6. Scanning electron micrograph (SEM) of an aluminum thin film photolytically deposited using an argon ion laser (514 nm) from TMAA on (A) GaAs (110) and (B) Si (111). The bar in the lower right corner indicates scale.
was found in the SEM for any laser induced damage of the substrate surface. In addition, pre-deposition surface defects in the Si (111) substrates were not observed to anneal in the post-deposition micrographs. Thus it appears that, under the deposition conditions employed here, very little surface heating occurs and what little heating does occur is limited to small local environments.

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