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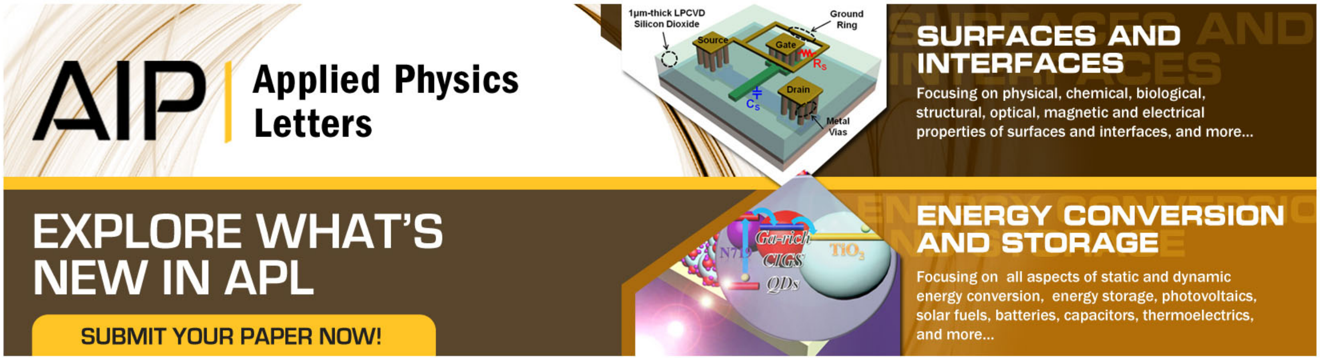

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Microstructure and deposition rate of aluminum thin films from chemical vapor deposition with dimethylethylamine alane

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Deposition of aluminum film from DMEAA in the temperature range of 100–300 °C has been studied. In this temperature range, there is a maximum deposition rate at around 150 °C. The film deposited at 190 °C has elongated blocklike grain shapes, which are ~600 nm in width and 930 nm in length. Grains in the film deposited at 150 °C showed an equiaxed structure with grain size in the range of 100–300 nm in a film with 600 nm thickness. Aluminum oxide particle inclusion was observed especially at high deposition temperature. Plausible reaction pathways of DMEAA dissociation were suggested to explain the experimental observations. © *1996 American Institute of Physics.* [S0003-6951(96)03825-9]

Aluminum has been widely used as a conducting material in the fabrication of integrated circuits. So far, most commercial Al films have been deposited by physical vapor deposition, but chemical vapor deposition usually gives more conformal coverage of a surface and allows a reactor design for multiwafer processing to give high throughput. For this reason, Al chemical vapor deposition (CVD) has been actively investigated for ULSI applications like 256 Mbit or 1 Gbit DRAM fabrication.

Previous works related to Al CVD precursors and reaction mechanisms have been reviewed comprehensively by Simmonds and Gladfelter.[1] For the deposition of aluminum, alkyl aluminum and amine-alane adducts have been used extensively. DMEAA, an adduct of alane (AlH_3) and dimethylethylamine [$N(CH_3)_2C_2H_5$], is the most recently introduced member of the amine family of precursors. Its relatively high vapor pressure at room temperature (1.5 Torr), its long shelf life, its ability to deposit carbon contamination-free films, combined with the advantages of being a liquid have recently made it the precursor of attention. The deposition behavior and chemistry of DMEAA,[2] have been studied including selective deposition[3,4] but study of the microstructure of Al films and data related to the deposition rate and chemical reaction kinetics is still lacking.

In this letter, experimental results, mainly the deposition rate and microstructure of the film as a function of deposition temperature, obtained from chemical vapor deposition of aluminum with DMEAA are described.

CVD of aluminum was carried out in a homemade, low pressure, cold wall, single wafer reactor. DMEAA was introduced directly without a carrier gas through vapor phase mass flow controller, MKS mass-flo type 1150. DMEAA with a rate of 0.01 ml/min in liquid volume was introduced from above through a cylindrical showerhead-type distributor and flowed down vertically toward the wafer surface. The gap distance between the showerhead and the susceptor was 3 cm. Al film was deposited on various substrate surfaces such as TiN, Al, Si, and SiO_2 with deposition temperature between 100 and 300 °C and pressure at 0.2 mbar. The base pressure before the deposition was 1.5×10^{-6} mbar. A substrate surface of TiN and Al was sputter deposited on a silicon wafer and the SiO_2 surface was obtained by thermal oxidation of a silicon wafer.

Figure 1 shows the amount of Al deposited on various substrate surfaces as a function of deposition time at a deposition temperature of 200 °C. The induction time, during which no appreciable deposition had been observed, was quite long on Si and SiO_2 surfaces. In that case, discontinuous film was formed and adhesion was very poor. On the TiN and Al surface, induction time was negligible and adhesion was good. From this observation, we could conclude that selective deposition is possible on TiN or Al over the Si or SiO_2 surface. As the deposition temperature goes up, the induction time becomes shorter and it becomes more difficult to achieve selective deposition. As the surface is covered with Al, the slope, i.e., the deposition rate, should be the same regardless of the substrate surface, but it seems that depending on the nucleation behavior at the initial stage, the deposition rate is slightly different.

Figure 2 shows the deposition rate of Al film on the TiN surface as a function of deposition temperature. The deposition rate increased to a maximum at around 150 °C and then

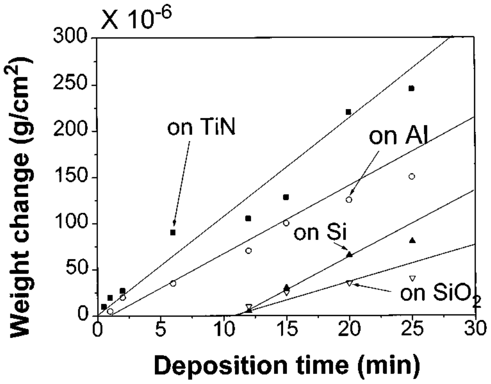

FIG. 1. Amount of Al deposited on various substrate surfaces as a function of deposition time at a deposition temperature of 200 °C and a pressure of 0.2 mbar.

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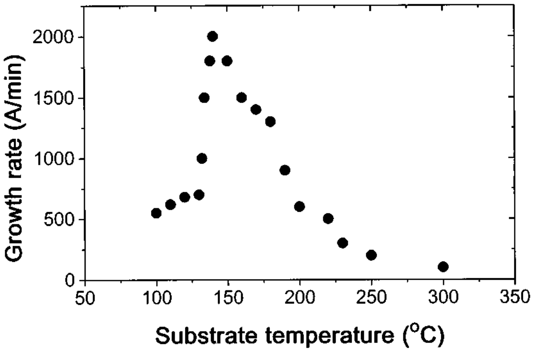

FIG. 2. Deposition rate of Al film on TiN surface as a function of deposition temperature.

decreased with the substrate temperature above 150 °C. It appears that DMEAA is very sensitive to the reaction temperature in this temperature range and gas phase reaction might become dominant when the deposition temperature is higher than 150 °C. It was reported that the mechanism in the deposition of Al from TMAA involved the adsorption of amine-alane adducts, dissociation of amine, and alane on the surface, dissociation of alane, deposition of Al, and desorption of hydrogen molecule.[5] The deposition of Al from DMEAA can be written as

$$[(CH_3)_2C_2H_5N]AlH_3(g) \rightarrow [(CH_3)_2C_2H_5N]AlH_3(ads), \quad (1)$$

$$[(CH_3)_2C_2H_5N]AlH_3(ads) \rightarrow AlH_3(ads) + (CH_3)_2C_2H_5N(ads), \quad (2)$$

$$AlH_3(ads) \rightarrow Al(ads) + 3H(ads), \quad (3)$$

$$3H(ads) \rightarrow 1.5H_2(g), \quad (4)$$

$$[(CH_3)_2C_2H_5N](s) \rightarrow [(CH_3)_2C_2H_5N](g), \quad (5)$$

as suggested by Han *et al.*[6]

For TMMA, the deposition rate was indicated to be controlled by reaction (2), the dissociation of amine–alane adducts on the surface,[5] whereas hydrogen desorption was proposed to be the rate limiting step for TEAA.[7] Han *et al.* suggested that DMEAA was likely to follow a behavior between those of TMAA and TEAA.[6]

We believe that, at substrate temperatures lower than 150 °C, adsorption of the precursor and surface chemical reactions were mainly involved in the deposition of aluminum and the deposition rate increased with increasing deposition temperature. We also believe that the amine–alane adduct can be dissociated in the gas phase as follows when the temperature is high enough. This may be the case when the substrate temperature is higher than 150 °C:

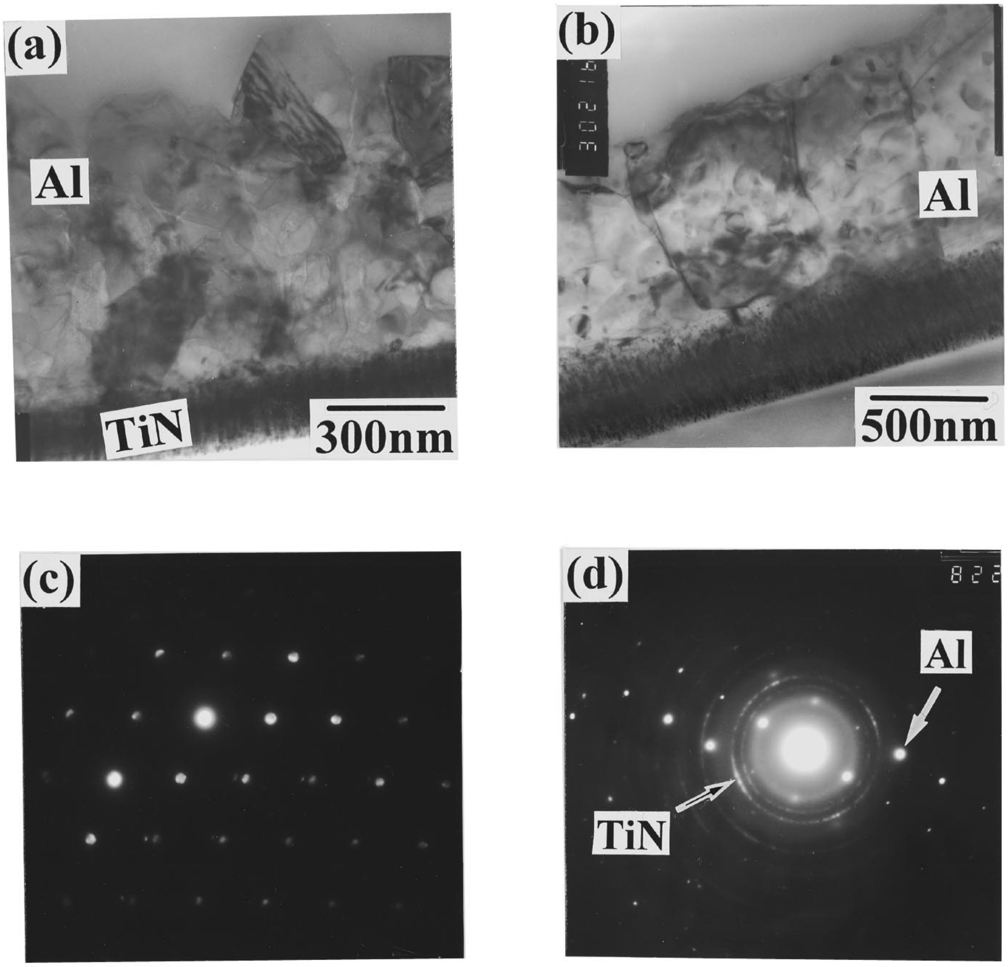

FIG. 3. Cross sectional TEM micrographs of the films deposited (a) at 150 °C and (b) at 190 °C. Selected area diffraction pattern of (c) Al grain and (d) Al/TiN interface in the film deposited at 150 °C.

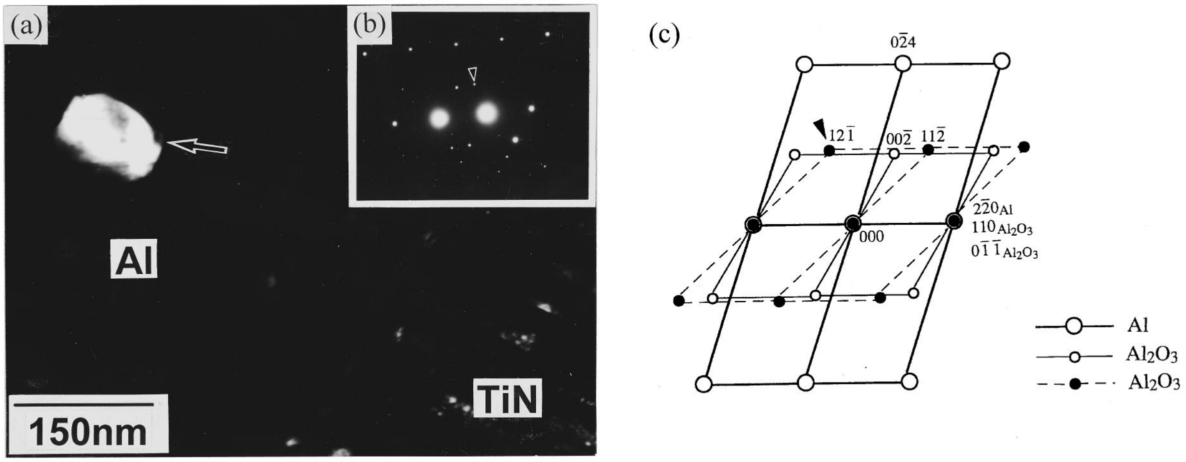

FIG. 4. (a) Aluminum oxide particle imbedded in the aluminum grain in the film deposited at 190 °C, (b) diffraction pattern, and (c) computer simulated pattern for the aluminum oxide particles. The dark field TEM image was taken from the spot indicated by the arrow.

$$[(CH_3)_2C_2H_5N]AlH_3(g) \rightarrow AlH_3(g) + (CH_3)_2C_2H_5N(g). \qquad (6)$$

It has been reported that powders were formed in the gas phase from DMEAA when the temperature is higher than 170 °C.[2,8] Alane is known to be unstable and forms a dimer, trimer, and even a polymer.[9] In a cold wall reactor used in this experiment, the temperature gradient exists between the hot substrate and the cold reactor wall and the gas phase can be heated by a hot substrate. When the substrate temperature is higher than 150 °C, the gas phase temperature is high enough so that part of DMEAA is presumably dissociated in the gas phase, as given in reaction (6), to form alane. Alane can be readily polymerized which, we believe, is not readily adsorbed on the surface to form aluminum film. The deposition rate above 250 °C is very low because gas phase reaction becomes very active. More study is needed to clarify this reaction pathway.

Another possibility is homogeneous nucleation through which powders are formed and precursors are consumed in the gas phase. Alane formed in the gas phase by reaction (6) may nucleate into a powder. In general, the deposition rate is decreased when there is powder formation and in this case, powders can be collected on the reactor wall after the deposition but we did not detect an appreciable amount of powders in our experiment.

The films deposited on TiN were polycrystalline with no detectable impurities as measured by AES. Figures 3(a) and 3(b) shows the cross sectional TEM micrographs of the films deposited at 150 and 190 °C. The film deposited at 190 °C shows that grains have elongated blocklike shapes, which are ~600 nm in width and 930 nm in height. It was also found that some grains formed at the nucleation stage at the interface were smaller. On the other hand, grains in the film deposited at 150 °C showed an equiaxed structure with grain size in the range of 100–300 nm in a film with 600 nm thickness. The grains formed at 150 °C were smaller and it may be due to the fact that the deposition rate is faster at 150 °C or the bulk diffusion is not fast enough for the grains to grow at this temperature. The preferred orientation of Al was confirmed to be ⟨111⟩ in the growth direction of the film and this may be due to the ⟨111⟩ preferential orientation of TiN (Ref. 10) on the silicon substrate as shown in Figs. 3(c) and 3(d).

We could also detect small particle inclusions imbedded in the aluminum grain in the film deposited at 190 °C and it was confirmed to be the aluminum oxide particle from the selective area diffraction pattern as shown in Fig. 4. We could not detect particle inclusions in the film deposited at 150 °C. These particles are not likely to be formed by the precipitation in the solid phase but more likely to be formed in the gas phase and incorporated into the film. It was pointed out that impurities such as H_2O, O_2, or CO caused an increase in the number of particles formed in the gas phase.[6] We believe that at higher temperatures above 150 °C, it is more likely that residual impurity gases react to form particles. Also, alane formed by the gas phase dissociation of the adduct is more likely to react with impurity. For example, with oxygen, alane can react as

$$2AlH_3 + 3/2O_2 \rightarrow Al_2O_3 + 3H_2. \qquad (7)$$

The oxide particle formation at high deposition temperatures is not believed to cause the decrease in the deposition rate, because the oxide powder formation is not intensive.

This research was supported by LG Semicon. Co., and the support of the Engineering Research Center for Interface Science and Technology of Materials is also acknowledged.

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