Characteristics of Aluminum Films Prepared by Metalorganic Chemical Vapor Deposition Using Dimethylethylamine Alane on the Plasma-Pretreated TiN Surfaces

Do-Heyoung Kim† and Byung-Yup Kim*††

Faculty of Applied Chemical Engineering and Research Institute for Catalysis, College of Engineering,
Chonnam National University, 300 Yongbong-dong, Buk-Ku, Kwang-Ju 500-757, Korea
*Central Research Laboratory, Hyundai Microelectronics Co., Ltd.,
50 HayangJeong-Dong, CheongJu-Si 360-480, Korea

Abstract—Aluminum films were prepared on H_2-plasma pretreated TiN substrates at deposition temperatures of 60-250 °C by metallorganic chemical vapor deposition using dimethylethylamine alane as a precursor. The films were highly pure and the growth rates were 3-50 nm/min, where the lowest deposition temperature was 60 °C. The resistivity was as low as 2.8 μΩcm. High substrate temperatures tended to favor a low resistivity and smooth surface morphology of the films, compared to films with a low temperature at a given thickness. Numerous empty pores appeared in the Al films deposited at a temperature below 150 °C when the film thickness exceeded 200 nm. The number of these pores tended to increase with decrease in temperature. However, in films deposited at temperatures above 200 °C, there were no pores and the large grains were interconnected to a high degree. Higher deposition temperatures yielded a greater preference of the (111) orientation of Al films.

Key words: Chemical Vapor Deposition (CVD), Aluminum, Dimethylethylamine Alane, Pretreatment, TiN

INTRODUCTION

As ultra large-scale integrated circuit (ULSI) devices are scaled down to a deep sub-quarter micron regime with increments of the device density, achieving adequate conformality is becoming extremely difficult by the currently used PVD techniques. During the past few years, chemical vapor deposition (CVD) aluminum has been widely investigated as an alternative to sputtering-aluminum because of its capability to achieve conformal films with various source chemicals, such as trimethylaluminum [Masu et al., 1990], triisobutylaluminum (TIBA) [Levy at al., 1984; Green and Gallagher, 1984; Lee et al., 1992; Amazawa, 1999; Jonnalagadda et al., 1999], dimethylaluminum hydride (DMAH) [Kondo and Ohta, 1995; Sugai et al., 1995, 1997; Naik et al., 1998], and amine-alane adducts such as trimethylamine alane [Gladfelter et al., 1989], triethylamine alane [Gross et al., 1991], dimethylethylamine alane [Simmonds et al., 1991, 1994; Kim et al., 1995; Yun et al., 1998; Jang et al., 1999]. However, CVD Al revealed the excessively rough topography of the film, regardless of the precursor used. This rough surface morphology is known to be caused by the slower nucleation of CVD Al compared with the subsequent film growth. To enhance the nucleation density and thus improve the surface morphology of Al films, it has been suggested to pretreat the substrate surface either physically or chemically before CVD Al [Cooke et al., 1982; Sugai et al, 1995; Jonnalagadda et al., 1999].

Although pretreatment was found to be effective at increasing Al nucleation, which resulted in a decrease in surface roughness of CVD Al films, there have been only few papers reporting the properties of Al films grown on pretreated substrate, and even these are lacking in detail [Sugai et al., 1995; Jang et al., 1999]. Therefore, in the present study, the properties of Al films grown on TiN that was pretreated by *in situ* hydrogen plasma were investigated by varying the deposition temperature.

EXPERIMENTAL

Al film growth was carried out at total pressure of 67 Pa using dimethylethylamine alane, $[(CH_3)_2C_2H_5N]AlH_3]$, (DMEAA) in a cold wall type, vertical reactor which was equipped with a load-lock system. Compared to other chemicals, the liquid DMEAA has been shown to deposit purer Al at low deposition temperatures of 100-270 °C [Simmonds et al., 1991; Kim et al., 1995; Yun et al., 1998]. The base pressure of the reactor was kept low at 1.32×10^6 Pa. Silicon wafers (200 mm) covered by sputtered TiN (50 nm, ~150 μΩcm) were used as substrates, which were heated with a resistance heater to temperatures of 60 to 250 °C. After loading the air-exposed TiN substrate into the reactor, *in situ* pretreatment was conducted using H_2-plasma for one minute at a treatment temperature of 120 °C, a power of 200 W, and a total pressure of 265 Pa before Al deposition.

DMEAA was bubbled in a stainless-canister at 30 °C and introduced into the reactor by a carrier gas, 350 sccm of He. The delivery line between the bubbler and inlet of the reactor, and the reactor wall were heated to 40 °C to prevent precursor condensation. Also, the temperature of the shower head in the reactor was strictly controlled at 45 °C to avoid the thermal decomposition of

†To whom correspondence should be addressed.
E-mail: kdhh@chonnam.chonnam.ac.kr
††Present Address: Jusung Engineering, Co., Ltd. 49 Neungpyeong-Ri, Opo-Myeun, KwangJu-Gun, Kyungggi-Do 464-890, Korea

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the precursor. Under these conditions, residues caused by condensation and decomposition on the interior reactor walls and the delivery lines were avoided.

Scanning electron microscopy (SEM) was used to study the surface morphology and also to measure the film thickness. Surface roughness was evaluated by measuring the relative reflectivity of the Al films based on a bare silicon wafer (100%) at a wave length of 405 nm and also by using atomic force microscopy (AFM). Resistivity and film purity were analyzed by using a four-point probe and Auger electron spectroscopy (AES), respectively.

RESULTS AND DISCUSSION

Since TiN is the most commonly used diffusion barrier in aluminum-based IC device fabrication, studies on the properties of CVD Al grown on the TiN are of great interest from various practical points of view.

The dependence of the film thickness on reaction time was first evaluated, and linear dependence of film thickness on time was observed which indicated that film growth rate was constant with respect to reaction time. Also, there was no differentiable incubation time in this work. To discern the controlling regime of the CVD reaction, the deposition rate of Al was examined as a function of the substrate temperature at the substrate temperatures of 60-250 °C. (Fig. 1). The other conditions for Fig. 1 were 30 °C bubbler temperature, 350 sccm of helium gas flow rate, and 67 Pa total pressure. The deposition time was 1 to 30 min and the thickness of the deposited aluminum was between 10 to 500 nm. Essentially all the films deposited were extremely pure regardless of the deposition temperature, and possible impurities in the bulk of the film were always below the detection limit of AES analysis, as shown in Fig. 2. The minimum deposition temperature for Al growth on the plasma-pretreated TiN was about 60 °C (under the conditions studied), which was 40 °C lower than the previously reported value of 100 °C, obtained from using the same precursor [Simmonds et al., 1994; Yun et al., 1998]. There seems to be a transition temperature in between 125-155 °C from surface reaction to gas-phase mass-transfer under the conditions investigated. Film growth rate increased linearly with increasing the deposition
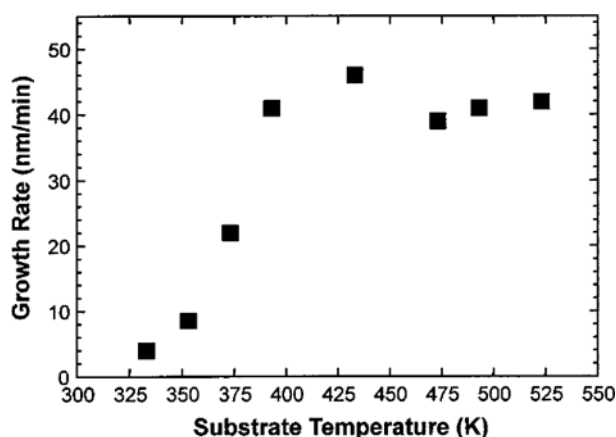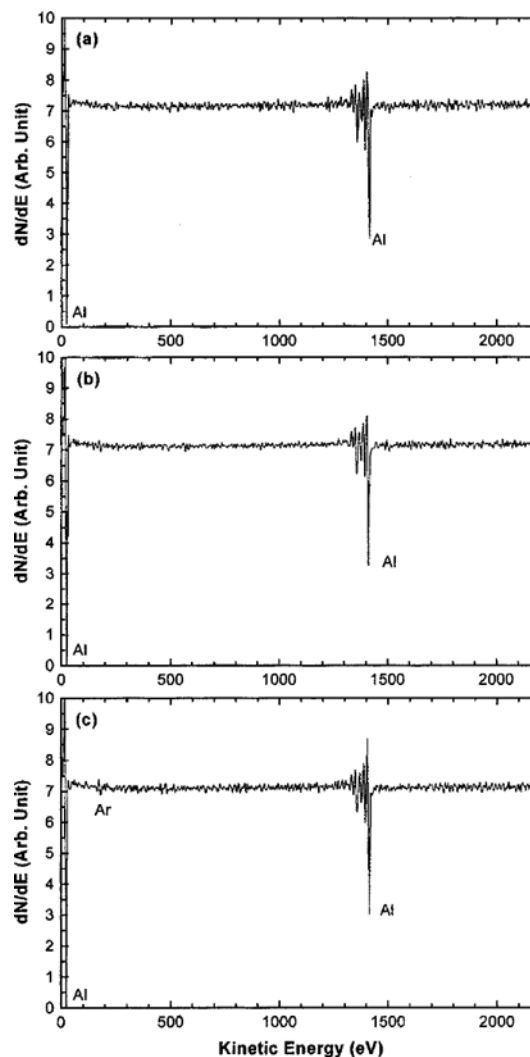

Fig. 2. AES electron spectrum of the Al films deposited at (a) 80 °C, (b) 160 °C, and (c) 250 °C (after 3 min sputtering).

temperatures of 60-120 °C, which reveals that the Al growth is controlled by the surface reaction. The activation energy for the film growth at this temperature range was estimated to be about 48 KJ/mol. The transition temperature and the value of the activation energy are similar to the results of Yun et al. (42 KJ/mol).

As the substrate temperatures were further increased above 150 °C, the growth rate leveled off, as shown in Fig. 1. This was contrary to the observations made by Kim et al. [1998] and Yun et al. [1995], who reported a rapid decline in the deposition rate as the substrate temperatures were increased above 150 °C. The decline of growth rate was explained by rapid dissociation of DMEAA in the gas phase. This difference is probably due to the different reactor systems. For example, our system has the capability to control the temperature of a shower-head in the reactor to suppress an excessive gas phase dissociation of DMEAA.

In order to study the morphological evolution of DMEAA-based CVD Al films, SEM analysis was conducted with Al films that were deposited at 120 °C, as shown in Fig. 3. The film thicknesses for Figs. 3a, b, c, and d were 10 (estimated by the deposition rate for a thick film), 40, 75, and 210 nm, respectively. It can be clearly

Fig. 1. Film growth rate dependence on substrate temperature at 67 Pa total pressure.
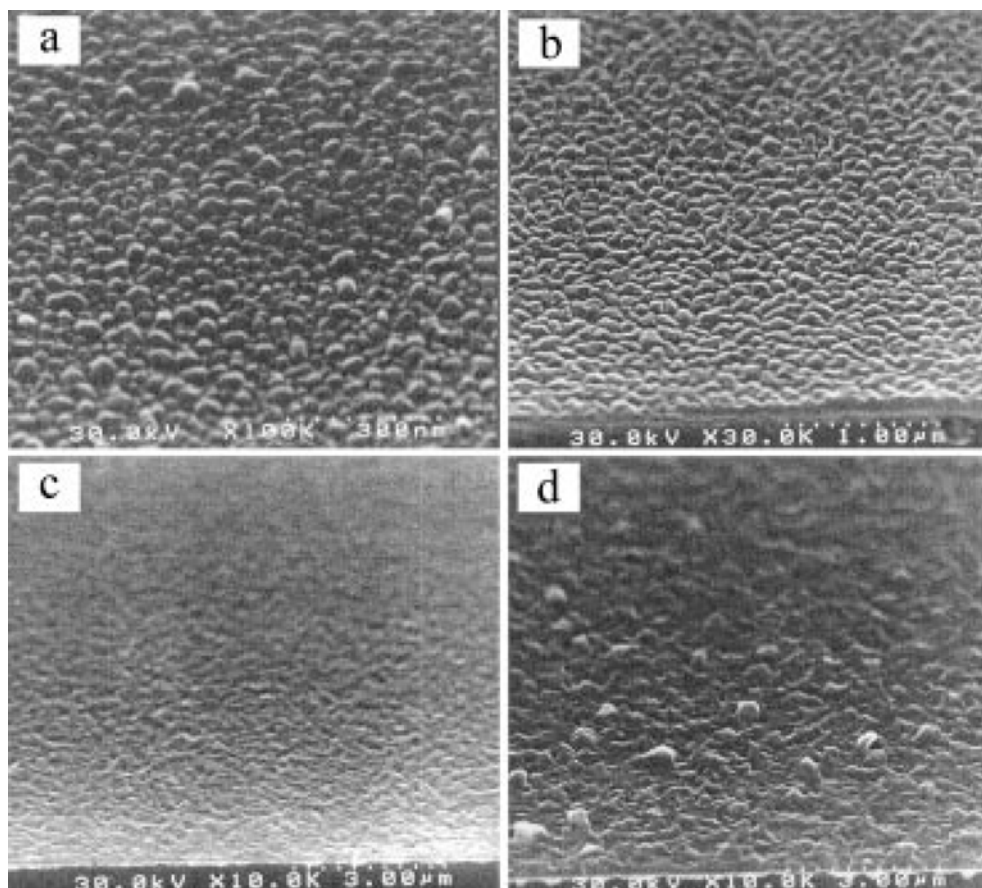
Fig. 3. Morphological evolution of the DMEAA-based Al film on the plasma pretreated TiN at 120 °C substrate temperature; (a) 10, (b) 40, (c) 75, and (d) 210 nm Al thickness.

seen that the growth of the CVD Al follows the Volmer-Weber three-dimensional mode on the TiN substrate. At the early stage of the Al film growth, reflectivity was low at 35%, due to the formation of discrete Al islands (Fig. 3a). As the coarsening of the separate Al grains progressed, reflectivity increased with increments of film thickness until the complete merging stage, i.e., continuous film formation. Reflectivities of the films of Figs. 3b and c were 88 and 140%, respectively. However, as the film thickness increased from 75 to 210 nm, reflectivity decreased to 31% due to grain growth; surface morphology revealed a grooved grain structure with many voids. The resistivity values of the samples in Figs. 3b, c, and d were 38.68, 4.60, and 3.47 $\mu\Omega$cm, respectively. As the films were highly pure, the main reason for the higher resistivity above bulk Al (2.67 $\mu\Omega$cm) would be the various structural defects in the deposited films, as appeared in Fig. 3.

Fig. 4 shows the root mean square (RMS) roughness of the films measured by AFM as a function of the Al film thickness. The values of peak to valley, $R_{(p-v)}$ and the surface grain size were summarized in Table 1. The RMS roughness, $R_{(p-v)}$, and grain size increased with increase in the film thickness. It should be noted that in the case where the film was 100 nm thick, the value of $R_{(p-v)}$ was more than four times the film thickness, but in cases where the film was 210 nm thick, the value of $R_{(p-v)}$ was close to the film thickness. This may suggest a relatively low nucleation rate of the Al on the TiN surface compared to the growth rate of the Al at the
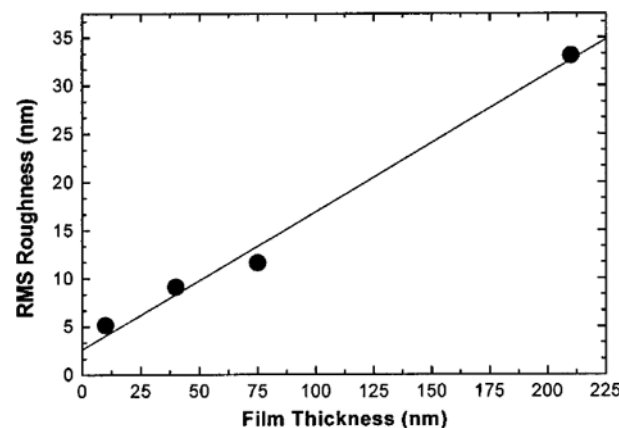
Fig. 4. Effect of film thickness on the RMS surface roughness for the Al films deposited at 120 °C.

Table 1. Dependence of peak to valley, $R_{(p-v)}$, and grain size on Al film thickness

Al thickness (nm)	$R_{(p-v)}$	Grain size (nm)
10	45.8	62.4
40	61.0	207.0
75	94.1	235.2
210	221.0	441.0

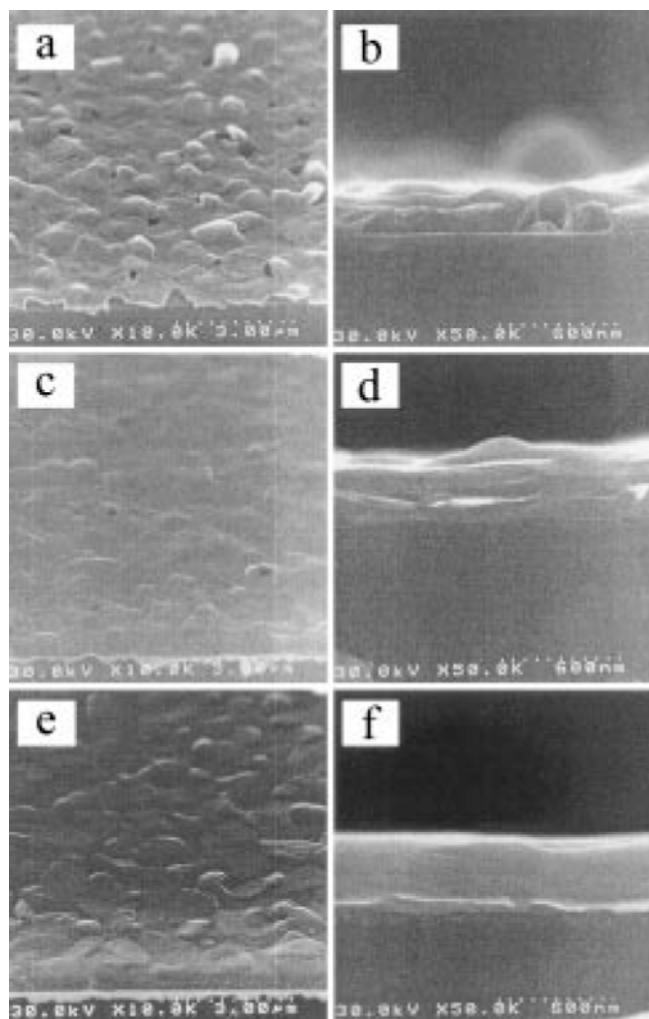Fig. 6. Resistivity of the Al films as a function of substrate temperature.

Fig. 5. SEM micrographs of the Al films deposited on the plasma pretreated TiN at (a and b) 100°C, (c and d) 160°C, and (e and f) 200°C.

early stage of film growth.

Fig. 5 shows an oblique view and cross-sectional views of the Al films deposited at substrate temperatures of 100, 160, and 200 °C. As observed in Fig. 5, the surface morphology of Al became smooth and faceted with increasing deposition temperature. It is interesting to note that many empty pores appeared in the Al films deposited at 100 °C. However, the number of empty pores greatly decreased as the deposition temperature was increased to around 160°C, and above 160°C the empty pores eventually disappeared.

Note also that there were no empty pores in the films deposited at the low temperature of 120 °C, in the case of thickness less than 80 nm, as shown in Fig. 3. Therefore, it may be inferred that such empty pores begin to form after the complete merging (i.e., continuous film) of the isolated Al crystal, due to intensive grain growth and agglomeration of the Al films relative to the growth rate of the Al. The low density of the Al nuclei and low surface mobility of the Al adatom on the TiN surface at temperatures below 160 °C, and also poor wetting between the Al films and the TiN surface could be considered as other possible reasons for this phenomenon, although there is no clear proof at present. The reflectivity of the Al films deposited at 200 °C and 100 °C was 92% and 31%,
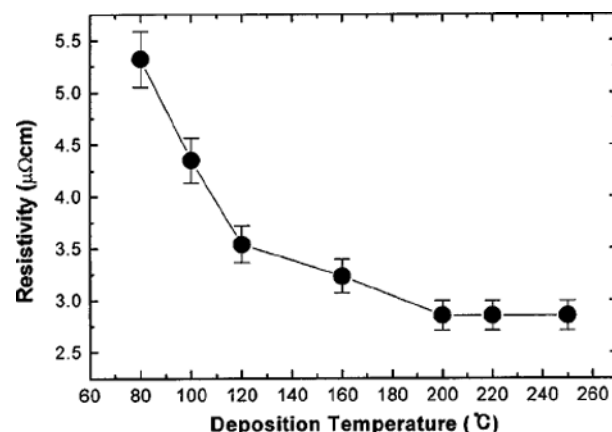
respectively. The deposition temperature also affects the grain size of the film. For films with the same thickness, the grain size of the film deposited at the higher temperature is larger. This might be attributed to the high degree of surface diffusion and grain growth at high temperatures.

Fig. 6 shows the resistivity of the Al films as a function of the substrate temperature. The value of the resistivity of the Al films that were 250-300 nm thick was in the range of 2.8 to 5.5 $\mu\Omega$cm. In particular, the resistivity of 2.8-2.9 $\mu\Omega$cm was routinely obtained for the films greater than 250 nm thick deposited at temperatures above 200 °C, due to the improved degree of interconnection between the Al grains at this high deposition temperature. This value is comparable to the bulk resistivity of Al (2.67 $\mu\Omega$cm) that suggests an extremely low defect density in the films deposited at a high temperature.

Microstructures such as texture, grain size, and grain size distribution are known to strongly influence the electromigration (EM) resistance [Murarka, 1992]; the median time to failure (MTF) increases in proportion to the cube of the intensity ratio of I(111)/I(200), where I is the corresponding x-ray diffraction peak. The crystal orientation of the Al films prepared at temperatures of 60-250 °C was examined by XRD. The deposited films were polycrystalline and showed a (111) preferential texture in all cases as shown in Fig. 7. This (111) preferred orientation could be explained by the minimization of the surface energy. Because (111) plane has the highest atomic packing density in face centered cubic (fcc) metals (such as Al, Cu and Pt) and the lowest surface energy, the atoms of the Al islands prefer to arrange themselves in the (111) orientation, in order to reduce the surface energy during the early stages of film growth when the separate Al grains are coarsened. As is common in the film growth process, subsequent film growth continues to replicate the initial texture of the growing film.

Fig. 8 shows the intensity ratio of (111)/(200) of XRD peaks as a function of deposition temperature. The appearance of the strongly preferred structure (111) at the higher temperatures may be attributed to the higher surface mobility of the adatoms at higher deposition temperatures in trying to establish an orientation with a low interface energy with respect to the substrate. However, contrary to the result of this work, opposite trends of the intensity ratio
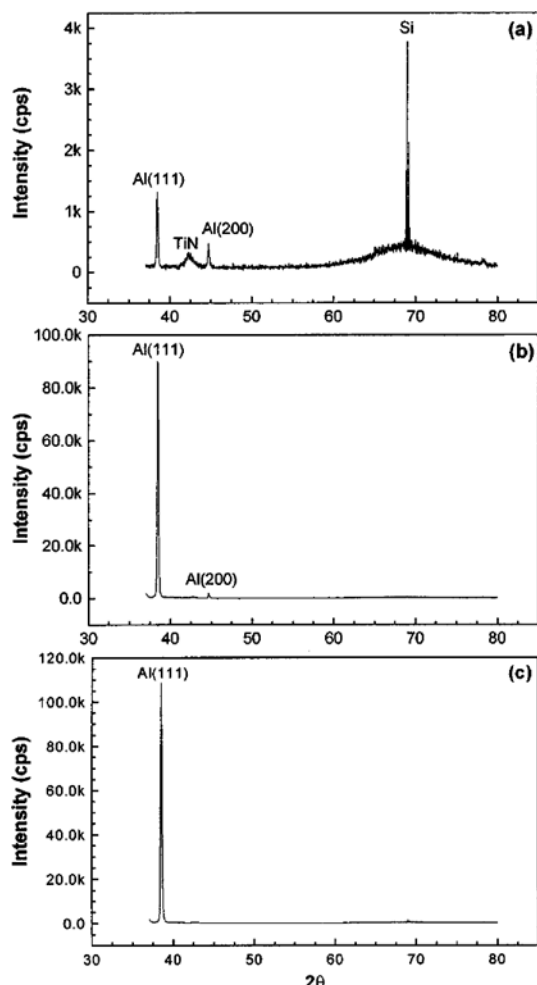
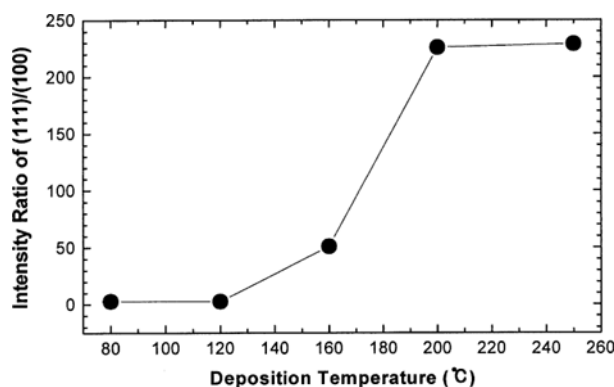**Fig. 7. X-ray diffraction patterns of the Al films deposited at (a) 80 °C, (b) 160 °C, and (c) 250 °C.**

Fig. 8. Intensity ratio of I(111)/I(100) of the Al films as a function of substrate temperature.

of (111)/(200) of XRD vs. deposition temperature were reported by Yun et al. [1998], who deposited the Al film on the "air exposed TiN" without plasma treatment. Despite any clear evidence, the suspected main causes of this discrepancy seem to be the different types of TiN and also difference in the degree of gas phase decomposition of DMEAA at high temperatures due to the different CVD reactor system.

CONCLUSION

Purity, the evolution of surface morphology, electrical resistivity, surface roughness, and the preferred orientation of the DMEAA-based CVD Al films deposited on the plasma pretreated air-exposed TiN substrate were evaluated. Highly pure Al films were grown at the substrate temperatures of 60-250 °C, and the of the Al films follows the three-dimensional growth mode on the plasma-pretreated TiN substrates. At high deposition temperature, the grain structure was highly interconnected, which led to its low resistivity of 2.8 $\mu\Omega$cm. Furthermore, the surface roughness was reduced significantly along with increment of the intensity ratio of (111)/(200) by increasing the deposition temperature.

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