JJAP Series 4
Proc. of 1990 Intern. MicroProcess Conference pp. 218–222

Study on Reaction Mechanism of Aluminum Selective Chemical Vapor Deposition with *In-situ* XPS Measurement

Hideaki KAWAMOTO, Hiroyuki SAKAUE, Shinobu TAKEHIRO
and Yasuhiro HORIIKE

Department of Electrical engineering, Hiroshima University,
Saijo Higashi-Hiroshima 724

(Received July 19, 1990; accepted for publication September 22, 1990)

Aluminum (Al) films have been deposited selectively on Si at a substrate temperature from 270 to 330°C under 1×10^{-3} Torr employing dimethylaluminum hydride (DMAlH). The experiments were carried out in a reaction chamber connected to an X-ray photoelectron spectroscopy (XPS) analyzer. The origin of selectivity was studied by *in-situ* XPS analysis, dopant dependency and surface treatments. The selectivity was independent of the dopant type and its concentration in Si substrate. *In-situ* XPS measurement revealed that the Al-hydrogen (H) bond was broken only on the Si surface. No Al film grew on the Si surface subjected to Ar^+ ion bombardment, while the Si surface exposed subsequently by hydrogen radicals was allowed to deposit the Al film. Eventually, it is considered that hydrogen (H) and/or fluorine (F) which terminates the Si surface after dipping in HF solution reacts with H atoms and methyl group in DMAlH, leading to the selective deposition of Al. Al did not grow on SiO_2 and Al_2O_3 surfaces because of the easy oxidation of Al due to the reaction of Al with oxide surfaces. Al could deposit on the TiN surface after the native oxide was reduced by hydroden radicals.

KEYWORDS: aluminum, CVD, reaction mechanism, *in-situ* XPS, hydrogen termination

§1. Introduction

Multilevel metallization is one of the key processes for VLSI to achieve a higher packing density. Continual shrinkage of device size requires high aspect ratio structure and subsequent planarization of the topology. A tungsten (W) selective CVD technology is developed intensively for submicron via-hole filling.[1,2] In recent years, an aluminum (Al)-selective CVD using organic sources such as a triisobtylaluminum (TIBA),[3] a diethylaluminum chloride (DEAlCl)[4] and a dimethylaluminum hydride (DMAlH)[5] has also been studied. In particular, the latter DMA1H is noted because it dissociates easily by replacing CH_3 in trimethylaluminum (TMA) by hydrogen bonding. However, the origin of this selectivity in the Al-CVD is not understood still, in contrast with the W-CVD mechanism. In this paper, a reaction process of the Al-selective CVD employing DMA1H is discussed using an *in-situ* X-ray photoelectron spectroscopy (XPS).

§2. Experimental

Figure 1 shows a schematic diagram of the experimental system. An Al CVD reactor was connected to a XPS system (Shimazu ESCA-750) through a gate valve. Samples of Si and SiO_2 with 5×5 mm^2 area after dipping in a diluted HF solution (5% HF, 1 min) were set on the XPS sample holder whose temperature was controlled from R.T. to 400°C. The reactor was evacuated to 1×10^{-7} Torr by a turbomolecular pump before experiments. The Al CVD was carried out by introducing DMA1H (Tosoh Akzo Co.) into the reactor at a pressure of 1×10^{-3} Torr. After the substrate temperature was reduced to room temperature by contacting a water-cooled Cu block to the sample holder, the sample was transported under the high vacuum to the XPS measurement system. Hydrogen (H) or fluorine (F) atoms generated by a remote microwave plasma of H_2 or NF_3 at a pressure of 1 Torr were irradiated on the samples for 1 min to investigate the dependence of the growth characteristic on the substrate surface condition.

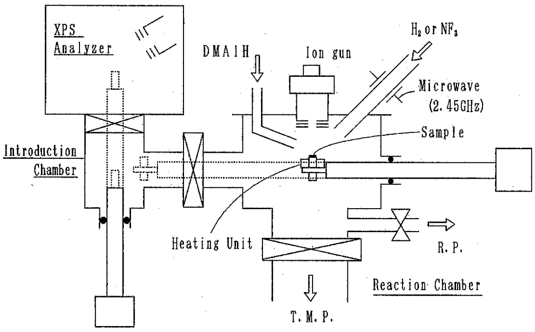

Fig. 1. A schematic diagram of the experimental system.

§3. Results and Discussion

Figure 2 shows the Al deposition rate for p-type Si(100) and SiO_2 substrates as a function of the substrate temperature, T_{sub}. The selective growth on Si was achieved at substrate temperature T_{sub} from 270°C to 330°C and had a maximum rate of 1500 Å/min around 300°C. Then the selectivity was lost above T_{sub}=about 360°C. The selective Al CVD was achieved as shown in the SEM micrograph of Fig. 3. The present filled Al structure is observed as a polycrystalline Al consisting of large Al grains, while a CVD of single-crystal Al with DMA1H is reported.[6] The SEM observation of as-grown Al surface morphology demonstrated large grains developed from micrograins with increasing deposition time. This apparently high deposition rate results from low-density

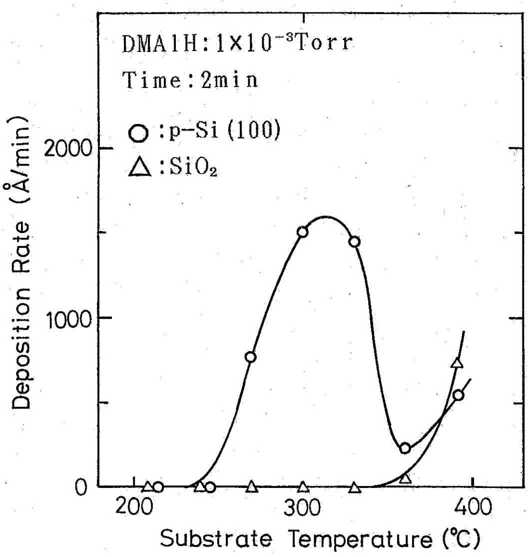

Fig. 2. The Al deposition rate of p-type Si(100) and SiO_2 substrates vs the substrate temperautre, T_{sub}.

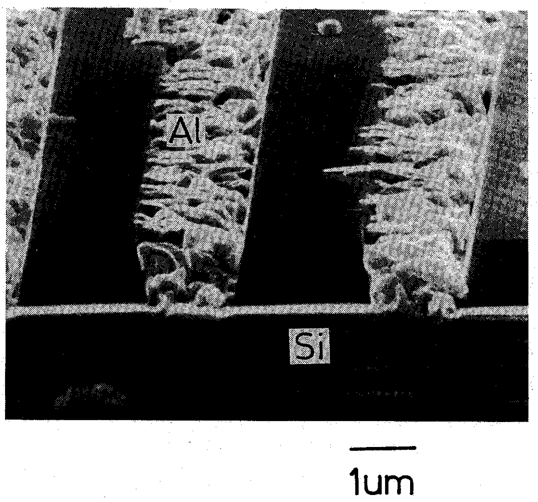

Fig. 3. The SEM micrograph of the selective Al CVD at $T_{sub}=300°C$.

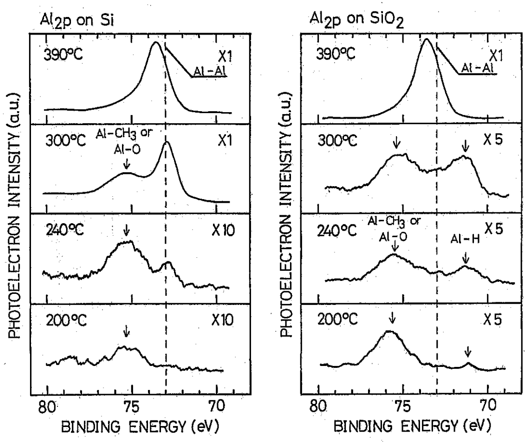

Fig. 4. The *in-situ* XPS spectra of Al_{2p} at varying T_{sub} of 240, 300 and 390°C.

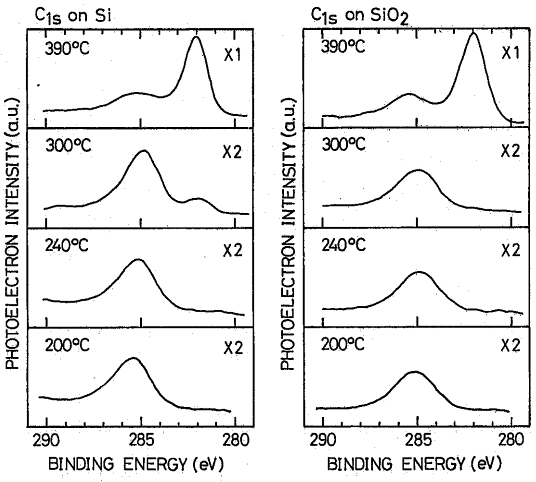

Fig. 5. The *in-situ* XPS spectra of C_{1s} at varying T_{sub} of 240, 300 and 390°C.

Al film due to the roughly grown Al grains.

The *in-situ* XPS of Al_{2p} and C_{1s} was measured on the Si and SiO_2 surfaces when T_{sub}'s were varied at 200, 240, 300 and 390°C, as shown in Figs. 4 and 5, respectively. The exposed time of DMA1H to both surfaces was fixed at 2 min. At T_{sub} of 200°C in which appreciable Al film growth did not occur, the Al–H bond was not observed on the Si surface but on the SiO_2 surface, while the Al–CH_3 peak (this peak is also assigned as Al–O because oxygen is usually detected, however, it may originate from an oxidized Al surface) was detected clearly on both surfaces. When T_{sub} was elevated to 240°C, the Al_{2p} spectra of 73 eV binding energy appeared for both Si and SiO_2 surfaces. The C_{1s} peak shows adsorbed carbon (C). With increasing T_{sub} to 300°C, the metallic Al peak increased and the Al-CH_3 peak decreased on the Si surface. However, Al-CH_3 and Al–H peaks were observed still on the SiO_2 surface. The C_{1s} spectrum at 300°C also indicates that a part of Al reacts with carbon. At 390°C, where selectivity is lost, Al strongly bonded to C or Al–C alloy is formed from shiftings of Al and C peaks to higher and lower binding energies, respectively.

A possible mechanism for the Al-selective CVD is discussed briefly focusing on an opposite behavior of the Al peaks on both surfaces. The Al–H bond is observed certainly on the SiO_2 surface on which Al does not grow. This result demonstrates that DMA1H does not decompose as long as the Al–H bonding exists in adsorbed DMA1H. In the case of the Si surface, the Al–H bond is not seen even at 200°C, where only a few monolayers of DMA1H are assumed to be adsorbed on the surfaces. Hence, a possible mechanism in which any driving force on the Si surface easily breaks the hydrogen bond of DMA1H and Al grows as a result of the pyrolytic decomposition of dimethyl Al at 240°C should be considered.

For deeper insight into the origin of this selective reaction, the dopant dependence of the deposition rate was investigated for the Si substrates of n^+ ($<0.015\ \Omega\cdot cm$), n ($7.5\sim12.5\ \Omega\cdot cm$), undoped ($>500\ \Omega\cdot cm$), p ($9.8\sim11.8\ \Omega\cdot cm$) and p^+ ($0.013\sim0.018\ \Omega\cdot cm$) types at $T_{sub}=300°C$, as shown in Fig. 6. However, significant dependence was not obtained. Also, no deposited Al film was obtained for the insulator surfaces of Si_3N_4 and Al_2O_3, and the Al, Cr and TiN surfaces which are usually covered by oxide films.

Much carbon contamination was observed by XPS on a Si sample subjected to the 10-minute-long water rinsing after diluted HF solution.[7] In addition, the Al CVD did not occur when the Si–O bond was observed in the Si_{2p} spectrum after such long rinsing. Therefore, the Si sample was dipped in diluted HF solution and subsequently dried by nitrogen gas flow. It was found that this H or F terminated Si substrate enabled us to realize the Al CVD only on the Si surface.

Hence, surface treatment conditions prior to the Al CVD were investigated concerning their effect on the selectivity. Table I shows the comparison for capabilities of the Al CVD on Si and SiO_2 whose surface conditions are altered by the diluted HF dipping, the Ar^+ ion sputtering (2 kV, 5×10^{-6} Torr, 1 min), and the Ar^+ ion sputtering and subsequent H or F treatment at T_{sub}=room temperature. Ar^+ ion sputtering was performed by an ion gun set in the XPS analysis chamber. These experiments were investigated by means of XPS, SEM and Taly step. For the HF dipped samples, Al deposits on the Si surface as a film, but Al grows as a large nucleus on the SiO_2 surface. When the F or H termination was removed by Ar^+ sputtering, a small amount of Al signal was observed for both Si and SiO_2 samples, while no film deposition occurred even on the Si at $T_{sub}=300°C$. In general, the Si surface which was subjected to Ar^+ ion bombardment is altered to the amorphous surface and is liable to be oxidized due to theresidual oxygen during heating up to 300°C. However, the Si–O peak which resulted in the formation of the native oxide was not detected even in a surface-sensitive XPS measurement for the heated Si sample. Once H or F radicals were exposed to the sputtered samples at room temperature for 1 min, the Al film was found to be deposited again on the Si surface and the samll Al nucleus was observed for the SiO_2 surface. It was considered that H radicals reduced the oxygen-adsorbing Si surface to terminate the Si surface, and F radicals etched Si in the thickness of about one hundred angstroms to generate also a fluorinated surface consisting of SiF_x (x=1–4) whose surface was terminated by F atoms.

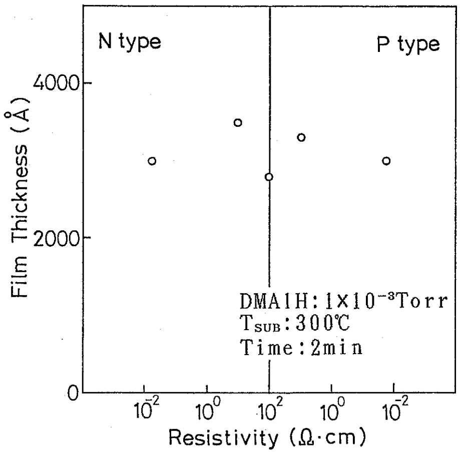

Fig. 6. The dopant dependence of the deposition rate for the Si substrates of n^+, n, undoped, p and p^+ types at $T_{sub}=300°C$.

Table I. The comparison for surface morphologies of Si and SiO_2 which adsorb a DMAlH after various surface treatments.

Surface treatments	a dipping diluted HF solution	Ar^+** sputtering	Ar^+ sputtering+H treatment**	Ar^+ sputtering+F treatment**
Si surface	Film deposited	Film* not deposited	Film deposited	Film deposited
SiO_2 surface	Nucleus observed	Film* not deposited	Film* not deposited	Film* not deposited

*However small nuclei which do not grow subsequent DMAlH adsorption were observed.

**A diluted HF dipping is performed before these treatments.

Based on these results, the above-mentioned driving force for the Al-selective CVD on Si is discussed. At first H or F atoms which terminate Si surface dangling bonds react with hydrogen of the DMA1H, desorbing it as H_2 or HF. Thus, the Al film deposits selectively on the Si surface. The dependence of the concentration of HF in diluted water on the Al deposition rate was not observed, as shown in Fig. 7. This is understandable from the recent result that at least 80% of the Si surface is always terminated by H atoms in spite of the widely changed HF concentration.[7] Once the Al film is deposited, CH_3 bonded to Al surface may react with hydrogen in DMA1H. Then, CH_3 is desorbed as CH_4 to grow Al on Al successively. Deposition thickness was measured as a function of time for Si and SiO_2 surfaces treated by the diluted HF dipping, Ar^+ ion sputtering and subsequent H or F radical exposure, as shown in Fig. 8. The deposition rate decreases after a rapid increase at the initial stage. This may be attributed to contamination of a part of the Al surface with carbon liberated from DMA1H or residual gases. Regarding SiO_2, a similar reaction between the DMA1H and chemisorbed H or F atoms in-

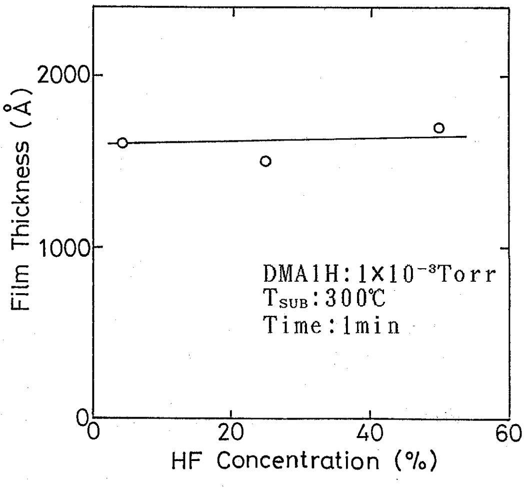

Fig. 7. Dependency of concentration of HF in diluted water on the Al deposition rate.

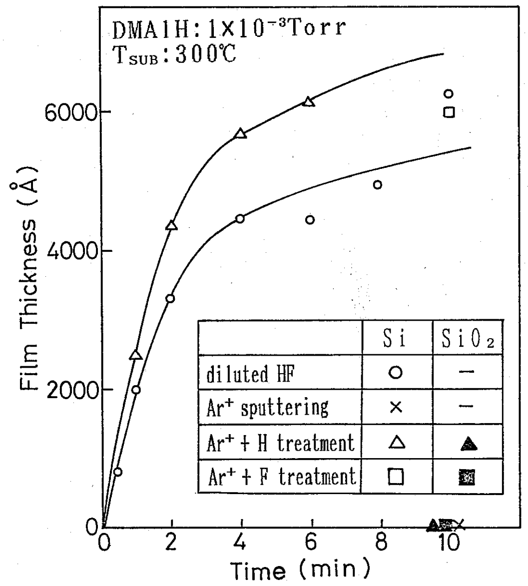

Fig. 8. Deposition thickness vs deposition time for Si and SiO_2 surfaces treated by the diluted HF dipping and Ar^+ ion sputtering and subsequent H radical exposure.

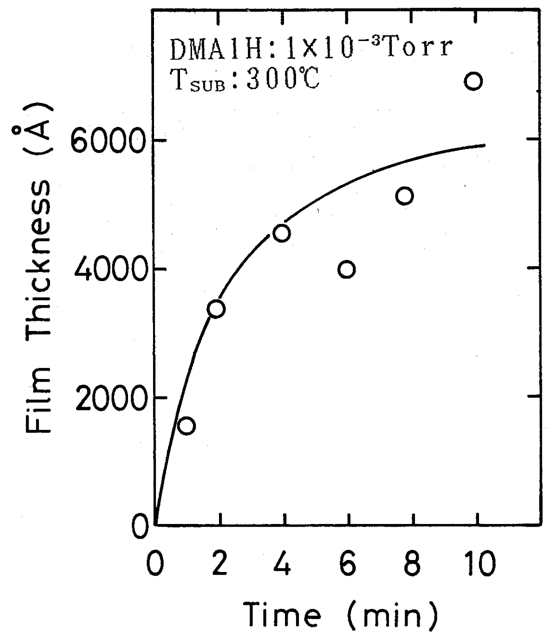

Fig. 10. Al film deposition thickness vs time at $T_{sub}=300°C$.

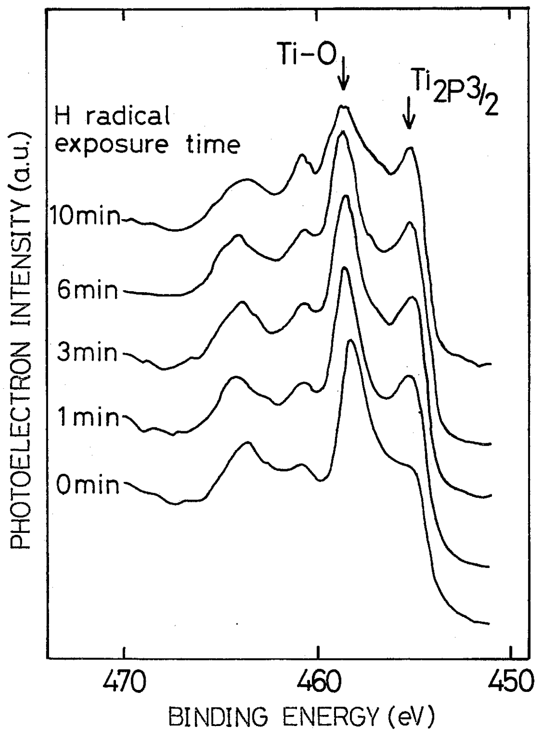

Fig. 9. Variation in Ti_{2p} XPS spctrum with exposure time of hydrogen radical at T_{sub}=room temperature.

itiates primarily the nucleation of Al, but the oxygen dangling bond generated after the removal of H or F atoms on the SiO_2 readily oxidizes Al to prevent the subsequent nucleation process.

The selective CVD of Al on Al or barrier metals such as titanium nitride (TiN) is required for the actual metallization process. The TiN film was made by reactive sputtering of a Ti target in nitrogen ambient at the pressure of 2×10^{-3} Torr. At first, Ar^+ ion sputtering was performed on the Al surface at 300°C employing the ion gun shown in Fig. 1, and then Al deposition on the Al surface was attempted immediately after exposure of H radicals. However, this Al-on-Al growth was not achieved because of the rapid oxidation of the Al surface due to a trace amount of water in the vacuum system. The Al CVD on TiN was also attempted. Figure 9 shows the variation in XPS spectrum of Ti_{2p} of the TiN with surface hydrogen radical exposure time as a parameter. The TiN surface which first was covered by a native oxide was removed with H radical exposure. When the Al CVD was carried out immediately after 10-min exposure, Al started to grow as shown in Fig. 10, while the same CVD tendency as Al on Si was observed. The Al CVD on TiN is considered as a result of the reduction of the TiN surface with the hydrogen exposure.

§4. Conclusions

The reaction mechanism of the selective Al CVD on Si with DMAlH has been studied employing a reactor directly combined with a XPS analyzer. The selective CVD was not realized on a Si surface until the surface was treated by diluted HF solution without following water rinse. No Al CVD took place for the Si surface bombarded by Ar^+ ion, while H or F radicals exposed to this surface enabled us to produced the Al CVD again. Accordingly, H and/or F terminated on the Si was considered to subtract the hydrogen or methyl in DMAlH, achieving the selective Al CVD on Si. On the other hand, even if DMAlH reacts with the SiO_2 surface, the produced Al is oxidized easily by oxygen in SiO_2. The CVD of Al on Al was difficult because of the rapid oxidation of Al surface by the residual water, while Al was deposited on TiN whose oxide was reduced by hydrogen.

References

1) H. Itho, R. Nakata and T. Moriya: *IEEE IEDM Technical Digest* (1985) p. 606.
2) T. Ohba and K. wada: *Digest of Papers 1988 1st MicroProcess Conf., Tokyo, 1988* (Business Center for Academic Societies Japan, Tokyo, 1988) p. 122.
3) T. Amazawa, H. Nakamura and Y. Arita: *Extended Abstracts of the 18th Conf. on Solid State Devices and Materials, Tokyo, 1986* (Business Center for Academic Societies Japan, Tokyo, 1986) p. 755.
4) C. Sasaoka, K. Mori, Y. Kato and A. Usui: Appl. Phys. Lett. **55** (1989) 741.
5) T. Shinzawa, S. Kishida and H. Okabayashi: *Extended Abstracts of the 50th Autumn Meeting, 1989* (The Japan Society of Applied Physics, Tokyo, 1989) p. 631.
6) K. Tsubouchi, K. Masu, N. Shigeeda, T. Matano, Y. Hiura, N. Mikoshiba, S. matsumoti, T. Asaba, T. Marui and T. Kajikawa: *Digest of Technical Papers, 1990 Symposium on VlSI Technology* (1990) p. 5.
7) T. Sunada, T. Yasaka, M. Takakura, T. Sugiyama, S. Miyazaki and M. Hirose: *Extended Abstracts of the 22nd Conf. on Solid State Devices and Materials, Sendai, 1990* (Business Center for Academic Societies Japan, Tokyo, 1990).