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# Precursor design and selective aluminum CVD

**K Tsubouchi and K Masu**, *Research Institute of Electrical Communication, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-77, Japan*

*Area-selective Al CVD technology has an excellent potential for filling via and contact holes of multilevel interconnection in Si ULSI. In this article, we discuss the selective Al CVD using metalorganic sources of trimethylaluminum [(CH₃)₃Al, TMA] and dimethylaluminum hydride [(CH₃)₂AlH, DMAH]. In order to deposit Al from TMA, the TMA molecule should be selectively excited into a reactive species of (CH₃)₂Al in the well controlled H₂/rf plasma. When using DMAH and H₂, Al can be deposited by low-pressure CVD; the features are (1) single crystal Al on Si surface, (2) filling capability into 0.3 μmφ/1 μm-deep contact holes, (3) low contact resistivity (2 × 10⁻⁷Ωcm²) to n⁺-Si, and (4) erosion free at the Al/Si interface after 450°C/30 min annealing. As a selective Al growth mechanism on the Si surface, we have proposed and experimentally confirmed a "surface electrochemical reaction model". In this model, terminated-H on the Si surface reacts with CH₃-radical of the DMAH molecule to produce volatile CH₄. The H atom of the DMAH remains on the newly deposited Al surface as a newly terminated-H atom. The terminated-H atom on the surface reacts repeatedly with CH₃-radical to deposit Al. It is noted that, in the DMAH molecule, two CH₃-radicals and one H atom are bonded to Al atom, i.e. "asymmetric" structure. Since the different radicals are bonded to the Al atom, Al can be selectively and repeatedly deposited on Si surface. The precursor which has "asymmetric" structure is considered to have an important role for selective growth.*

## 1. Introduction

Miniaturization of an Si device according to the scaling rule has resulted in high speed, high density and high performance. The lateral dimension has been shrunk, while the thickness of the insulating layers has not been shrunk because of maintaining the high electric field endurance. The aspect ratio of contact and via holes for interconnections becomes larger and larger. The deposition of metal into deep submicron contact and via holes with a high aspect ratio is the most important issue for the multilevel interconnection. A high crystal quality is also required for high electromigration and stress-migration endurance. Aluminum and its alloy are still choice interconnect materials because of their stability and low resistivity.

Chemical vapor deposition (CVD) of Al is promising for the multilevel interconnection because of its capability of achieving the conformal step coverage[1-3], selective deposition[4-7], and single crystal growth on the Si surface[8]. As precursors of the Al CVD, metalorganic sources have been used; trimethylaluminum [(CH₃)₃Al, TMA], dimethylaluminum hydride [(CH₃)₂AlH, DMAH], triisobutylaluminum [(i-C₄H₉)₃Al, TIBA], etc. However, the Al CVD technologies are not yet suitable for practical use, because they have not provided full control of the selective and the nonselective deposition of high quality Al. The selective growth mechanism should be thoroughly investigated and it is necessary to give a guiding principle of precursor design for the selective deposition.

The authors have investigated the selective Al growth tech-

nology using TMA and DMAH. It has been clarified that, in the case of TMA, Al is selectively deposited on the Si surface when TMA is selectively excited into (CH₃)₂Al in the well-controlled H₂/rf plasma[6,9]. Furthermore, in the case of low-pressure CVD using DMAH, Al can be selectively deposited on the electrically conductive surface such as Si, Ti, TiN, TiSi₂ and Al[10-15].

In this paper, we describe the selective Al deposition using TMA and DMAH, and the selective Al growth mechanism. Furthermore, we discuss what kind of precursor is promising for selective deposition.

## 2. Selective Al deposition

**2.1. Al CVD apparatus.** Figure 1 shows a schematic of the Al CVD system[6,13]. Metalorganic (MO) source (DMAH or TMA) and the H₂ carrier gas are introduced into a horn-type quartz reactor. TMA is a clear liquid with a vapor pressure of 1.3 × 10³ Pa at room temperature and DMAH is a clear viscous liquid with a vapor pressure of 2.7 × 10² Pa at room temperature. The vapor pressures of these MO sources are 10–100 times higher than that of TIBA (27 Pa at RT). The shape of the reactor is one important point because a vortex flow can be effectively reduced and a laminar flow can be realized in this type of reactor[16]. A 4 in diameter Si wafer is placed on a heated susceptor. The rf (13.56 MHz) excited plasma can be generated using a three-separate ring electrode.

Plain Si wafers and SiO₂-patterned Si wafers are chemically cleaned by H₂SO₄ : H₂O₂ (4 : 1) solution with an intermediate rinse
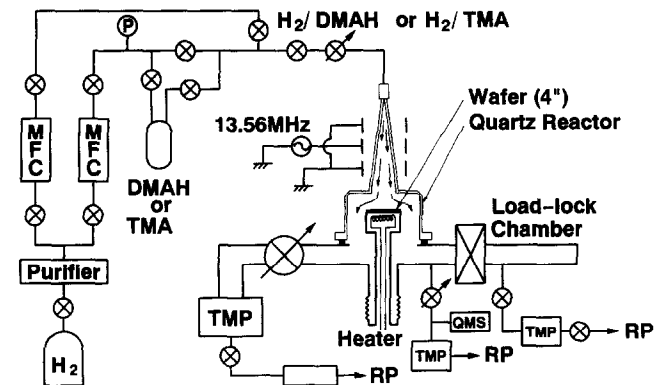
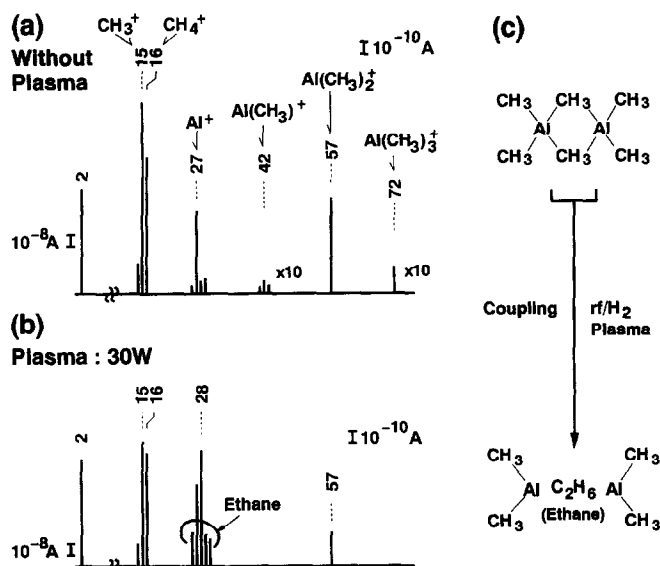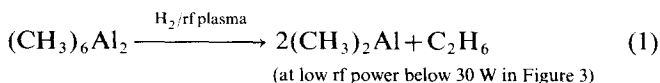Figure 1. Schematic of the low-pressure Al CVD system.



Figure 2. Typical mass spectra of TMA in $H_2$ with and without rf plasma, respectively. Ionization energy of QMAS is 70 eV, 80 mm$\phi$ straight quartz tube is used in this measurement.
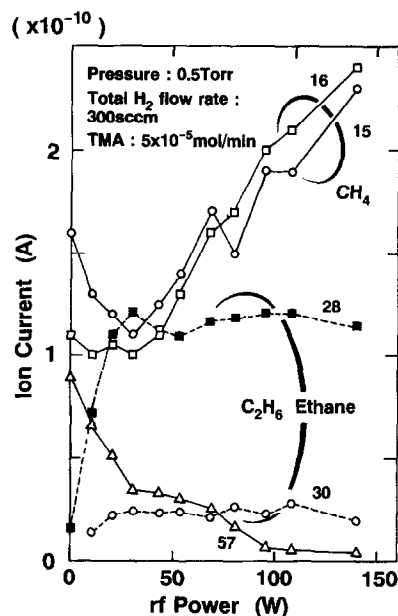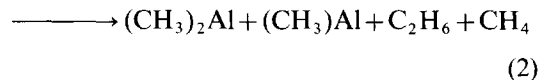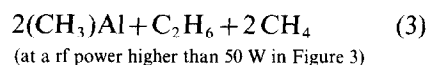


Figure 3. Intensity of several mass peaks as a function of rf plasma power.

in ultrapure water. The wafers are then pretreated just before Al deposition by a short dip in $HF:H_2O$ (1:50–1:100) solution in order to remove residual oxide on the Si surface, followed by an ultrapure water rinse. The typical rinsing time is 10 min. After the above cleaning, the cleaned Si surface is mainly terminated by hydrogen [17]. The terminated hydrogen plays an important role in the selective growth of Al on Si using DMAH as discussed later.

## 2.2. Al deposition using trimethylaluminum.

When TMA/$H_2$ was supplied to the heated substrate with a total pressure of 93 Pa and a TMA partial pressure of 0.33 Pa, Al could not be deposited; no deposition was observed on the Si substrate below 300°C, while the interference aluminum carbide was deposited at 480°C[18]. It was reported that Al was deposited by rf plasma CVD using TMA and $H_2$[1,19]. However, several % of carbon was incorporated in the film and the selective deposition was not realized. We had recognized that TMA should be excited and/or decomposed into $(CH_3)_2Al$ or $(CH_3)Al$ which might readily react on a substrate surface, and into stable and gaseous species such as $CH_4$, $C_2H_6$, etc. in order to eliminate the carbon incorporation in the film. We have found that TMA can be selectively excited and/or decomposed into $(CH_3)_2Al$ and $C_2H_6$ in the well-controlled $H_2$/rf plasma[9].

Figure 2 shows typical mass spectra of TMA in $H_2$ measured with the quadrupole mass analyzer (QMAS). With the rf plasma excitation, a remarkable change was observed at 28, 29 and 30 amu. From standard fragment patterns, it has been confirmed that ethane ($C_2H_6$) is generated. Figure 3 shows the rf power dependence of the intensities of several peaks. The intensities of 28 and 30 amu were saturated in the range over 30W. 30W plasma power corresponds to the power density of about 0.05 W/cm$^3$. The ratio of $C_2H_6^+$ (30)/$C_2H_4^+$ (28) was 0.2 i.e. the ethane is generated. The intensity of 15 and 16 amu increased with an increase in the rf power in the range over 50 W. Since the ratio of $CH_3^+$ (15)/$CH_4^+$ (16) was about 0.8, these peaks were fragments of methane ($CH_4$). It is noted that TMA has a dimer structure in the vapor phase. We have reported that $C_2H_6$ is generated by coupling of bridge $CH_3$ radicals in photolysis of TMA[20]. In the plasma excitation, it is considered that $C_2H_6$ is generated by coupling of the bridge $CH_3$ radical as shown in Figure 2(c). The $H_2$/rf plasma excitation of TMA is summarized as follows:

$$(CH_3)_6Al_2 \xrightarrow{\text{$H_2$/rf plasma}} 2(CH_3)_2Al + C_2H_6 \qquad (1)$$

(at low rf power below 30 W in Figure 3)

$$\longrightarrow (CH_3)_2Al + (CH_3)Al + C_2H_6 + CH_4 \qquad (2)$$

or

$$2(CH_3)Al + C_2H_6 + 2CH_4 \qquad (3)$$

(at a rf power higher than 50 W in Figure 3)

In the $H_2$/rf plasma, $H_2$ is considered to be excited to $H_2^+$, $H_2^*$, $H^+$, and $H^*$, so that there remains the possibility that TMA is excited into $(CH_3)_2AlH$ in equation (1). We have also evaluated the excitation and/or decomposition of TMA in Ar/rf, $H_2/\mu$-wave (2.4 GHz), and Ar/$\mu$-wave plasmas. For these three kinds of
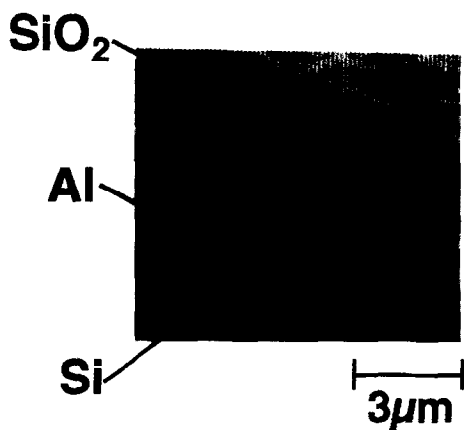
**Figure 4.** Selectively deposited Al into $SiO_2$ windows using the selectively excited TMA. The thickness of Al is 3000 Å.

plasma, clear $C_2H_6$ generation was not observed in the mass analysis; TMA was excessively decomposed into $Al(CH_k)_h$, Al and $C_mH_n$. Thus, we have confirmed that the TMA molecule can be excited into $(CH_3)_2Al$ in the $H_2/rf$ plasma with a power density of 0.05 $W/cm^3$.

We have deposited Al from the selectively excited TMA in $H_2$[6]. Total pressure and TMA partial pressure were 93 Pa and $2 \times 10^{-2}$ Pa, respectively. The plasma was almost confined within the three-separate ring electrode. The plasma power density was between 0.03 and 0.06 $W/cm^3$. In this plasma power density, the excited species are considered to be mainly $(CH_3)_2Al$. Typical deposition temperature was 230–260°C. At a constant plasma power density, the deposition rate DR had the surface-reaction-limited form: $DR = DR_0 \exp(-E/kT)$, where $E = 1.1 - 1.6$ eV. Figure 4 shows the SEM micrographs of the selectively deposited Al into $SiO_2$ contact windows. The thickness of Al is 3000 Å. Carbon and oxygen were not incorporated in the deposited film according to the ESCA (Electron Spectroscopy for Chemical Analysis) depth profile. The resistivity of the deposited film was as low as 2.7 $\mu\Omega$ cm. The Al film on (100)Si was (100) oriented polycrystal. From these results, we confirmed that the selectively excited TMA, i.e. $(CH_3)_2Al$, is a precursor for the selective Al deposition.

### 2.3. Al deposition using dimethylaluminum hydride.

We have investigated Al CVD using dimethylaluminum hydride

(DMAH), which has a similar molecular structure to "the selectively excited TMA; $(CH_3)_2Al$".

Figure 5 shows the selectively deposited Al into contact holes using DMAH and $H_2$. total pressure and DMAH partial pressure were 160–400 Pa and 0.4–0.9 Pa, respectively. The rf plasma was not used. The typical deposition temperature was 270°C and the typical deposition rate was about 800 Å/min selectively into contact holes on Si. The deposition rate $(DR)$ on Si had a surface reaction limited form: $DR = DR_0 \exp(-E/kT)$, where $E = 0.3$ eV in the temperature range 230–350°C. The activation energy of 0.3 eV is lower than that of the selectively-excited TMA case. At the present time, the difference in the activation energies has not been clarified. The ESCA depth profile has revealed that carbon and oxygen are absent from the bulk of the film. The resistivity of the deposited film was 3 $\mu\Omega$ cm.

In Figure 5(a), the 0.3 $\mu m\phi$ deep-submicron contact hole with an aspect ratio larger than 3 is completely filled with the selective Al. We have also confirmed that 0.18 $\mu m\phi/0.4$ $\mu m$-deep contact holes are filled with the selective Al. In Figures 5(b) and 5(c), the Al was intentionally overgrown after filling the contact holes. From the shapes of the overgrown Al, it can be confirmed that single crystal Al is deposited on Si; (111)Al on (100)Si and (100)Al on (111)Si. The crystallographic orientation of single crystal (100)Al on (111)Si is determined to be $\langle 011 \rangle/Al\langle 11\bar{2} \rangle$Si and $\langle 01\bar{1} \rangle Al/\langle 1\bar{1}0 \rangle$Si.

The other important features are (1) the specific contact resistivity of as-deposited $CVD$-$Al/n^+$-Si contact is as low as less than $2 \times 10^{-7}\Omega$ $cm^2$[12], and (2) erosion was not observed at the interface between the selectively deposited single-crystal Al and Si after the annealing at 450°C/$N_2$/30 min[10,13]. Furthermore, we have proposed a new MOSFET structure called $SAL^2$ (Self-ALign Selectively-deposited AL)-MOSFET, where the poly-Si gate electrode as well as source/drain regions are selectively covered with Al, resulting in the dramatic reduction of the sheet resistances[14].

### 3. Selective Al growth mechanism

We have proposed and experimentally confirmed "a surface electrochemical reaction model" as a selective growth mechanism of Al on the Si surface as shown in Figure 6[12–15]. The most important points of this model are (1) catalytic contribution of surface free electrons, (2) a surface terminated-H atom, and (3) selective
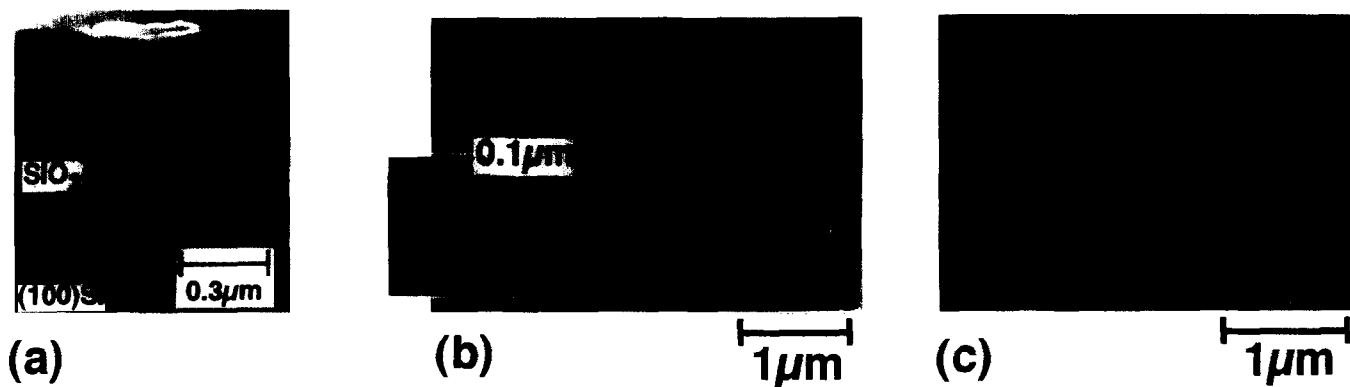


**(a)** **(b)** **(c)**

**Figure 5.** SEM photographs of selectively deposited Al into via holes using DMAH. In this case, plasma was not used. (a) Al in a 0.3 $\mu m\phi$ diameter via hole, (b) (100)Al on (111)Si, and (c)(111)Al on (100)Si. In (b) and (c), Al was intentionally overgrown after filling the via holes. The diameter and depth of the via holes are 0.8 and 1 $\mu m$, respectively. The insert of (b) is a 0.1 $\mu m$ pyramid of Al.
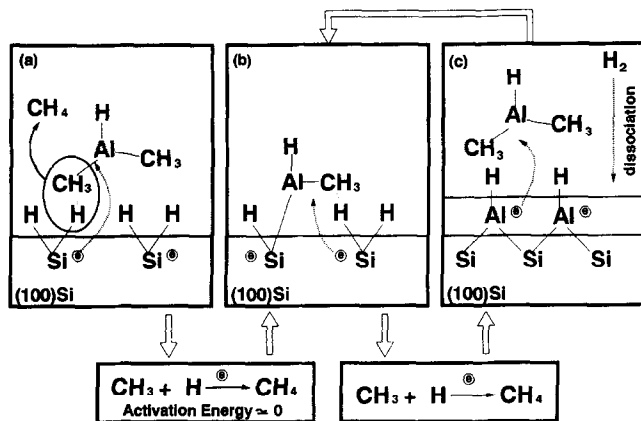
**Figure 6.** Surface electrochemical reaction model proposed for the selective Al CVD on Si. Free-electron, H-terminator and $CH_3$ radical are three essential elements for selective reaction.
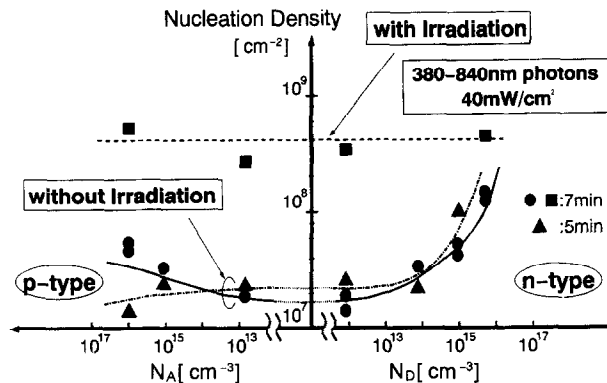


**Figure 7.** Nucleation density of Al at the initial growth stage as a function of dopant density of a (111)Si wafer with and without photo-irradiation.

reaction between the terminated-H and $CH_3$-radical of the DMAH molecule.

At first, the Si surface is mainly terminated by a H atom after the diluted-HF dip followed by a pure water rinse as shown in Figure 6(a). Since terminated dihydride and monohydride are considered to be desorbed at 410°C and 535°C, respectively[21], the Si surface remains to be terminated by H at the growth temperature of 270°C. When the DMAH molecule adsorbs on the H-terminated Si surface as shown in Figure 6(a), Al-$CH_3$ bond is weakened (or dissociated) because of the catalytic contribution of free-electrons. Then the $CH_3$-radical of the DMAH reacts with the terminated-H atom to produce volatile $CH_4$ molecules; $CH_3 + H \rightarrow CH_4$. Thus, Al is deposited on the Si surface (Figures 6(a) and (b)).

Since the bonding energy of Al-H is larger than that of Al-$CH_3$[22], Al-H remains after depositing Al, i.e. the H atom remains on the newly deposited Al surface as a new terminated-H atom. The terminated-H atom on the surface reacts repeatedly with the $CH_3$-radical to deposit Al (Figures 6(b) and (c)). The overall reaction for DMAH to produce Al requires an additional H atom. The additional terminated-H atom is supplied by the dissociation of $H_2$ molecules because of the catalytic contribution of surface free electrons at the heated metal surface.

For the reaction on $SiO_2$, there is no free electron that can catalytically contribute to the reaction. The $H_2$ molecule can not be decomposed to supply the terminated H atom, if the $H_2$ molecules are supplied to the $SiO_2$ surface. Therefore, the reaction of $CH_3 + H \rightarrow CH_4$ does not occur on $SiO_2$, so that Al is not deposited on the insulating surface.

The fundamental results concerning the contribution of free electrons to the surface reaction are (1) Al is deposited on the electrically conductive materials such as Si, Al, Ti, TiN, Ti-silicide, etc. and (2) Al is not deposited on an electrically insulating surface such as $SiO_2$, PSG, BPSG, etc. and (3) Al is deposited on the insulating material when free electrons are supplied from the rf plasma[13].

Figure 7 shows the Al nucleation density on P-doped n-type and B-doped p-type (111)Si wafers at the initial growth stage[13]. Al was deposited at 160 Pa and 270°C. Without the photo-irradiation, the nucleation density dramatically increased at $N_A > 10^{15}$ cm$^{-3}$. For the Si wafer with $N_D < 1 \times 10^{15}$ cm$^{-3}$, since the intrinsic carrier density at 270°C is $n_i(270°C) = 1 \times 10^{15}$ cm$^{-3}$,

the dependence of the nucleation density on $N_A$ and $N_D$ is considered to be masked by the intrinsic carrier density. On the other hand, for the Si wafer with $N_D > 1 \times 10^{15}$ cm$^{-3}$, the electron density is larger than $n_i(270°C)$, the increase in the nucleation density is considered to be the contribution of the surface free electrons. When the Si wafer was irradiated by light, the nucleation density increased and became independent of n-type and p-type, and independent of the dopant density of the Si wafer. This increase in the nucleation density is attributed to the photo-excited electrons. Thus, we have experimentally confirmed that free electrons at the surface actively contribute to the surface reaction to produce Al.

The crystal quality of Al on Si is considered to be dependent on the hydrogen termination conditions. We have carried out Al deposition for various hydrogen termination conditions, which are obtained by changing the rinsing time after diluted HF-dip and by changing the baking temperature before Al deposition[12]. Figure 8 shows the half width of X-ray rocking curve $\Delta\theta_{(111)Al}$ of deposited Al films as function of the baking temperature before Al deposition. The thickness of Al was 8500-9500 Å. $\Delta\theta_{(111)Al}$ increased with an increase in baking temperature, because the terminated dihydride and monohydride were considered to be desorbed at 410°C and 535°C, respectively[21]. The incomplete H-termination deteriorates the crystal quality of Al. Therefore, it has been confirmed that terminated-H atom actively contributes to the reaction of selective Al CVD. The reaction between the $CH_3$-radical and the terminated-H has been confirmed by
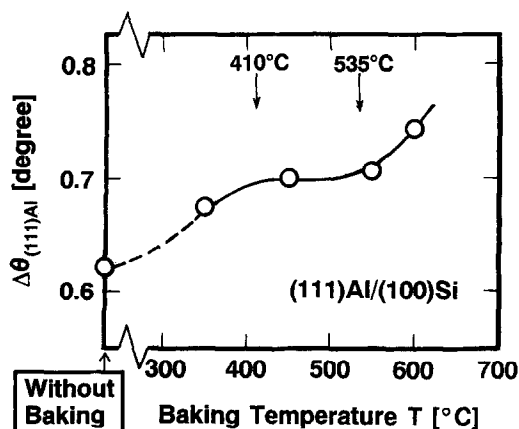


**Figure 8.** Half width of X-ray rocking curve as a function of baking temperature before Al deposition. Al was deposited at 270°C.

the Fourier-transform-infrared-spectroscopy attenuated-total-reflection (FT-IR ATR) method[23].

Finally, we discuss the molecular structure of precursors for the selective deposition. At first, we assume that the molecule $M$–$A_n$ is "symmetric", and the molecule $A_m$–$M$–$B_n$ is "asymmetric", where $M$ is a metal and $A$ and $B$ are different radicals. DMAH in which two $CH_3$-radicals and one H atom are bonded with Al atom is just "asymmetric", so that the reaction chain to produce the selective Al continues automatically as explained in Figure 6. For a continuous and stable reaction during the selective deposition, the requirement for the "asymmetric" molecule can be said that (1) one of the radicals (for example "A") reacts with the terminator on the substrate surface, (2) another radical "B" remains on the newly deposited surface as a new terminator, and (3) the remaining radical "B" reacts with the radical "A" of the newly adsorbed molecule. From this point of view, it can be summarized the "asymmetric" structure has an important role for the selective deposition.

## 4. Summary

We have investigated area selective CVD of Al using MO sources of TMA and DMAH. In the case of TMA, it has been found that the TMA molecule should be selectively excited into a reactive species of $(CH_3)_2Al$ in the well-controlled $H_2$/rf plasma in order to deposit Al without carbon incorporation. In the case of DMAH, Al can be deposited by low-pressure CVD. Single crystal Al can be selectively deposited on Si surface and deep-submicron contact holes are completely filled with the selective Al. We have proposed and experimentally confirmed the surface electrochemical reaction model as a selective reaction mechanism. It has been summarized that the "asymmetric" molecule has an important role as a precursor for the selective deposition, where the "asymmetric" means $A_m$–$M$–$B_n$ ($A$ and $B$ are different radicals and $M$ is a metal) such as DMAH.

## Acknowledgements

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