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Al-Selective CVD Induced by Hydrogen Desorption on Si

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We studied a influence of a chemical structure of silicon-hydride species on Al deposition rate in Al-CVD employing DMAlH on hydrogen-terminated Si surface. It was revealed that the peak temperature of hydrogen desorption from Si-H_2 and Si-H_3 in TDS spectra well coincides with the peak temperature of the Al deposition rate. We found that the hydrogen thermal-desorption from di-hydride and/or tri-hydride species induced the Al selective deposition reaction. Mono-hydride is not useful for the deposition at 240-290°C because of its higher desorption temperature of 350°C. In the early stage of the Al deposition, a lower density of Al nuclei on the NH_4F treated surface compared with on the HF treated surface suggests that the Al nucleation occurred at step edges on which di- and tri-hydride species exit.

1. Introduction

Aluminum (Al)-selective CVD on the Si surface using a dimethylaluminum hydride (DMAlH) gas has been noted for its high capability of filling in contact and via-holes with high aspect ratio for ULSI metallization. The previous works[1,2] showed that Al did not deposit on the Si surface on which terminate hydrogen atoms were removed by Ar^+ ion bombardment, while Al deposition was observed again on the hydrogen re-terminated surface employing atomic hydrogen exposure after the ion bombardment. As a result, it is concluded that the terminated hydrogen atoms on the Si surface are indispensable for the Al selective deposition employing DMAlH.[1,3] In this work, a reaction mechanism in Al deposition on the hydrogen terminated Si surface was investigated. We examined the relation between a temperature dependence of Al deposition rate in Al-CVD employing DMAlH and the thermal desorption behavior of the hydrogen atoms on hydrogen-terminated Si surface.

2. Experiment

We used Si(111) wafers with off-angle of 0.2° whose surface were terminated by hydrogen atoms[4] and the samples covered by thermally grown oxide layer were also used. The hydrogen-terminated surfaces were prepared by immersing in 5% HF or 40% NH_4F solution. Figure 1 shows AFM (atomic force microscope) images of the surfaces prepared using (a) 5% HF and (b) 40% NH_4F solution. The latter surface has an atomically flat and the terrace/step periodic morphology and the former surface has a rough morphology.[5] Figure 2 shows a schematic illustration of experimental apparatus used for Al deposition. Al was deposited on the Si wafers set on a Cu holder whose temperature was controlled from room temperature to 400°C. DMAlH was introduced into the

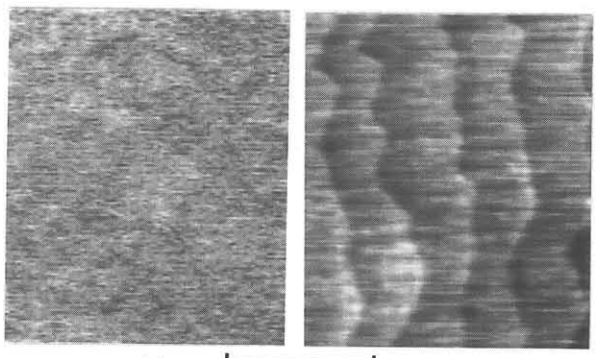

Fig. 1 AFM images of the surfaces prepared using (a) 5% HF and (b) 40% NH_4F solution.

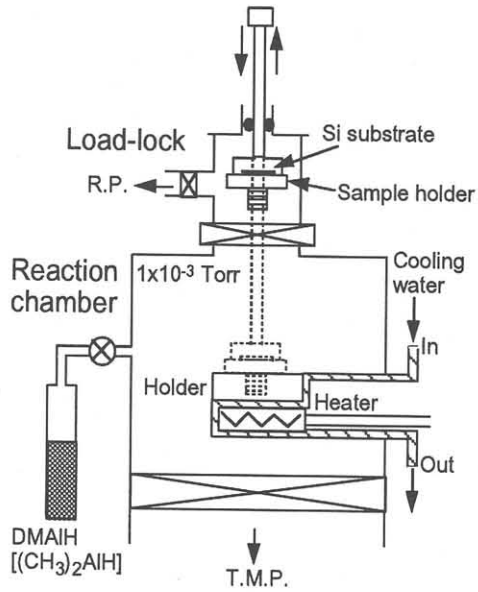

Fig. 2 A schematic illustration of experimental apparatus.

CVD chamber through a variable leak valve at a pressure of 1×10^{-3} Torr. The hydrogen desorption was observed using UHV-TDS (thermal desorption spectroscopy) whose base pressure was 1×10^{-9} Torr.

3. Results and discussion

Figure 3 shows the temperature dependence of the Al deposition rate on H-terminated and thermally oxidized surfaces. The Al deposition did not occur at substrate temperature below 220°C on the both of H-terminated and oxidized surfaces. The Al deposited on the H-terminated Si surface at 240°C and the deposition rate had maximum value at 270°C. The deposition rate on the H-terminated surface increased at temperature above 320°C and the deposition on the SiO_2 surface was observed at this temperature. In-situ XPS measurement showed that the films deposited at temperature below 290°C and above 320°C were composed of a pure Al film and a carbon contained Al film, respectively.[1] Thus, the selective growth on the H-terminated Si surface was achieved at substrate temperature from 240°C to 290°C. It is noticeable that the deposition rate of Al film on NH_4F treated Si surface is lower than that on HF treated surface.

Figure 4 (a) shows TDS spectra of the hydrogen molecules with mass number of 2 of Si(111) wafers treated by 5% HF and 40% NH_4F. The two peaks were clearly observed at 270°C and 450°C in the spectrum of HF treated wafer. In the spectrum of NH_4F treated Si wafer, the peak

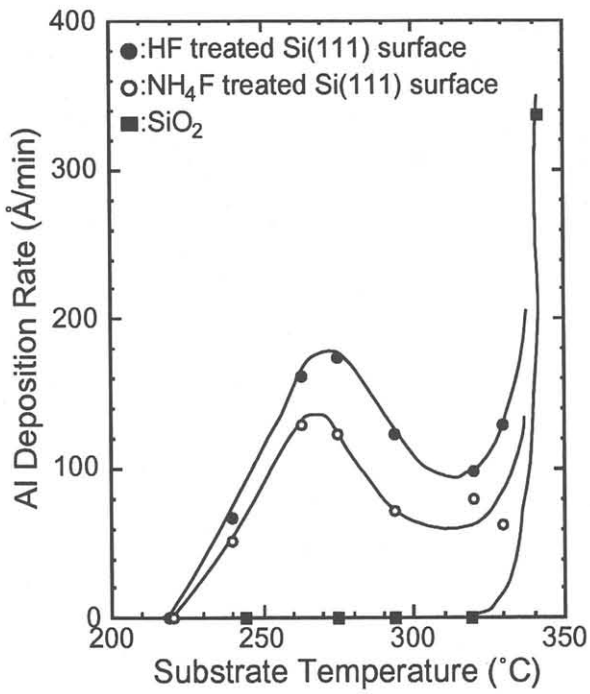

Fig. 3 The temperature dependence of the Al deposition rate on H-terminated and thermally oxidized surfaces.

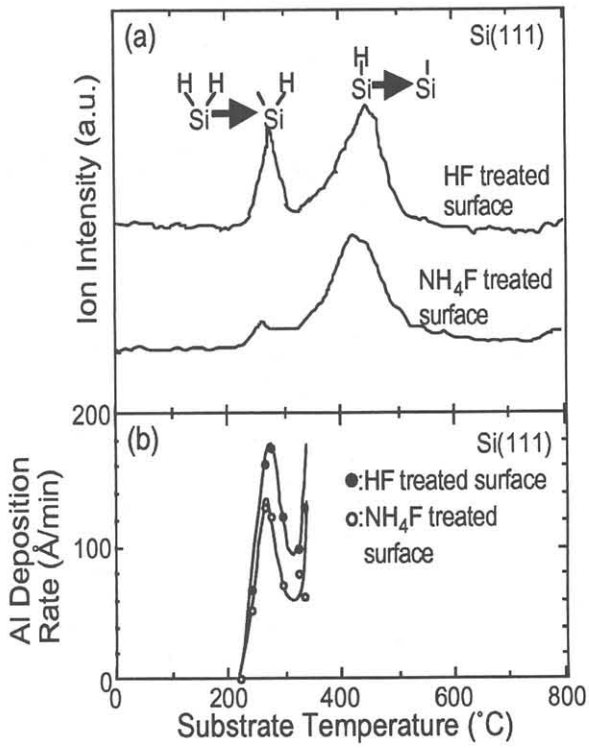

Fig. 4 (a) TDS spectra of the hydrogen molecules of Si(111) wafers treated by 5% HF and 40% NH_4F and (b) replotted Al deposition rate.

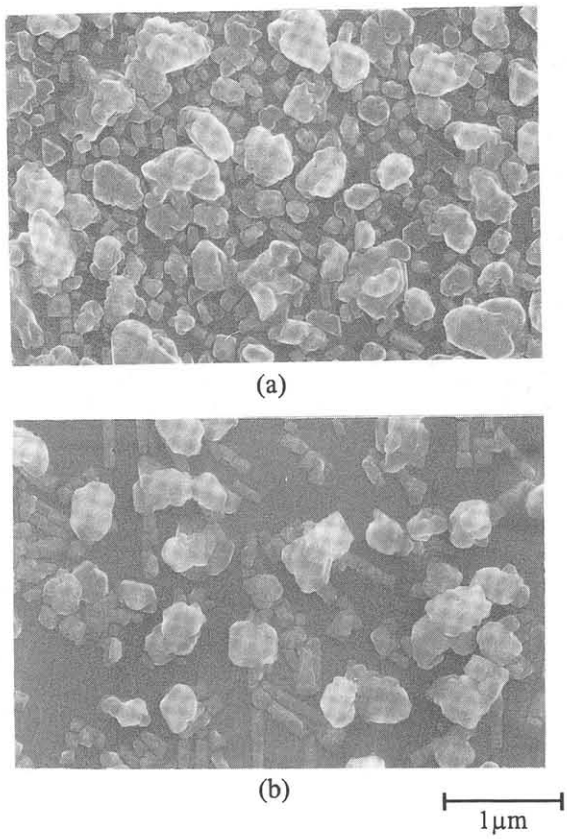

Fig. 5 SEM photographs of Al nucleus on the surface prepared by (a) 5% HF and (b) 40% NH_4F.

at 450°C is dominant and the peak at 270°C is small. The higher temperature component is assigned to the hydrogen desorption from mono-hydride (Si-H). The lower temperature component is assigned to the hydrogen desorption from di- and tri-hydride ($Si-H_2$ and $Si-H_3$). These species are considered to exist at step edges on the Si surface. In Fig.4 (b), we replotted the Al deposition rate on the H-terminated Si surface at the same temperature range of TDS results in order to compare with the hydrogen desorption behavior. The peak temperature of hydrogen desorption from $Si-H_2$ and $Si-H_3$ in TDS spectra well coincides with the peak temperature of the Al deposition rate in Fig.4 (b).

In addition, we tried to deposit Al to the HF treated Si surface at 280°C after heat treatment in the UHV chamber at 320°C. On the basis of a result of TDS measurement, it is considered that the Si surface has no $Si-H_2$ and $Si-H_3$ and has only Si-H on the surface and then hydrogen does not desorb from the surface at a temperature range between 250°C and 300°C. We can not observe the Al growth on the Si surface after the deposition treatment by SEM observation. The results suggest that in-situ hydrogen desorption from the substrate is essential for the Al deposition employing DMAlH at a temperature range between 250°C and 300°C.

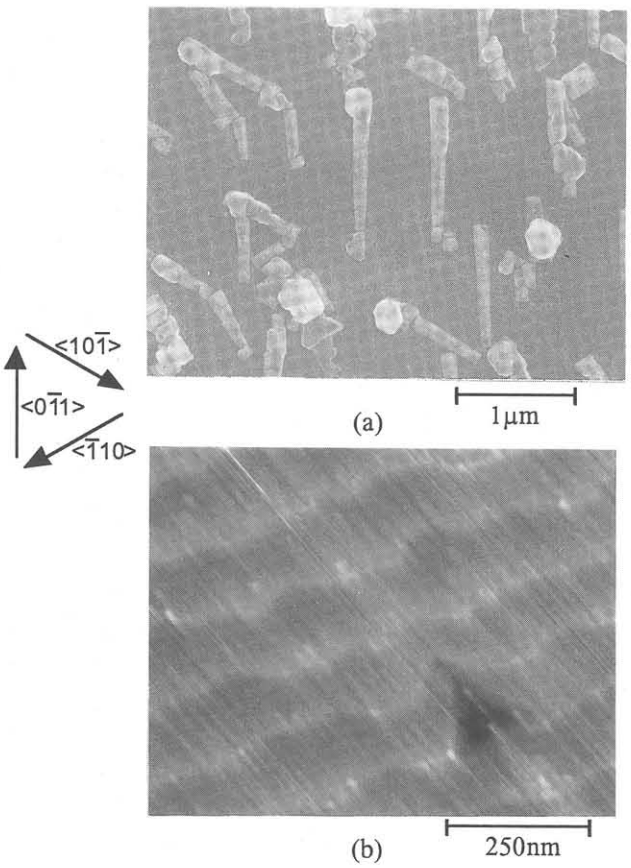

Fig. 6 (a) A SEM image of Al deposited surface at deposition time of 6 minutes and (b) an AFM image of Si substrate surface.

SEM photographs in Figure 5 show a growth behavior of Al crystal on the surfaces prepared by (a) HF and (b) NH_4F solution in the condition of deposition temperature of 270 °C and deposition time of 20 minutes. A density of Al nuclei on the surface treated by NH_4F was lower than that on the surface treated by HF. Two kinds of nucleus are observed on the NH_4F treated surface as shown in Fig. 5 (b). One of them is primary nucleation which is considered to epitaxially grow on Si(111) because of its definite growth direction. Another one without clear growth direction observed to grow on the primary Al nucleus. We estimated the growth direction of the primary Al nucleus in a SEM image of Al deposited surface at deposition time of 6 minutes shown in Fig. 6, that is compared with an AFM image of Si substrate surface. As shown Fig. 6 (a), the primary nuclei grow along [110] direction to which a lattice miss match is small in the case of Al(100) on Si(111). Moreover, the growth direction has the preferential order of <0$\bar{1}$1>, <10$\bar{1}$> and <$\bar{1}$10>. This order is proportional to an angle between the growth direction and the step edge shown in Fig. 6 (b).

4. Conclusions

The results intensively suggest that the Al deposition reaction is induced by the hydrogen desorption from Si surface. Thus the hydrogen desorption from di- and tri-hydride is essential for the Al selective deposition at 240-290°C on the Si surface employing DMAlH and hydrogen of the mono-hydride, that is desorbed at 350°C, dose not induce the Al deposition reaction at 240-290°C. We found a new mechanism of Al-Selective deposition that the Al deposition is induced by hydrogen desorption on the H-terminated Si surface. In the early stage of Al deposition, a lower density of Al nuclei on atomically flat surface compared with on the rough surface suggests that the Al nucleation occurred at step edges on which di- and tri-hydride species exit.

References

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