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Selective Aluminum Chemical Vapor Deposition Using DMEAA

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This paper presents the use of a new precursor dimethylethylamine alane (DMEAA) to grow high-purity aluminum selectively on Si, TiN, MoN,$TiSi_2$ and CVD-W in the presence of SiO_2. The choice of DMEAA was based on its excellent thermal stability and relatively high vapor pressure of 1.2 torr at room temperature. The deposition rate on CVD-W followed the Arrhenius' equation down to 90 °C with an activation energy of 0.75 eV, which is consistent with the binding energy of Al-N. The resistivity of the film is about 3 μΩ-cm. The temperature effects on the selectivity for contact and via hole fillings were studied.

I. INTRODUCTION

One of the most challenging goals in ULSI metallization is the filling of small diameter, high aspect ratio contact and via holes. Selective and non-selective low-pressure chemical vapor deposition of aluminum is of continuing interest, because of the potential advantages of conformal coverage of irregularly shaped surfaces. Up to now, TIBA ($Al(C_4H_9)_3$) [1,2] and DMAH ($AlH(CH_3)_2$) [3,4] have been used to as a precursor for Al CVD. The selective growth onto the electrically conductive surface, and single crystal growth on the Si wafer are among the most distinguishable features of Al CVD technology [5,6].

Here we investigate Al CVD with a new precursor, dimethylethylamine alane (DMEAA, $(CH_3)_2C_2H_5N{:}AlH_3$) that has the advantages of being a liquid, high thermal stability and relatively high vapor pressure at room temperature, designed to decompose cleanly to high purity aluminum.

II. EXPERIMENTS

Aluminum was deposited by low-pressure CVD using DMEAA. Fig. 1 shows schematic of a cold-wall Al CVD system. The base pressure of the reactor was below $5x10^{-6}$ Torr. DMEAA used is a clear viscous liquid and has vapor pressure of 1.2 Torr at 20 °C, which is comparable to the DMAH vapor pressure and is almost eight times higher than that of tri-isobutylaluminum. DMEAA was synthesized according to the published procedures from dimethylethylamine hydrochloride and lithium aluminum hydride diethyl ether [7]. DMEAA, kept in a heat bath, was evaporated into the quartz reactor without using carrier gas. If argon was used as the carrier gas to bubble through the precursor, the high deposition rate would degrade the surface morphology.

The substrates used for evaluating CVD characteristics consist of conventional sputtered TiN layer, CVD MoN and CVD-W layers, on thermally oxidized Si wafers, plain Si and $TiSi_2$ wafers as well as BPSG-contact patterned Si, PECVD-via patterened aluminum wafers. Before deposition each sample was dipped in HF:H_2O (1:50) solution for 30 sec in order to remove residue oxide, followed by a deionized water rinse for 2 min.

Substrate temperature controlled by the lamp heating, ranged from 90 to 320 °C. Aluminum film was deposited at a chamber pressure of 0.2 Torr and the precursor DMEAA typically was held at 0° or 17 °C.

The film resistivity was measured with a four-point probe, and the film thickness was calibrated by a Dektak stylus profilemeter and Scanning Electron Microscope (SEM). The reflectivity of the film was measured in the Nanospec Optoreflectometer at wavelength of 365 nm, using a 5000 Å Al film as the

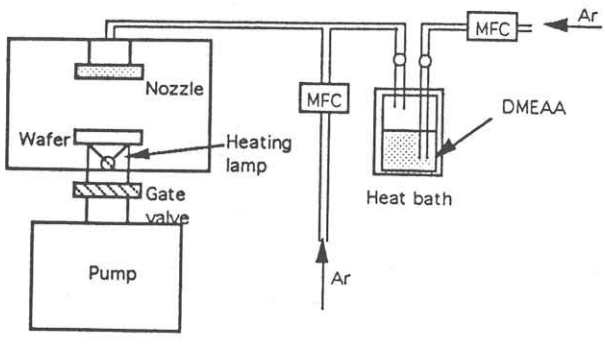

Fig.1 Schematic of the low-pressure Al CVD system.

reference. Surface morphology and the step coverage in the contact hole or via hole were characterized by SEM. Film purity was analyzed by Auger Electron Spectroscopy.

III. RESULTS AND DISCUSSION

Fig. 2 shows the deposition rates versus reciprocal deposition temperatures. CVD-W layer was used for evaluation because it has a short incubation time, as compared with sputtered TiN films. As the chamber pressure is at 200 mtorr, the deposition rate on CVD-W surface follows the Arrhenius equation down to 90 °C. Deposition rates in excess of 1800 Å/min have been obtained at temperatures of 200 °C. Above 200 °C the growth rate levels off with an activation energy of about 0.1 eV. Below 200 °C the reaction rate is completely controlled by the surface reaction with an activation energy of 0.75 eV. This value is probably is consistent with a rate-limiting Al-N bond cleavage in the case of deposition using TMAA as a precursor [8]. As the chamber pressure is lowered to 50 mtorr (the source temperature is kept at -10 °C), there is no apparent transition knee point between diffusion-limited and surface reaction-limited process. The activation energy is approximately 0.2 eV. This may be attributed as the source-limited reaction.

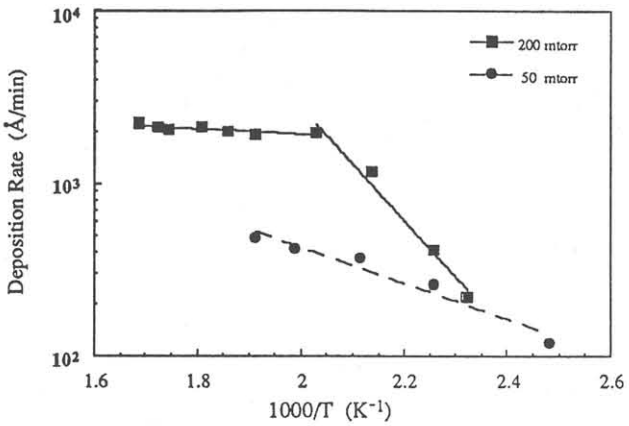

Fig.2 Deposition rate vs. reciprocal substrate temperature for CVD Al on CVD-W

Fig. 3 (a) and 3 (b) show SEM photomicrographs of CVD aluminum growth by thermal decomposition at 250 °C on Si and TiN layer, respectively. Al was not found on the electrically insulating SiO_2 surface, while it is selectively deposited on electrically conductive materials such as n-Si, p-Si, and TiN. On Si, however, the deposition rate drops rapidly with decreasing temperature and becomes practically zero below 200 °C. The average grain size for Al on Si is approximately 50 nm, ten times smaller than that found on TiN, indicating that Al nuclei are much more easily formed on more conductive materials such as TiN.

Fig. 4 shows a cross-sectional SEM photograph of 0.6 μm trench patterns after 2000 Å blanket CVD Al in-situ deposited at 200 °C on a 200 Å MOCVD-MoN layer. The trench filling profile is uniform and the aluminum surface is quite smooth. The conformal deposition can easily achieve filling unity aspect-ratio contact holes.

The purity of the film was confirmed by the AES analysis shown in Fig. 5. The carbon and oxygen levels in the Al film are below the detection limit. The MoN barrier metal layer is clearly indicated

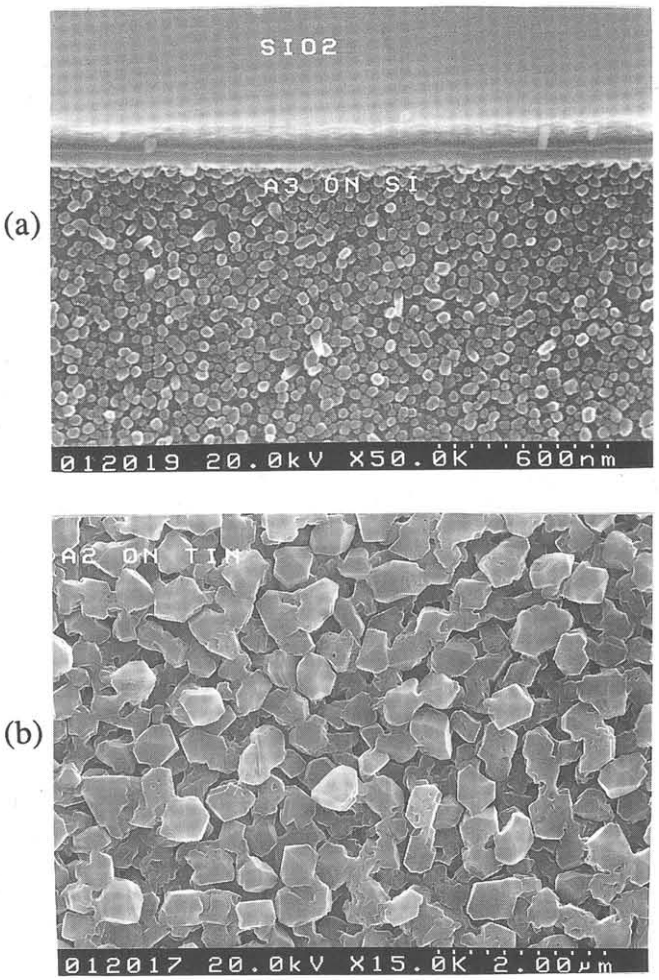

Fig.3 SEM photomicrographs of CVD Al grown (a). selectively on Si, not on SiO2, (b) on TiN

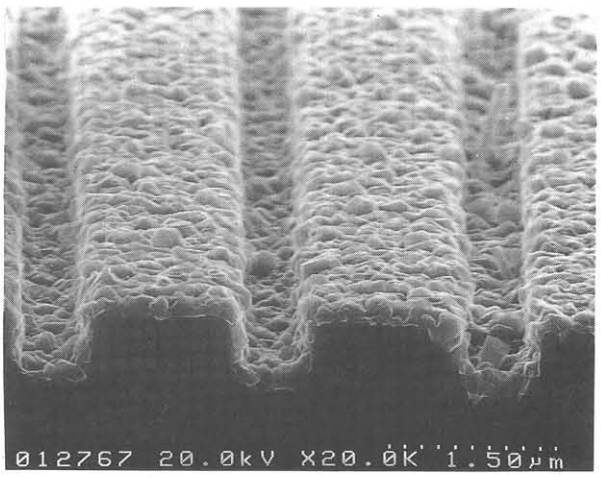

Fig.4 Cross-sectional SEM photograph of CVD Al grown non-selectively on in-situ CVD-MoN layer. Oxide trench patterns are 0.6 μm high and 0.6 μm wide.

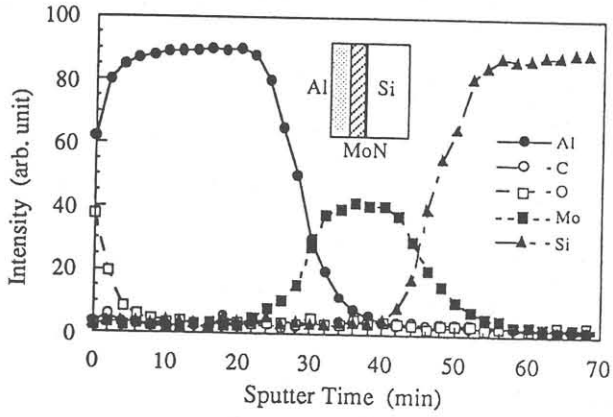

Fig. 5 AES depth profile of a 3000 Å CVD Al on in-situ deposited MoN.

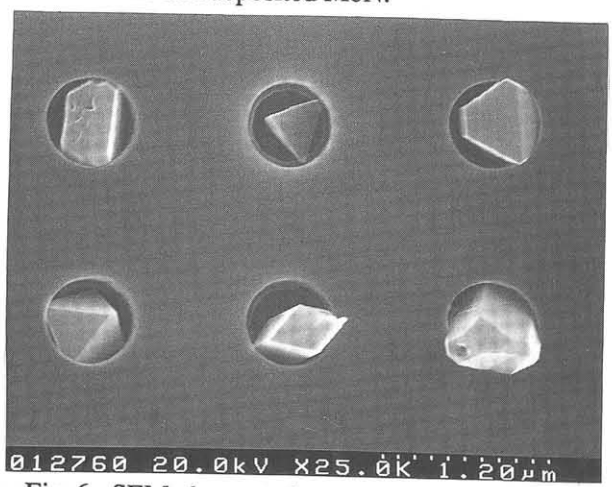

Fig.6. SEM photograph of contact hole filling by CVD Al. The contact hole is on (100) Si silicided with $TiSi_2$.

in between CVD Al and Si substrate. Resistivity measurements indicated that films with thickness between 1000 Å and 2000 Å have resistivitiy values around 2.8 to 3.0 μΩ-cm. As the films grow thicker, the surface becomes fairly rough. This will significantly affect the accuracy of film thickness measurement, and thus the resistivity estimation.

Fig. 6 shows selectively deposited Al into borophosphosilicate glass (BPSG) contact holes on (100) Si which was silicide with Ti. Diameter and depth of contact holes were 0.5 μm and 0.6 μm, respectively. The single crystal (111)-oriented Al exhibited a triangular terrace. However, a big single grain may indicate an non-uniform nucleation on the bottom of the contact hole. Therefore the voids are clearly visible from the SEM photograph. The variation of single crystal structure of CVD Al on different Si orientations has also been reported using a different precursor DMAH [3].

Increased substrate temperatures led to a reduction in selectivity. Selectivity is determined by using SEM to examine the relative amount of aluminum on the SiO_2 and on the conductive patterns. At a substrate temperature of 120 to 260 °C, Al was deposited with nearly perfect selectivity onto CVD-W patterns on SiO_2. Above 260 °C, selectivity started dropping off and by 320 °C the process was still able to maintain 90% selectivity. By comparison, above 140 °C, selectivity for gold on SiO_2 dropped off rapidly and by 180 °C the process was unselective [9]. If PECVD oxide instead of thermal oxide as mentioned in the above CVD-W/SiO_2 was used, the *critical temperatures* of selectivity loss would be lower. If this PECVD oxide received 450 °C thermal treatment, we were able to raise the critical temperature. Therefore, it is believed the moisture or O-H bonds on the surface may play an important role in the selectivity loss. This may also explain the difference of critical temperature between our data and that of Ref.9.

IV. CONCLUSIONS

We have demonstrated the selective deposotion of CVD Al using dimethylethylamine alane in advanced metallization applications. At -10 °C source temperatures, the deposition process was limited by the availability of source vapor. As the source temperature was increased to 0 °C and above, the deposition rate was found to follow Arrhenius' equation at wafer temperatures down to ~90 °C. Since Al-N bond is weak, this results in a fast growth rate. Nucleation on a variety of substrates of technological importance has been demonstrated but a more thorough understanding of this process is needed to better control film morphology. Wafer temperature has a dramatic effect on the selectivity loss. Tunsgten on SiO_2 was found to have a higher critical temperature for the selectivity loss than that of gold on SiO_2.

V. ACKNOWLEDGEMENT

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