Note

Surface Observation of Aluminum Evaporated on Silicon as Immersed in $\text{HF}:\text{NH}_4\text{F}$ Solution

Katsuro SUGAWARA* and Hiroo TOCHIKUBO*

Silicon dioxide films are deposited by the gaseous reaction of SiH_4 and O_2 on aluminum to effect mechanical protection of the metallization and insulation of the multilevel interconnections for use in integrated circuits. To open holes in these SiO_2 films for revealing the bonding pads or for forming through-holes, parts of the SiO_2 thin films are etched off by $\text{HF}:\text{NH}_4\text{F}$ buffer solution. When the surfaces of specimens thus treated are examined through an optical microscope, specific parts of the aluminum sometimes appear black or brown. An investigation of the cause of this "discoloration" has been conducted and the results are reported herein.

Surfaces of the aluminum in MOS integrated circuits were examined by an optical and/or an electron microscope after the specimens were immersed in 1 vol. $\text{HF}:\text{20 vol. NH}_4\text{F}$ buffer solution. Furthermore, to clarify the mechanism of "discoloration", the following experiment using a simplified structure was carried out aluminum was evaporated at room temperature by the resistance heating method to the thickness of 1 micron on Czochralski-grown, boron-doped, (100) oriented silicon wafers with resistivity of 7.3 ohm-cm.

As shown in Fig. 1, a dark "C" part and a white "E" part on the same wafer with MOS integrated circuit structures were observed under the microscope. Fig. 2 (a) and 2 (b), electron micrographs, corre-

spond with "C" and "E" in Fig. 1, respectively. The white "E" region is comparatively flat as seen in Fig. 2 (b) but the dark "C" region etched by the buffer solution, becomes irregular and appears black under the optical microscope due to diffused reflection on the uneven aluminum surface.

(a)

(b)

Fig. 2 Surfaces of aluminum observed through an electron microscope

Fig. 2 (a) and (b) correspond to the dark "C" part and the white "E" part, respectively, in Fig. 1

Fig. 1 Surfaces of an MOS integrated circuit after immersion into 1 vol. $\text{HF}:\text{20 vol. NH}_4\text{F}$ buffer solution

* Semiconductor & Integrated Circuits Div., Hitachi, Ltd. (1450 Josuihon-cho, Kodaira-shi, Tokyo)

Different surfaces of aluminum on the same wafer were observed after immersion into the buffer solution. To investigate this cause, a voltaic potential difference between aluminum and silicon in the buffer solution was measured with a potentiometer. As a result, a potential difference of about 0.6 V was obtained, silicon being anodic and aluminum cathodic.

The standard electrode potential of Eq. [1] is -2.1 V when Al becomes AlF_6^{3-} , while that of Eq. [2] is -1.2 V when Si becomes SiF_6^{2-} ,¹⁾ so that the difference between two potentials is fairly consistent with the experimental result.

This measurement indicates the formation of an electric cell between the silicon and aluminum in the solution. Then the electric current between these two substances was measured. One electrode was silicon and the other was aluminum evaporated on silicon, the back side of which was covered with wax. The change of electric current between aluminum and silicon was recorded. Fig. 3 is an example of curves thus obtained. The abscissa shows the time after immersion of the aluminum into the buffer solution and the ordinate shows the current density passed between the two electrodes. Soon after the aluminum electrode was immersed into the buffer solution, large elec-

Fig. 3 An example of transient electric current passed between the silicon and aluminum in 1 vol. HF : 20 vol. NH_4F buffer solution

tric current was recorded and about 20 seconds later it decreased, leveling off at about one-tenth of the maximum current. This phenomenon can be explained by the competition between aluminum dissolution and passivation reactions. Thus, the passive film²⁾ was formed on the aluminum surfaces, resistant to HF solution, caused by reaction between the aluminum and NH_4F . Moreover, it was observed that the surface roughness depended on the quantity of electricity passed to reach the constant current. When the quantity flowed was more than 2×10^{-3} Coulomb/cm², the reflectivity diminished. In Fig. 1, the white "E" part is connected to the "gate" SiO_2 insulating film, which lies between silicon and aluminum to prevent the formation of the local electric cell in the buffer solution, while the dark "C" aluminum part is connected with silicon directly to allow electric current pass. This difference of the passage caused the "discoloration" of the aluminum pads evaporated on the same silicon wafer.

More details concerning aluminum surfaces relating to composition of the buffer etching solution, the existence of a *P-N* junction in a silicon electrode and the annealing of aluminum will be reported in the near future

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