Corrosion at the Grain Boundary and a Fluorine-Related Passivation Layer on Etched Al-Cu (1 %) Alloy Surfaces

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After etching Al-Cu alloy films using SiCl4/Cl2/He/CHF3 mixed gas plasma, the corrosion phenomenon at the grain boundary of the etched surface and a passivation layer on the etched surface with an SF6 plasma treatment subsequent to the etching were studied. In Al-Cu alloy system, corrosion occurs rapidly on the etched surface by residual chlorine atoms, and it occurs dominantly at the grain boundaries rather than the crystalline surfaces. To prevent corrosion, the SF6 gas plasma treatment subsequent to etching was carried out. The passivation layer is composed of fluorine-related compounds on the etched Al-Cu surface after the SF6 treatment, and it suppresses effectively corrosion on the surface as the SF6 treatment pressure increases. Corrosion could be suppressed successfully with the SF6 treatment at a total pressure of 300 mTorr. To investigate the reason why corrosion could be suppressed with the SF6 treatment, behaviors of chlorine and fluorine were studied by various analysis techniques. It was also found that the residual chlorine incorporated at the grain boundary of the etched surface accelerates corrosion and could not be removed after the SF6 plasma treatment.

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I. INTRODUCTION

Aluminum and its alloys are widely used as the interconnection material for the VLSI circuits because of their good characteristics, such as low resistivity, low cost, and good adhesion, etc. As feature sizes of the device become smaller, chip areas become larger and the metal lines become finer. For a high performance and reliability of the metallizations, Al-Cu alloy films are utilized because the Cu atoms in Al-Cu alloy system improve the resistance to electromigration [1]–[3]. Plasma etching technique using chlorine contained gas chemistries is commonly used for patterning Al and its alloy films. However, there is a serious problem in Al and Al-alloy plasma etching processes, such as corrosion by the residual chlorine atoms on the etched metal surface. Corrosion on the etched surface occurs rapidly upon atmospheric exposure and degrades the performance and reliability of the device. There has been intensive research in the corrosion phenomena to prevent or to avoid it [4]–[8]. It was well known that the corrosion effects might be prevented by substitution of fluorine for the residual chlorine atoms with the SF_6 treatment [9]–[10]. Recently, however, there are fresh reports for the corrosion mechanism, which corrosion is suppressed by the passivation layer of the fluorine-related compounds on the etched surface [11]–[14].

In this study, the corrosion phenomenon at the grain boundary of the etched Al-Cu film surfaces has been investigated by scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). An existence of the passivation layer, which is composed of the fluorine-related compounds on the etched surfaces, was demonstrated by transmission electron microscope (TEM).

The effect of the SF_6 plasma treatments subsequent to etching, which suppresses corrosion effectively by the fluorine-related passivation layer, was investigated.

II. EXPERIMENTAL

The samples were prepared using (100) boron doped 125 mm Si wafers in the resistivity ranges of 0.85–1.15 Ωcm. After dilute HF cleaning, an oxide layer was deposited in the thickness range of 6000 Å by low pressure chemical vapor deposition (LPCVD). The Al-Cu alloy films were deposited successively in the thickness range of 8000 Å by the sputtering system. The sputtering target was an Al-alloy containing 1 wt.% Cu. Plasma etch of the Al-Cu alloy films was carried out by SWE 654 etching system of Balzers Co. Etching of the Al-Cu films was carried out under $SiCl_4/Cl_2/He/CHF_3$ mixed gas plasma at a pressure of 600 mTorr. The lower electrode and chamber wall temperatures of 20 °C and 70 °C, respectively, were utilized during etching the Al-Cu alloy films. The helium gas was used for carrier gas and the partial pressures of the $SiCl_4$, Cl_2, and CHF_3 were 210, 16, and 9 mTorr, respectively. At the same time, the RF power was 240 watts at each etching condition. The Al-Cu films were etched partially to a thickness of 6000 Å, and corrosion was investigated on the remaining surfaces after exposure to air for 10 minutes. For some samples, to investigate the SF_6 treatment effects on corrosion, the SF_6 plasma treatments subsequent to etching were carried out immediately in the same reaction chamber and the temperatures were also the same as those of the Al-Cu etching step. The treatments were carried out at the total pressure of 100, 200 and 300 mTorr, respectively. The flow rate of SF_6, RF power, and treatment time were kept constant by 50 sccm, 50 watts, and 30 seconds, respectively. After the SF_6 plasma treatments, samples were exposed also to the atmospheric environment. The etched metal surfaces with or without the SF_6 treatment were compared with those of as-deposited ones by SEM. To investigate the composition and the chemical bonding states on the etched surface, XPS narrow scan analyses were carried out. The AES point analyses were carried out to investigate the corrosion phenomena between at the crystalline surface and at the grain boundary regions. To demonstrate the existence of the passivation layer, TEM analysis was carried out.

III. RESULTS AND DISCUSSION

1. Corrosion at the Grain Boundary

Figure 1 shows the SEM images of the Al-Cu alloy surface. Figure 1(a) shows the as-deposited surface. Figure 1(b) shows etched surface, which was treated with the SF_6 plasma at a pressure of 300 mTorr and then exposed to air for 10 minutes.

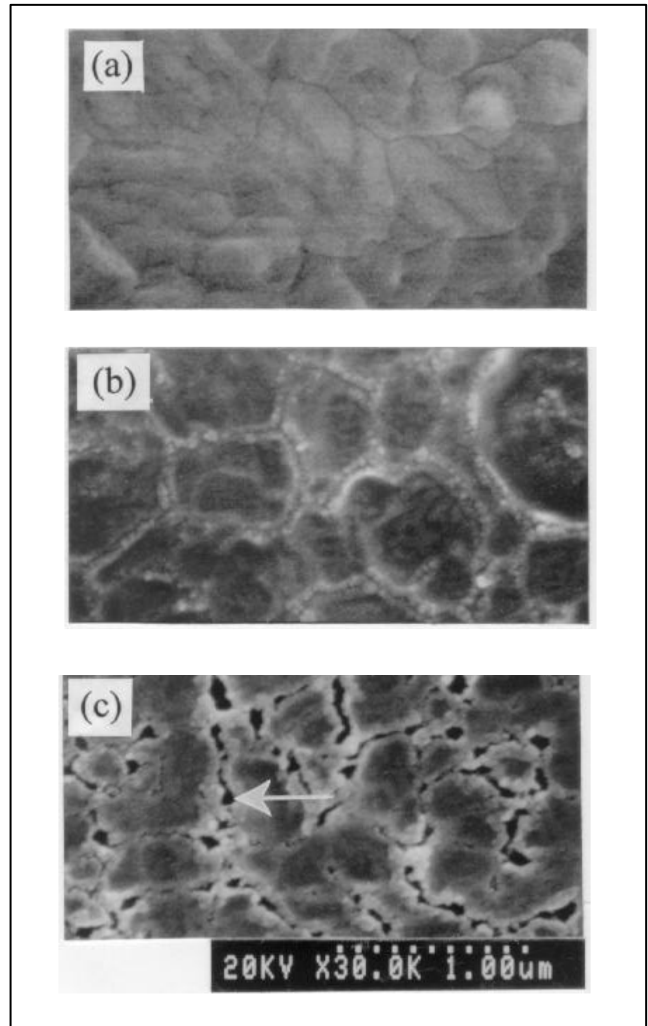

Fig. 1. SEM photographs of the Al-Cu alloy film surface: (a) as-deposited surface, (b) etched surface with the SF_6 plasma treatment in the pressure of 300 mTorr, and (c) etched surface without the SF_6 treatment.

This shows that the grain boundaries are clearer than that shown in Fig. 1(a), but corrosion on the surface does not occur. Figure 1(c) shows the typically corroded surface which was exposed to air subsequent to etching without a SF_6 plasma treatment. The arrow shown in the Fig. 1(c) indicates the corroded position. Figure 1(c) shows that corrosion occurs rapidly on the etched surface by residual chlorine atoms, and it occurs dominantly at the grain boundaries rather than the crystalline surfaces. Corrosion is due to HCl, which is produced by reaction of the residual chlorine atoms with moisture in air. However, the SF_6 treatment subsequent to etching successfully suppresses corrosion on the etched surface as shown in Fig.1 (b).

Figure 2 shows the AES point spectra for chlorine and fluorine atoms in the different regions. The intermediate regions shown in Fig. 2 (a) and (b) represent the area between the crystalline and the grain boundary region. The samples were

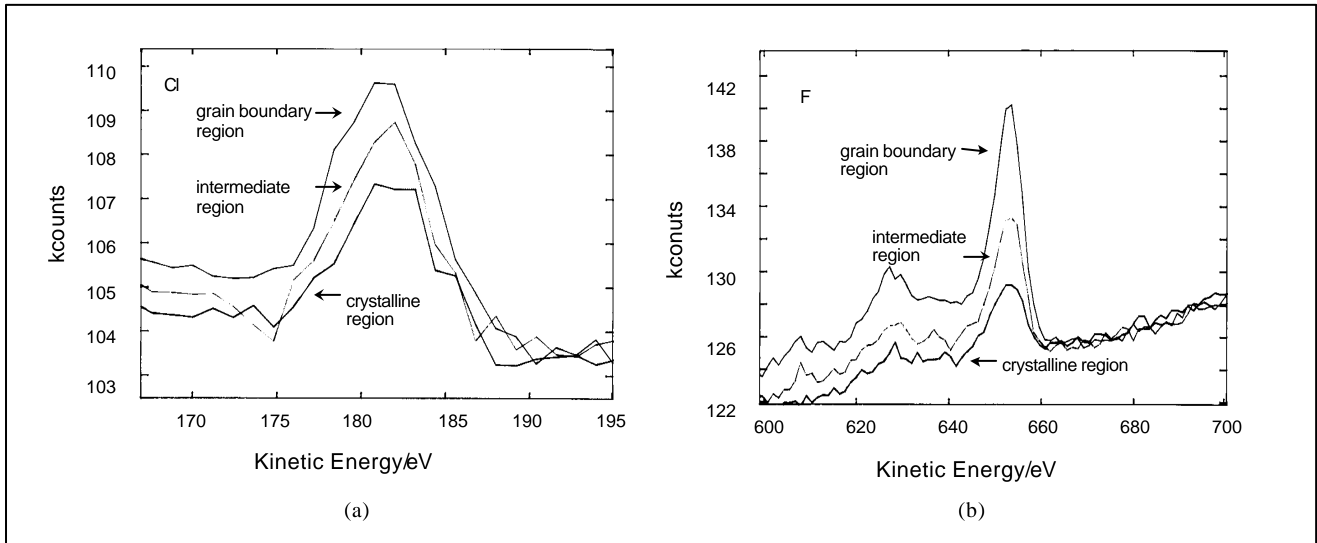

Fig. 2. AES spectra on different regions at etched Al-Cu alloy film surfaces for: (a) chlorine, (b) fluorine.

treated with the SF_6 plasma subsequent to etching at a pressure of 300 mTorr. If the sample surface is flat and smooth, from AES results it can be confirmed that there exist relatively large amounts of the chlorine and fluorine atoms at the grain boundary compared with those in the other regions. There seem to be due to the structural imperfection of the grain boundary. The residual chlorine atoms incorporate into the grain boundary and they could not be removed easily during the SF_6 treatment. Even though there still exists many chlorine atoms in the grain boundary region, corrosion does not occur in the SF_6 treated samples. However, in the case of non-treated samples, corrosion occurs rapidly with exposure to air as the previous discussion shown in Fig. 1(c). For the fluorine spectra as shown in Fig. 2(b), the results are same as for the case of the chlorine atoms. There is large amount of fluorine atoms at the grain boundary after the SF_6 treatments. With the consideration of Fig. 2(a) and (b), there exists relatively large amount of chlorine and fluorine atoms in the grain boundary region, corrosion does not occur in the SF_6 treated samples. This implies that the remaining chlorine atoms do not react with moisture by a fluorine-related compound layer on the etched surfaces after the SF_6 treatment.

2. Passivation Layer Due to Fluorine-Related Compounds

Figure 3 shows the atomic species and their contents on the etched surface determined by XPS analyses. The etched surface was treated with the SF_6 plasma by the various treatment pressures. The atomic content of fluorine on the surface increases as the treatment pressure increases, while that of oxygen atom decreases. The oxygen atoms may come from exposure to air. In the case of chlorine, however, the atomic content is not affected with the SF_6 treatment. This is very interesting. If

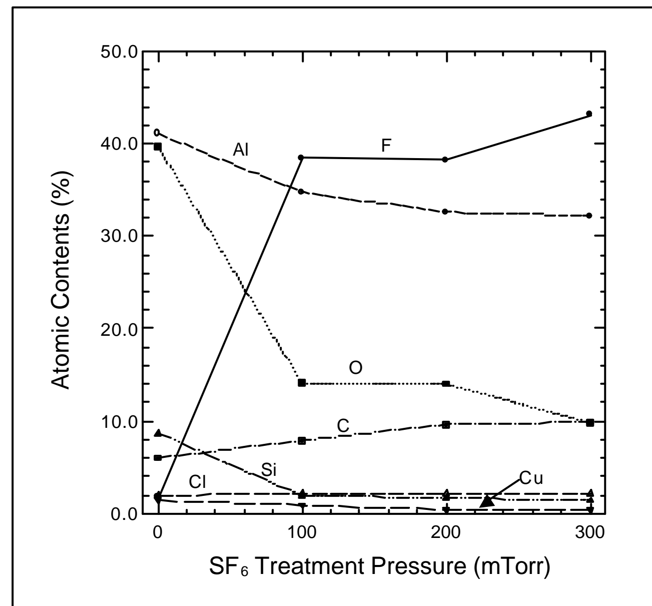

Fig. 3. Atomic species and their contents variation on etched Al-Cu surface with the SF_6 treatment pressure. Zero mTorr in the x-axis means non-treated case.

the fluorine atoms substitute for the chlorine atoms, the atomic content of chlorine should decrease as that of the fluorine atom increases. However, the atomic content of chlorine does not change. With the above considerations of fluorine, oxygen and chlorine atoms on the Al-Cu surface, it is appropriate to assume that a passivation layer on the surface would be formed by fluorine-related compounds, and the layer becomes more ef fective as the SF_6 treatment pressure increases. The passivation layer prevents the oxygen and moisture in air from penetrating, and the residual chlorine under the passivation layer does not react with moisture. So, corrosion is significantly suppressed.

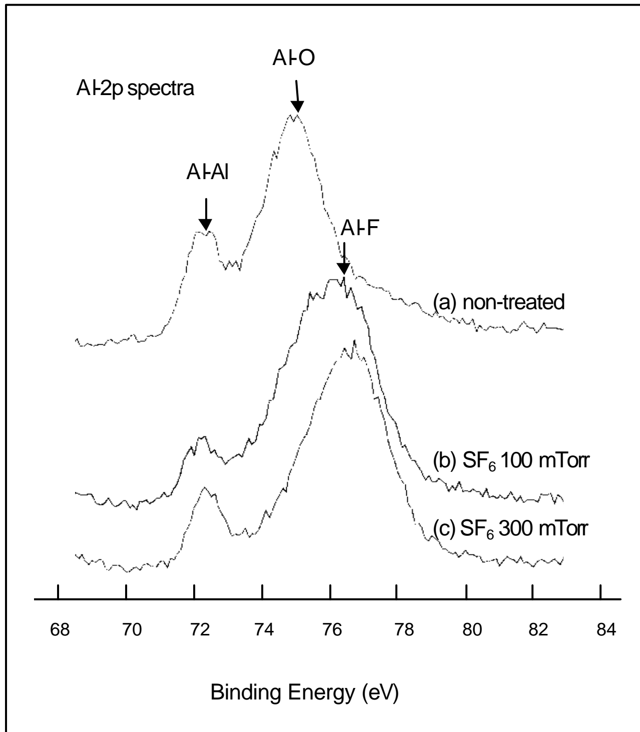

Fig. 4. Al-2p narrow scan spectra for the samples: (a) non-treated sample, (b) with the SF_6 treatment in the pressure of 100 mTorr, and (c) with the SF_6 treatment in the pressure of 300 mTorr.

To confirm the validity of the above assumptions, an XPS narrow scan analysis for aluminum was carried out in order to investigate the chemical bonding states with the SF_6 treatment pressures. Figure 4 shows the narrow scan spectra of Al-2p states on the etched surfaces. Figure 4 (a), (b), and (c) represent the spectra for non-treated sample, for a sample treated with 100 mTorr, and for a sample treated with 300 mTorr, respectively. All the samples have been also exposed to air for 10 minutes. In the case of non-treated sample, there is a peak for the Al-O chemical bonding states, which is shown at Al_2O_3 peak position in Fig. 4(a). For treated samples as shown in Fig.4 (b) and (c), the peak for the Al-F states shifts gradually to the AlF_3 position as the SF_6 treatment pressure increases, while the peak for Al-O states diminishes. For the aluminum bonding states, however, the peak position is not changed in all the samples with or without SF_6 treatment. This means that the Al-F states on the SF_6 treated surface prevent the oxygen penetration from air, and they also suppress corrosion effectively by prevention of moisture penetration. The results shown in Fig. 4 are coincident with those in Fig. 3. That is, the atomic content of oxygen in Fig. 3 decreases as the SF_6 treatment pressure increases, while the fluorine content increases.

To investigate the behavior of chlorine atoms in this system, a narrow scan analysis for chlorine was also carried out. Figure 5 shows the spectra of Cl-2p. Figure 5 (a), and (b) represent the spectra for the non-treated sample and for the SF_6 treated sample, respectively. The peak position and shape of Cl-2p spectra do not change with or without the SF_6 treatment. This means that the chlorine atoms still exist on the etched surface in spite of the SF_6 treatment, and the amount of chlorine atoms is nearly the same as that in non-treated sample. We have already discussed this result for chlorine atoms as shown in Fig. 3. It is noted the facts that the SF_6 treatment could not eliminate the residual chlorine atoms, however, corrosion was not observed for the sample treated at the SF_6 pressure of 300 mTorr. So it can lead to conclude that a certain layer would be formed on etched Al-Cu surface after the SF_6 treatment, called passivation layer.

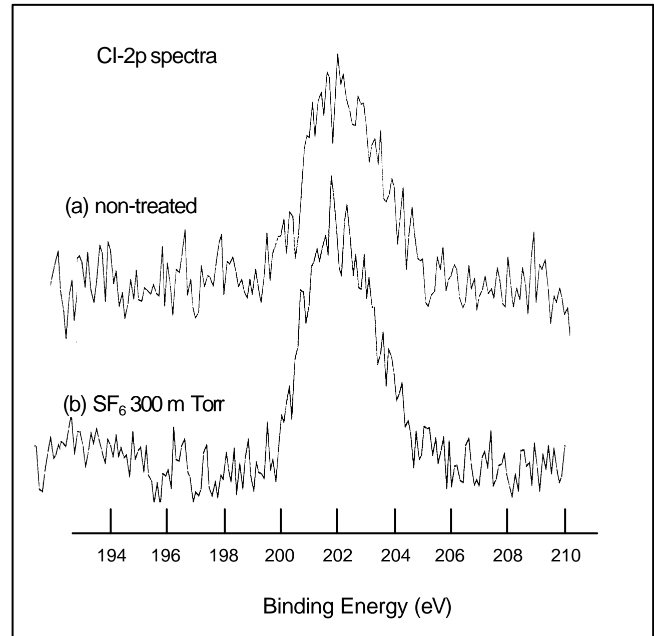

Fig. 5. Cl -2p narrow scan spectra for the samples: (a) non-treated sample, (b) with the SF6 treatment in the pressure of 300 mTorr.

To demonstrate the existence of the passivation layer, the TEM analysis has been carried out on the etched surface after the SF_6 treatment. Figure 6 shows cross sectional view of the etched Al-Cu surface for the SF_6 treated sample. It shows that the passivation layer exists on the etched Al-Cu surface in the thickness ranges of several 100 Å The passivation layer during the SF_6 treatment is formed on the etched surface, which contains the large amount of the residual chlorine atoms and may be composed of the Al-F compounds. The passivation layer prevents the moisture penetration from air, and corrosion is successfully suppressed not by the fluorine substitution for the chlorine but by this passivation layer.

IV. CONCLUSIONS

Corrosion of Al-Cu alloy surfaces after etching using $SiCl_4/Cl_2/He/CHF_3$ gas plasma was studied with SEM, AES,

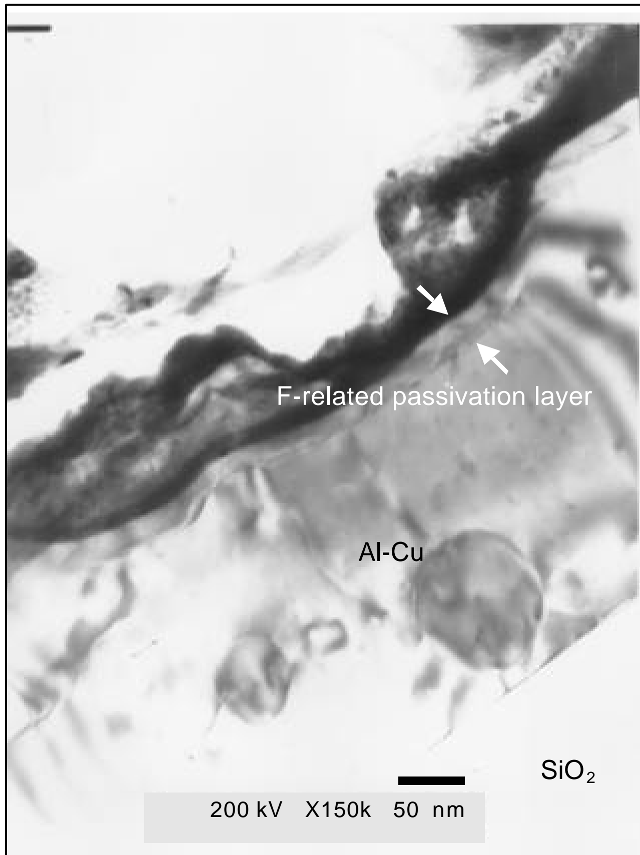

Fig. 6. TEM image of the fluorine-related passivation layer on the etched Al-Cu alloy surface.

XPS, and TEM. For the sample without the SF_6 treatment, corrosion occurs significantly at the grain boundary rather than at the crystalline surface by residual chlorine atoms after air exposure. An SF_6 plasma treatment subsequent to etching effectively prevents corrosion when the SF_6 gas pressure is 300 mTorr. However, the SF_6 treatment could not eliminate the chlorine atoms on the etched surface. Corrosion prevention mechanism, which the fluorine atoms on the etched surface are not substituted for chlorine atoms but would form a passivation layer on the surface composed of fluorine-related compounds during the SF_6 treatment, is found. The existence of the passivation layer on the etched surface is demonstrated by TEM analysis. The passivation layer prevents the penetration of moisture onto the etched surface and suppresses corrosion successfully.

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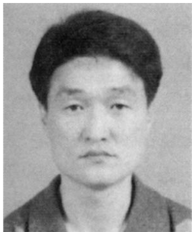

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