Extended Abstracts of the 16th (1984 International) Conference on Solid State Devices and Materials, Kobe, 1984, pp. 51-54

Surface Morphology and Corrosion in Aluminum Alloy Thin Films

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A new method has been proposed which is easily able to evaluate the degree of corrosion of Al and Al alloy films. It has been demonstrated that Al-Si films sputtered in the condition that the H2O partial pressure in residual gas is low,have much resistance to corrosion. The role of Mg or Cu in Al alloy which is effective for improvement of surface morphology has been also clarified.

1. Introduction

In VLSI devices,Al multi-level interconnection technology comes to be one of the most important technologies. Many problems about Al metallization in the technology have been pointed out. For example,(1)Al spikes in case of shallow junction (2)resistance increase in small-area contact (3)poor step coverage at via hole edge (4)hillock growth which reduces the dielectric breakdown strength of interlevel insulator. From also a reliability point of view, (5)electromigration failure of Al fine line at steps and via hole edges (6)Al corrosion failure accompanied with spreading of plastic packages.

This paper describes the results examined in order to find out Al film properties with strong corrosionproof. It proposes,first, a new method which is easily able to evaluate the degree of Al corrosion and demonstrates ,second,the relation between corrosionproof and surface morphology and examines, lastly, the deposition condition to get the Al film with strong corrosion resistance.

2. Experimental

Various Al alloy films were deposited onto oxidized Si wafers 1 μm thick by dc magnetron sputtering, monitering the residual gas in the chamber with a quadrapole mass spectrometer. Subsequently following photolithography, their films were sintered at 500°c for 20 min. in H_2 gas. Then they were exposed to high pressured saturated water vapor ambience containing NaCl or no in the wafer state (hereafter saying Pressure Cooker Test: PCT).

Evaluation of Al corrosion resistance was by mainly spectroreflectivity and surface morphology was observed with SEM, and impurities in Al alloy films were measured with SIMS and XPS.

3. Results and Discussion

3.1 Evaluating method of Al corrosionproof

Optical reflectivity (R) of as-sputtered Al alloy film at wavelength (λ) between ultra violet and visible light monotonically decreases as wavelength becomes short as shown in Fig.1. On the other hand, spectroreflectivity curve of Al alloy film after PCT indicates an interference between reflection ligtht (R1) from the corroded layer surface and reflection light (R2) from uncorroded Al layer surface. And the mean slope of spectroreflectivity curve changes from plus to minus according to the degree of corrosion at wavelength between 400 nm and 500 nm. The change in the reflectivity at short wavelength is due to formation of $Al(OH)_3$ near the surface of Al alloy film which has large optical absorption coefficient. According as corroded layer becomes thick, R1 becomes dominant in short wavelength region. As a result, it might be considered that reflectivity increases at short wavelength. Consequently, the degree of Al corrosion could be evaluated by the difference of spectroreflectivity curve between before PCT and after PCT.

Quantitative method to evaluate Al corrosion resistance in this experiment is as follows; (1)thickness (d) of the corroded layer formed on Al metallization area and (2)change rate of mean slope of spectroreflectivity curve. The former is able to be estimated from (1) equation by measuring peak to peak difference in wavenumber of interference fringe.

$$d = 1/(2n \cdot \Delta k) \qquad (1)$$

where n; refractive index

Δk; difference in wavenumber

The latter is able to be estimated with (2) equation

$$\Delta R/dt \quad (\Delta R \text{ gradient}) \qquad (2)$$

where $\Delta R \equiv (R400-R500)/R500$

R400,R500; Reflectivity at wavelength 400nm,500nm respectively

Next electric resistance change in Al alloy stripes without capping in ceramic packages after PCT were measured to verify the validity of the method mentioned above. Fig.2 shows both the results estimated by the method and voltage change at constant current. ΔR of all Al alloy film are minus before PCT, it turns however, to plus gradually after PCT. It can be judged from $\Delta R/dt$ that the degree of corrosion of pure Al and Al-Si-Mg is rather heavy. It also can be indicated that almost all of pure Al layer is corroded but Al-Si film is hardly corroded. On the other hand, the voltage change agreed with the results mentioned above as shown in Fig.2(c).

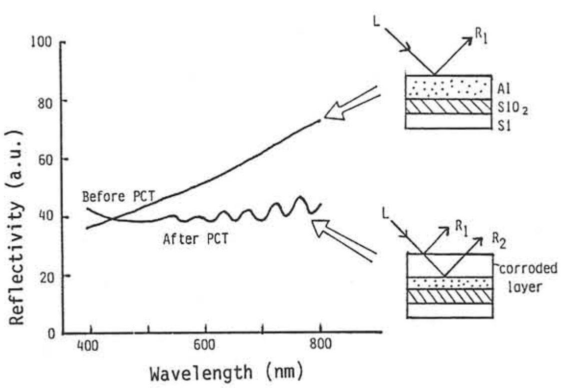

Fig.1 Spectroreflectivity curve of Al alloy film both before PCT and after PCT

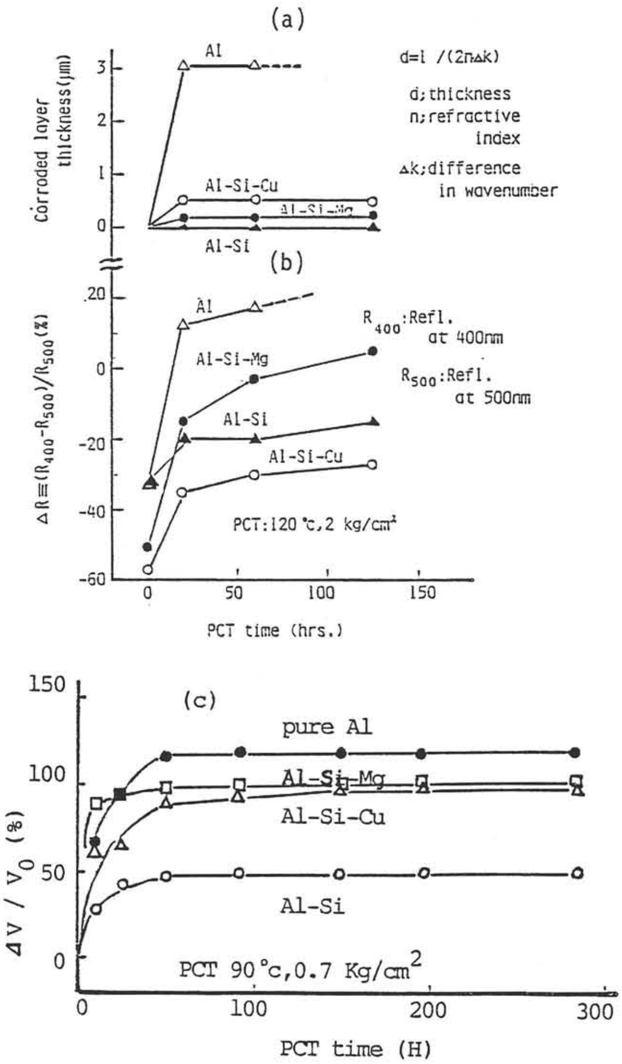

Fig.2 Effects of PCT on (a)thickness (b)ΔR of corroded Al surface and (c)electric resistance in Al alloy stripes

3.2 The relation between corrosionproof and surface roughness

Effects of PCT on ΔR and $\Delta V/V_0$ of Al-Si films with different reflectivities are shown in Fig.3. ΔR of the film with reflectivity 26%,29% which surface is rough, changes more quickly than that of the film with reflectivity 59% by PCT in Fig.3(a). ΔR gradient at PCT time till saturation shown by arrows are indicated in the table of Fig.3(a). It is clear from the results that the lower reflectivity is, the larger ΔR grad. is. And it is indicated that the lower reflectivity is, the larger $\Delta V/V_0$ at const. current becomes in Fig.3(b).

The result under high pressured saturated water vapor ambience containing 900 ppm NaCl had also the same tendency with those under ionized water ambience as shown in Fig.4. So it is concluded that Al-Si films with low reflectivity are easy to be corroded.

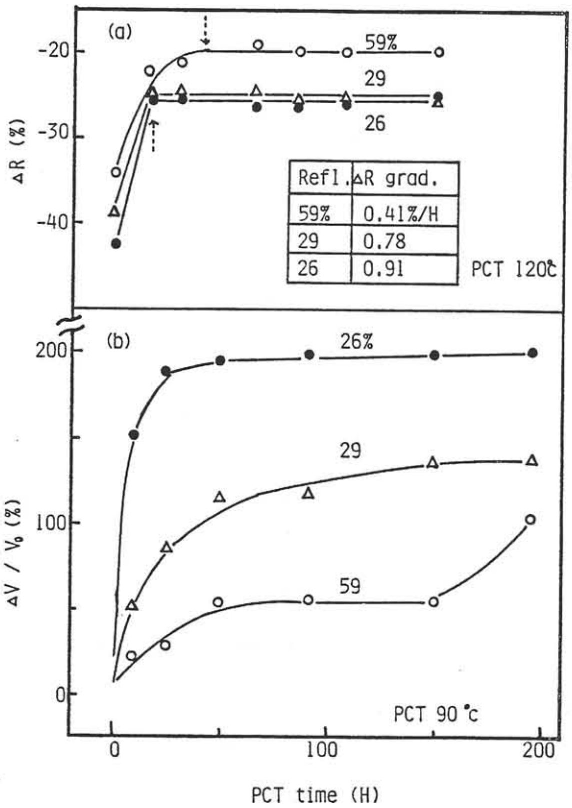

Fig.3 Effects of PCT under ionized pure water ambience on (a) ΔR and (b) $\Delta V/V_0$ of Al-1.5%Si films with different reflectivities

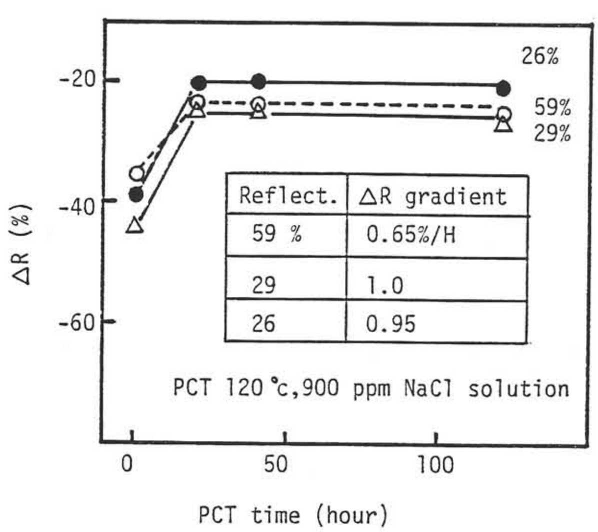

Fig.4 Effects of PCT under water containing 900 ppm NaCl on ΔR of Al-1.5%Si films with different reflectivities

And also the result has been obtained that reflectivity of Al alloy film is inversely proportional to the hillock density as shown in Fig.5 Therefore surface morphology should be smooth to improve the corrosionproof.

3.3 Factors effected on Al surface morphology

The relation between reflectivities of Al alloy films and residual gas before deposition were examined with a quadrapole mass spectrometer. It was clarified that water vapor, O2 , N2 in residual gas has harm influence on reflectivity of Al-Si film. As shown in Fig.6, however, Al-Si-Mg and Al-Si-Cu films are insensitive against water vapor. Next the correlation between impurities in Al alloy films and reflectivity was examined. Fig.7 shows oxygen ion intensity normalized by Al ion intensity measured with SIMS in Al alloy films with different reflectivities. AS a result, it was obtained that oxygen,perhaps produced by dissolution of water vapor,is the most correlative with reflectivity and reflectivity is inversely proportional to the oxygen intensity and even if the oxygen intensity of Al-Si-Mg and Al-Si-Cu film is higher than that of Al-Si film by more than 1 order, their reflectivities are higher than Al-Si's. Therefore it can be concluded that Al-Si-Mg and Al-Si-Cu films are insensitive against impurities particullarly water vapor.

Impurity redistributions in Al-Si-Mg and Al-Si-Cu film by annealing were measured with SIMS to examine the reason why Al-Si-Mg and Al-Si-Cu films are insensitive against water vapor. Oxygen was redistributed in correspondence with Mg and Cu, respectively in Fig.8. Moreover Mg2p and Cu2p spectra at 500 Å depth from their film surface were analized with XPS. Metallic Mg and Cu peak were not detected but MgOx and CuOx peak were observed as shown in Fig.9. Consequently it can be considered that Mg or Cu is combined with water vapor in residual gas and precipitates in the form of MgOx or CuOx at the Al grain boundary and as a result, hillocks which cause the decrease of reflectivity might be suppressed.

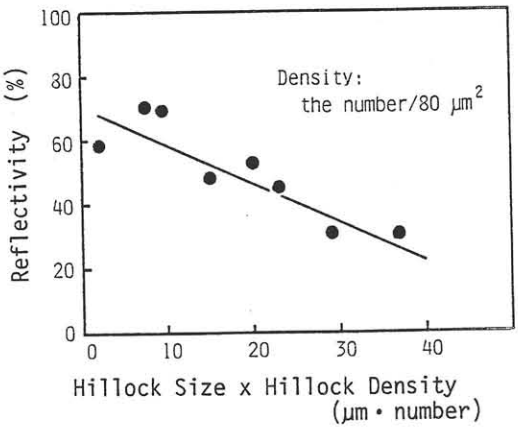

Fig.5 The relation between reflectivity and hillock density

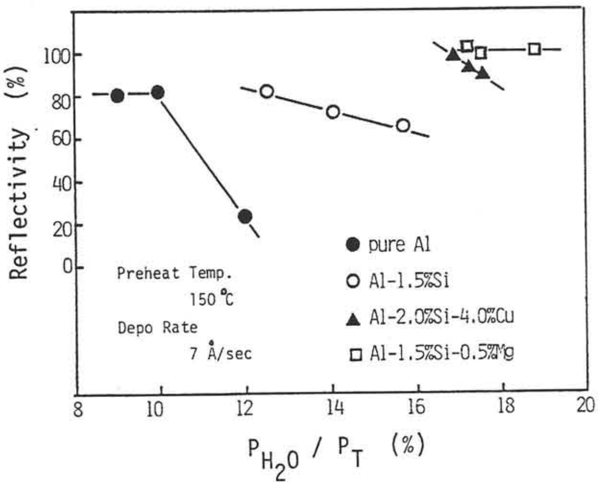

Fig.6 Effects of water vapor in residual gas before deposition on reflectivity of various Al alloy films

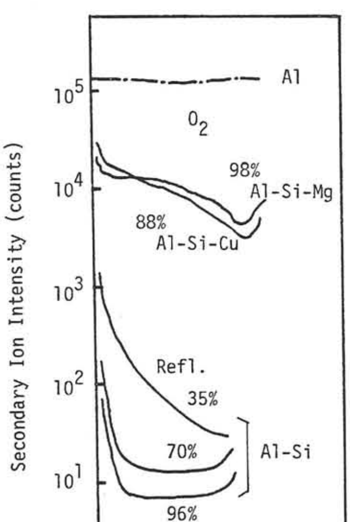

Fig.7 Normalized oxygen intensity in Al alloy films with different reflectivities

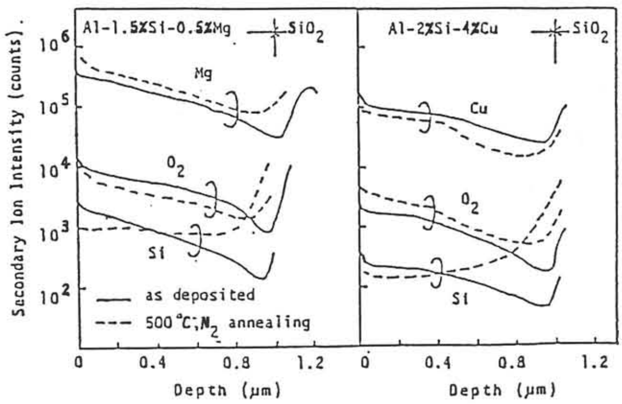

Fig.8 Impurity redistributions measured with SIMS in Al-Si-Mg and Al-Si-Cu films by annealing

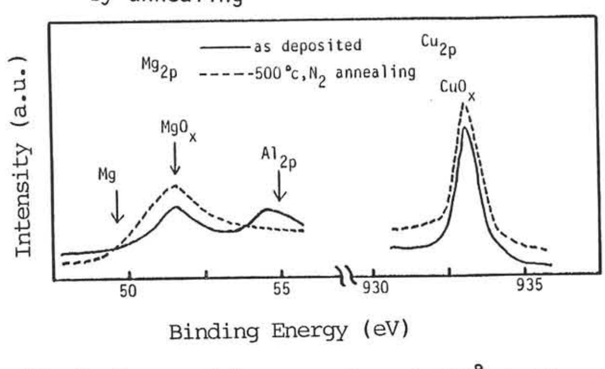

Fig.9 Mg_{2p} and Cu_{2p} spectra at 500Å depth from Al-1.5%Si-0.5%Mg and Al-2%Si-4%Cu film surface, respectively with XPS

4. Conclusion

We proposed an effective method to evaluate the degree of the corrosionproof easily and verified the validity. We also demonstrated strong correlation between corrosionproof and smoothness of Al alloy film surface by this method. And deposition conditions for high reflectivity were investigated to get Al alloy film with high corrosionproof. As a result,it was obtained that water vapor in residual gas is the most correlative with low reflectivity and that adding Mg or Cu to Al alloy films is effective for improvement of surface morphology.

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