Electrochemical Analyses for Corrosion Mechanism of Al-Cu Alloy Thin-Films

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Abstract

Corrosion mechanism of Al-Cu alloy thin films has been investigated dynamically by means of electrochemical methods in 1.0 mol/l HCl aqueous media. It was found that anodic corrosion potential (Ecorr) shift and degradation of breakdown potential of oxide layer of Al-Si-Cu surfaces were key processes for the corrosion of Al-Si-Cu thin-films.

1. Introduction

Al alloy thin-films containing Cu are used as inter-connection to obtain good reliability characteristics in ULSI. Addition of Cu into Al, however, increases susceptibility to corrosion after dry etching with etchants containing halogens, due to the formation of a local cell between Cu depleted region and Cu precipitates in Ai-Si-Cu films¹⁾. Corrosion of Ai-Si-Cu metallization will cause significant yield loss and reliability lowering in device characteristics²). To avoid these problems, it is important to understand corrosion mechanism of Ai-Si-Cu thin-films. In order to investigate the corrosion mechanism, electrochemical analyses are very There have been several works useful. concerning with corrosion mechanisms for Alalloy thin-films¹⁻⁶⁾. However, there exist few works investigating dynamic mechanism of corrosion for the films.¹⁻⁶⁾

In the present study, we have presented a dynamic mechanism of corrosion for Ai-Si-Cu thin-films induced by means of an electrochemical method.

2. Experimental

An electrochemical cell used in this study is shown in figure 1. All test samples (ca. 12x60 mm square) were sectioned from silicon wafers after deposition of Ai-1%Si-0.5%Cu films of 800nm thickness on 600nm-thick th-SiO2. The samples were covered with an insulating film except an 100 mm2 area. Time dependencies of potential (OCP) and DC Open circuit polarization were measured with a potentiostat. Aqueous solutions of 1.0 mol/l HCl and ca. 3x10⁻⁴ mol/l CuSO₄ were used as electrolytes. All polarization scans had a set scan rate of 10mV /sec. A typical polarization curve is shown in figure 2. Surface analyses through this experiments were carried out by SEM and EDX observations.

3. Results and Discussion

Figure 3 shows the time dependence of OCP for Ai-Si-Cu in 1.0 mol/l HCl. After the

measurement, localized corrosion were observed on the surface of the samples. The OCP result indicates that three phases exist in the corrosion process of Ai-Si-Cu thin-films. From the time dependent DC polarization measurements (figure 4), it is obvious that phase I corresponds to degradation of breakdown potential (Ebd) of the oxide layer on Ai-Si-Cu surfaces and anodic shift of corrosion potential (Ecorr). Phase II corresponds to Ecorr shift to Ebd and an increase of corrosion current (Icorr) indicating localized corrosion caused by breakdown of oxide layers of Ai-Si-Cu surface Phase III corresponds to a continuous increase of Icorr and cathodic shift of Ecorr due to the exposure of the metallic surface to HCl solutions. Time variations of Ecorr in DC polarization mesurements are consistent with the OCP result. Time dependences of Ecorr, Ebd, and Icorr are shown in figure 5. In phase II, where Ecorr is equal to breakdown potential, corrosion current abruptly increases. This fact clearly indicates that breakdown of oxide layer initiates corrosion of Ai-Si-Cu. These findings are also supported by SEM observations as shown in figure 6, which show localized thinning of oxide layer (figure 6a) in phase I, deterioration of oxide layer (figure 6b) and pitting corrosion (figure 6c) in phase II, and serious localized corrosion due to dissolution of oxide layer (figure 6d) in phase III.

In order to clarify the reason why Ecorr anodically shifts in phase I in DC polarization we investigated measurements, the time dependence of OCP of Ai-Si-Cu film in ca. 3x10⁻⁴ mol/l CuSO₄ aqueous solution. In figure 7, a time-dependent anodic-shift of OCP of Ai-Si-Cu was observed. This anodic shift of OCP is supposed to be caused by Cu deposited on the surface, acting effective cathodes^{3,4)}. as

Therefore, the Ecorr shift for Ai-Si-Cu in HCl solution may be attributed to the increase of effective area of Cu precipitates, caused by dissolution of Cu-oxide formed on the surface of Cu precipitates by HCl with time.

4. Conclusion

Corrosion mechanism of Ai-Si-Cu in 1.0 mol/l HCl was electrochemically determined. Corrosion of Al-Si-Cu thin-films in aqueous HCl solution proceeds through three phases as follows. Phase I: Degradation of Ebd caused by dissolution of the oxide layer of Ai-Si-Cu surface, and anodic shift of Ecorr caused by the increase of effective area of Cu precipitates by dissolution of surface oxide. Phase II: Corrosion induced by breakdown of oxide layer of Ai-Si-Cu surface. Phase III: Corrosion caused by exposure of metallic surface of Ai-Si-Cu to HCl solution.

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Figure 1. Assembly of Electrochemical Cell.







Figure 5. Time Dependence of Ecorr, Ebd, and Icorr for AlSiCu in 0.1mol/I HCI.



Figure 7. Time Dependence of OCP for AlSiCu in 2.4x10⁻⁴ mol/l CuSO₂ solution.







Figure 4. Time Dependent DC Polarization Measurements for AlSiCu in 1.0 mol/l HCl Solution.

300 pm

(a) After 30 sec





(b) After 600 sec

(c) After 600 sec



(d) After 1800 sec

Figure 6. SEM Photographs of the Surface of AlSiCu Treated in 1.0 mol/l HCl Solution.