Abstract #680, 223rd ECS Meeting, © 2013 The Electrochemical Society

Corrosion improvement of oxidized Co by using silane thin films

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Semiconductor devices, magnetic disks, and optical instruments use thin film ranging from a few nanometers to several dozen nanometers in thickness. It is necessary to develop an anti-corrosive technology that works at the nm level to improve the reliability of these products. Chromate treatment is a conventional anti-corrosion technique for metals. However, since it controls corrosion with a reaction product formation, it easily dissolves substrate thin metal. To enable this treatment to be used on thin film, we “pre-treated” several metals with silane coupling agents to form self-assembled anti-corrosion layers[1, 2].

In this study, we used 100-nm cobalt-sputtered polysilicon wafer samples. The silane coupling agents were 1.2-bis [triethoxysilyl]ethane (BTSE), 1.2-bis [triethoxysilylpropyl]amine (BTSPA), and 1.2-bis [triethoxysilyl]tetrasulfide (BTSPS) with ethanol as a solvent. An appropriate amount of hydrogen peroxide (H_2O_2) was added to the solution. The reason for adding hydrogen peroxide is that the cobalt surface must be covered with a thin film of cobalt oxide to make it efficiently adsorb BTSE [3]. To form this coupling layer, the sample was immersed in the various silane solutions for different periods of time. Corrosion was evaluated in a borate mixture solution using the electrochemical method. The Co surface was observed by SEM and AFM. The deposits on the Co surface were analyzed by XPS.

Table 1 shows the corrosion current density of cobalt after the treatments (including no treatment). The corrosion current density of cobalt treated in 10% (30% H_2O_2) for 1 h was slightly smaller than that of the non-treated surface. The corrosion current density of cobalt treated in 0.2 % BTSE + 10 % (30% H_2O_2) for 1 h was also smaller than that of the non-treated cobalt. But the corrosion current density for the 24 h immersion was less than 1/100th that of the non-treated cobalt. The corrosion current density was extremely small after the 1 h immersion in 0.2% BTSPA + 10% (30% H_2O_2). However, the corrosion current density increased with the immersion time. The results of the 1 and 24 h immersions in 0.2% BTSPS + 10% (30% H_2O_2) were nearly the same as the no–treatment case. Therefore, a protective layer did not form when BTSPS was used.

Table 1 Corrosion current density of cobalt with several treatments.

Treatment conditions		Corrosion current density (μA/cm^2)
Solution	Immersion time (h)	
None		7.50
10%(30% H_2O_2)	1	5.86
0.2%BTSE+10%(30% H_2O_2) pH:4.62	1	1.16
	24	0.057
0.2%BTSPA+10%(30% H_2O_2) pH:6.46	1	0.0163
	24	0.100
0.2%BTSPS+10%(30% H_2O_2) pH:3.58	1	1.69
	24	4.45

Figure 1 shows an SEM image on a non-pretreated Co surface and one treated with only hydrogen peroxide for 1 h. The non-pretreated Co surface was uniformly covered with Co particles that were about 10 nm in diameter. In contrast, the treated sample by 10% (30% H_2O_2) was covered with a rice-formed deposit that was composed of larger particles.

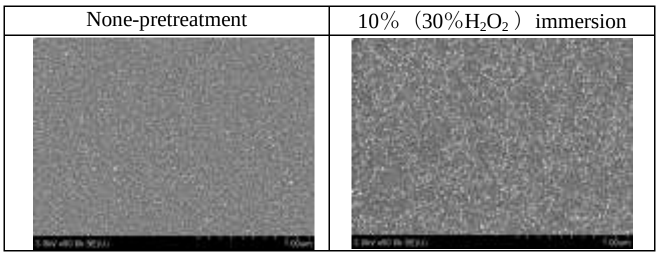
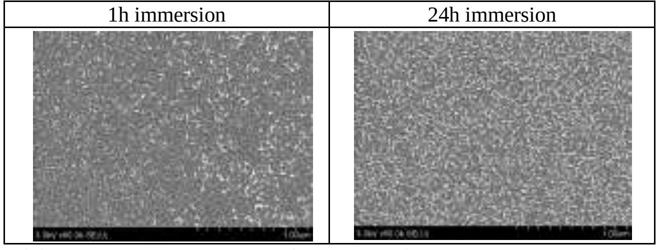


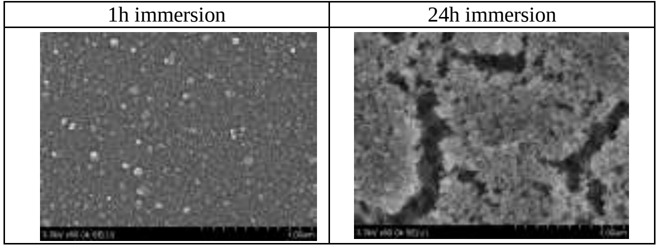
Fig. 1 SEM images of non-treated Co surface and surface treated with H_2O_2 for 1h.

Figure 2 shows SEM images of surfaces treated with different silane coupling agents and 10% (30% H_2O_2) for 1 and 24 h. The surface topography of the Co immersed in BTSE was similar to the surface immersed in hydrogen peroxide. As the corrosion current density decreased, the surface became uniformly covered with a very thin BTSE layer. The topography of the surface immersed for 1 h in 0.2% BTSPA + 10% (30% H_2O_2) was unchanged from that before immersion. However, after the 24 h immersion, the surface was covered with thick products. This was a cause of the increase in corrosion current density. A thick product precipitated on the surface that was immersed in 0.2% BTSPS + 10% (30% H_2O_2). This deposit was too crude to provide corrosion resistance.

(1) 0.2 % BTSE + 10 % (30% H_2O_2)



(2) 0.2% BTSPA + 10% (30% H_2O_2)



(3) 0.2% BTSPS + 10% (30% H_2O_2)

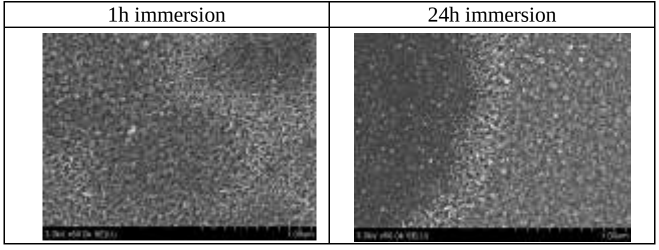


Fig. 2 SEM images of Co surfaces treated with different silane coupling agents in a 10% (30% H_2O_2) solution for 1 and 24 h.

The relationship between silane coupling film formed on cobalt and corrosion resistance was discussed from the viewpoint of the HSAB principle.

References

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