Sn-Ag 2step activation process for electroless copper plating

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Abstract: - An Sn-Ag 2step activation method for electroless copper plating is presented in this study. When the Sn-Ag activation process was applied, the amount of the Ag catalysts adsorbed on substrate surfaces was higher than Pd catalysts adsorbed by conventional Sn-Pd 2step activation process. With this activation method, it was also shown that the adsorbed Pd species with a size of about 3 nm were uniformly distributed on the surfaces, thus a smooth and uniform coating on the surfaces was obtained by subsequent electroless copper plating. The samples after each step were characterized by AFM, XPS, FIB, and SEM

Key-Words: - Electroless copper, Silver activation, Interconnect, Electrical resistivity

1 Introduction

Electroless plating had been used for a long time as an industrial process, and Brenner and Riddell [1] did the first experiments in 1944 during the Second World War. The applications of this technique were found in the field of providing conductive or decorative coating on the surface. Before electroless plating, a palladium (Pd) activation step that introduces the catalytic sites onto the surface has to be preceded. The conventional " two-step " activation process utilizes successively the acid solutions of $SnCl_2$ then $PdCl_2$, while the " one-step " process uses a colloidal mixture of $SnCl_2$ and $PdCl_2$ [2],[3].

According to the previous results, large clusters of Pd species (Pd atom, ion) were absorbed on the surface during Pd activation processes mentioned above. Zhu et al. [4] reported that Pd clusters with size scattering from 10 to 200 nm were absorbed on the Si wafer by one-step activation process. Chang et al. [5] showed that Pd clusters with sizes over 10 nm were loosely spread on the two-step activated $Si/SiO_2/Ta_xN$ surfaces. As the width of interconnects for semiconductor devices is decreasing under 30 nm, it is essential to develop the new activation process that can distribute tiny Pd clusters on the trench for the electroless gap-filling.

In this study, silver is used catalytic element. Sn-Ag two step process are used as activation process for enhanced gap-filling property.

2 Experimental Procedures

The $Si/SiO_2/Ta$ substrates were first sensitized using an acid $SnCl_2$ solution (20 g/l SnCl2, 10 ml/l HCl) with constant agitation for 1 min. at 25 ◦ C. The sensitized substrates were rinsed with de-ionized water subsequently. After cleaning, the Sn2+ ion-sensitized samples were then immersed into the activator, which was composed of 1.4×10^{-3}M $AgSO_4$ and 0.1M H_2SO_4 in order to achieve surface activation. The activation of samples was carried out in 25 ◦ C, and the activated substrates were rinsed with de-ionized water and dried. Activation was performed either mechanical agitation. Afterwards, the activated substrates with Pd catalysts were then electrolessly Cu plated in the solution of copper sulfate ($CuSO_4$), potassium sodium tartrate ($KNaC_4H_4O_6\cdot4H_2O$) as complexing agent, and some minor surfactant of 2,2' -dipyridyl and SPS with formaldehyde (HCHO, 37%) as a reductant at 25 °C. Scanning Electron Microscope (FEI, SIRION-400) was used to examine the surface morphologies after activation processes and Cu electroless deposition. In order to obtain the cross-sectional images of 26 nm trenches after Cu gap-filling, samples were milled using FIB (FEI, NOVA-600) system, and then observed by FE-SEM.

3 Results and Discussion

Fig. 1 shows the morphologies of the surfaces after activation process with different methods of conventional Sn-Pd 2step process and Sn-Ag 2step process. It was shown from Fig. 1(a) that large Pd clusters with diameter over 15 nm were absorbed on the surface activated using conventional process. In contrast, when the Sn-Ag 2step process was applied, the SEM image of the surface indicated smaller Ag catalyst with

a diameter of about 3 nm uniformly distributed on the surface.

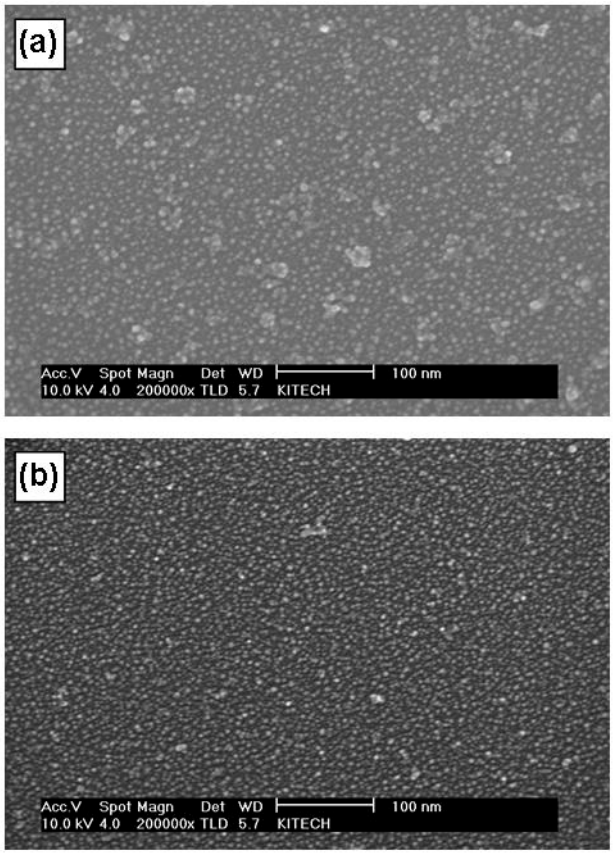

Fig. 1 SEM images of activated substrates: (a) after conventional Sn-Pd 2step activation process and (b) Sn-Ag 2step activation process

Table 1 shows the XPS quantitative analysis of the sample surface from the Sn-Pd conventional activation process and that from the Sn-Ag activation process. When Sn-Ag activation method was applied, amount of Ag adsorbed on the surface was greater. Therefore, it is confirmed that the Sn-Ag activation method effectively enhance the adsorption of catalysts.

Table 1 Surface composition of activated surfaces

at.%	Ta	C	O	Cl	Pd	Ag	Sn
Sn-Pd	51.2	21.6	18.7	0.7	1.5	-	6.4
Sn-Ag	51.8	20.4	16.0	0.1	-	6.4	5.4

Fig. 2 indicates the electrical resistivity of the copper film electrolessly deposited on the wafer after activation process with different methods of conventional Sn-Pd 2step process and Sn-Ag 2step process as a function of the film-thickness. Cu film on Sn-Ag activated surface show lower electrical resistivity than that on Sn-Pd activated surface. It is considered to be from lower resistivity of silver than copper.

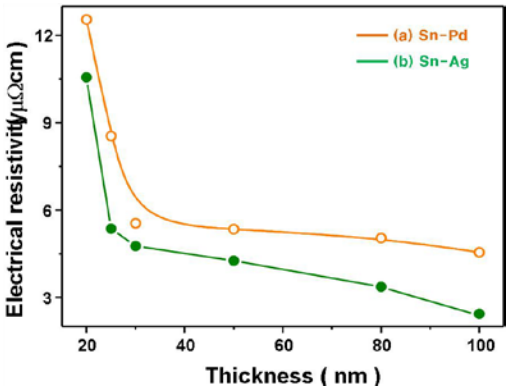

Fig. 2 Electrical resistivity of the copper film electrolessly deposited on the wafer after Sn-Pd and Sn-Ag activation processes.

Electroless Cu gap-fill is attempted on 26 nm trench prepared by two methods above. The trench samples were prepared by forming oxide layer on the Si pattern wafer with AR 3.5 and width 26 nm, and finally forming 3 nm thick Ta layer using ALD method. Indicated in Fig. 3, the sample using the conventional method reveals irregular deposition due to large Pd clusters, thus resulting void within the trench. Alternatively, gap-fill is successfully performed without void when the sample was activated with Sn-Ag method.

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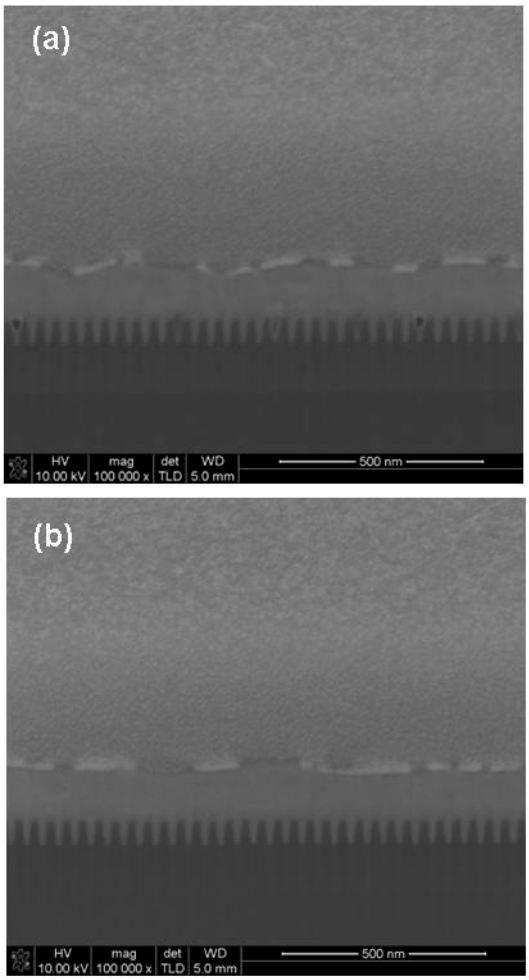

Fig. 6 Cross-sectional SEM images of 26 nm trench after electroless Cu plating: (a) with conventional Sn-Pd activation (b) Sn-Ag activation

4 Conclusion

This study examined how Sn-Ag activation method affects the distribution of Ag catalysts, copper electroless desposition, and the gap-fill property. According to the SEM analysis, when Sn-Ag 2step activation method was implemented, smaller Ag particles are homogeneously distributed. Homogeneous distribution of Ag particles led decrease in the electrical resistivity. Using the above result 26 nm trench Cu gap-fill becomes successful.

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