

Optimization of Surface Layers for Suppression of Agglomeration in Ag Films

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We previously reported that Al, Ti, and Nb surface layers can effectively suppress agglomeration in Ag films, which is dominated by the surface diffusion of Ag atoms. In this study, Ag films with Pd, Ni, and W surface layers were prepared by RF magnetron sputtering, and the properties of these films were compared with previous observations of the effects of Ti and Nb surface layers. The most important properties of the appropriate surface layers for the suppression of agglomeration in Ag films are a high cohesive energy or a high Gibbs free energy of formation of the oxide, and a low solid solubility in Ag.

Recently, Ag thin films have attracted increasing attention in the electronics industry because Ag has the lowest bulk resistivity of all metals.^{1, 2)} Because Ag films easily agglomerate at high temperatures, it is necessary to improve the thermal stability of Ag thin films while maintaining their low resistivity. Since more than thirty years ago, much research has shown that the agglomeration of Ag thin films is dominated by surface diffusion mass transport.^{3, 4)} Therefore, the suppression of surface diffusion could be a highly effective means of suppressing agglomeration. It has been confirmed that passivation layers can be formed at the surfaces of silver-titanium (Ag-Ti) and silver-aluminum (Ag-Al) alloy films to protect the Ag films from agglomeration.⁵⁻⁷⁾ However, using alloying elements causes a higher resistivity because of the impurity scattering effect.^{5, 6)} Regarding this issue, we reported that surface layers of Al and Ti deposited on pure Ag films can effectively suppress agglomeration and avoid the introduction of impurities, because these materials are relatively insoluble in Ag and are oxidized to form passivation layers during the annealing process.^{8, 9)} However, we recently found that a niobium (Nb) surface layer, regardless of the chemical state of the metal or oxide, effectively suppresses Ag agglomeration.¹⁰⁾ These previous results suggest that the cohesive energy, the Gibbs free energy of formation of the oxide, and the solid solubility with Ag of a surface metal are closely related to the metal's ability to suppress Ag agglomeration. The properties of Ag, Pd, Ni, Ti, Nb, and W, which were used for comparison in this study, are listed in Table 1.¹¹⁻¹⁴⁾ All of these metals have higher cohesive energies than Ag, and those of W and Nb are extremely high. Ag and Pd have very low free energies of oxide formation, so they were not expected to be easily oxidized. The free energy of oxide formation for Ni is slightly higher than that of Pd, but is much lower than those of W, Ti, and Nb. Although Pd can form a complete solid solution with

Ag, the other metals are difficult to dissolve in Ag. Among these metals, the bulk resistivity of W is the closest to that of Ag, and that of Ti is the highest. Our goal in this study was to clarify the relationship between the above-mentioned properties of the surface layers and their effects on the suppression of Ag agglomeration, and to determine which metals are appropriate as surface layers for the suppression of agglomeration in Ag films.

60-nm-thick Ag, Pd, Ni, W, Ti, and Nb films and 100-nm-thick Ag films with various surface layers (5 nm thick) of Pd, Ni, and W were deposited using RF magnetron sputtering. A Si (100) wafer with a 100 nm thick thermally grown SiO₂ layer was used as a substrate without heating during sputtering. Annealing was carried out at 500 or 600°C in a lamp-heated furnace for 1 hour after evacuation to less than 1.0×10^{-6} Torr. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to investigate the surface morphology of the films. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical bonding state of the surface layers. X-ray diffraction (XRD) was carried out to investigate the crystal structure of the Ag films beneath the various surface layers. The resistivities of the films were measured at room temperature by the four-point probe method.

The primary role of the surface layer is to inhibit the surface diffusion of the Ag films during annealing, which contributes to the suppression of Ag agglomeration. Therefore, a high morphological stability is required for the surface layer. Figure 1 shows SEM images of 60-nm-thick Ag, Pd, Ni, Ti, Nb, and W films after annealing at 600°C in a vacuum. All of the as-deposited films had very smooth surfaces, which are not shown here. The annealed Ag film exhibited the most severe agglomeration of all the films. Part of the substrate was exposed, and the rms roughness reached 29.2 nm. The annealed Pd

and Ni films had similarly irregular surfaces, which contained numerous small voids and hillocks, showing poor morphological stability, even though these films did not agglomerate as severely as the Ag film. In contrast, the very smooth surfaces of the W, Ti, and Nb films after annealing indicate their excellent morphological stability. In particular, the rms roughnesses of the annealed Nb and W films were 1.4 and 0.9 nm, respectively, both lower than that of Ti (2.5 nm). This suggests that Nb and W films have a higher morphological stability than Ti.

Figures 2(a) – 2(e) show SEM images of Ag (100 nm) films with 5-nm-thick Pd, Ni, W, Ti, and Nb surface layers after annealing at 600°C. As expected, the annealed Pd/Ag and Ni/Ag films had rough surfaces with many voids and hillocks. On the contrary, the annealed W/Ag film had a continuous flat surface, as did the Nb/Ag film. The resulting W surface layer was slightly better than that of the Ti surface layer, as it had smaller voids and a lower surface roughness. If surface layers with a higher morphological stability can better assist in the suppression of Ag agglomeration, then W and Nb are appropriate surface layer materials.

The reasons for the above results are discussed based on the properties of these metals, as shown in Table 1. First, it is easy to understand that the formation of a solid solution with Ag would reduce the thickness of the surface layer and reduce its effectiveness. The interplanar spacing of Ag(111) for all of the double-layer films as a function of annealing temperature was investigated by XRD. Only the Pd/Ag film showed a sharp decrease in the interplanar spacing of Ag(111) with increasing annealing temperature. It is obvious that large amounts of Pd dissolved in the Ag after annealing, which caused the Pd surface layer to provide the weakest suppression of Ag agglomeration. Next, as shown in Fig. 1 and Table 1, metals with a low Gibbs free energy of oxide formation and a low cohesive

energy, such as Pd and Ni, had poor morphological stability, which is disadvantageous for a surface layer intended to suppress the agglomeration of an Ag film. XPS analysis confirmed that the Pd surface layer was not oxidized before or after annealing; a very thin Ni oxide layer was formed at the surface by natural oxidation, but this was completely reduced to Ni metal after annealing at 500°C. This indicated that Pd and Ni, with low Gibbs free energies of oxide formation, cannot easily form a stable oxide passivation layer to resist surface diffusion. Moreover, the low cohesive energies of Pd and Ni result in easier migration of their atoms at high temperature, which facilitates metal agglomeration. Therefore, Pd and Ni thin films in their metallic state showed poor morphological stability, so that as surface layers of Ag films they were less effective in suppressing agglomeration.

Ti, on the other hand, can easily form an oxide passivation layer by natural oxidation, because of its large Gibbs free energy of oxide formation.⁹⁾ This Ti passivation layer contributes to the high morphological stability of Ti single-layer films and Ti/Ag multilayer films, despite the relatively low cohesive energy of Ti. W and Nb have similar properties. They exhibited a higher morphological stability than Ti, and this was likely caused by the combined effect of a high Gibbs free energy of oxide formation and a high cohesive energy. We used the same method as was described in our previous paper describing a Nb surface layer¹⁰⁾ to study the effect of a W surface layer in the metallic state. A W (5 nm)/Ag (50 nm) film was sequentially annealed at 450°C for 1 h after deposition in a sputtering chamber, without exposure to air before annealing, and its SEM image is shown in Fig. 2(f). The W (5 nm)/Ag (50 nm) film showed a significant improvement in thermal stability, as did the Nb (5 nm)/Ag (50 nm) film. This indicates that W and Nb surface layers in the metallic state can maintain good morphological stability to effectively suppress Ag agglomeration, because of their high cohesive energies.

Low resistivity is another important feature of modified Ag films. Figure 3 shows the resistivities of Ag films with various surface layers as a function of annealing temperature. The resistivities of all as-deposited films except for the Ti/Ag film were close to that of the Ag single-layer film. Comparing this result with Table 1, it is apparent that surface layers with a low bulk resistivity have little influence on the sheet resistance of as-deposited modified Ag films. The resistivity of the Pd/Ag film increased remarkably with increasing annealing temperature, because of the impurity scattering effect of dissolved Pd atoms. After annealing at 600°C, the Ag films with Ti, Nb, and W surface layers maintained resistivities as low as those observed after annealing at 500°C, but the Ni/Ag film developed a higher resistivity. It is clear that the maintenance of a low resistivity can be attributed to a significant improvement in the thermal stability of the Ag films.

In conclusion, metals with a high cohesive energy or a high free energy of oxide formation and a low solid solubility in Ag are suitable surface layers for Ag films and can effectively improve the thermal stability of the films and avoid increased resistivity due to impurity scattering effects. In addition, among the candidate surface layers, those with a low bulk resistivity have a smaller influence on the sheet resistance of the modified Ag films. In this work, W satisfies all of these essential properties, confirming it is the best surface layer of an Ag film for the maintenance of low resistivity and the improvement of thermal stability.

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Figures:

Figure 1 SEM images of 60-nm-thick (a) Ag, (b) Pd, (c) Ni, (d) W, (e) Ti, and (f) Nb films after annealing at 600°C.

Figure 2 SEM images of Ag (100 nm) films with various surface layers (5 nm) of (a) Pd, (b) Ni, (c) W, (d) Ti, and (e) Nb after annealing at 600°C in a lamp-heated furnace, and (f) a W (5 nm)/Ag (50 nm) film after annealing at 450°C in a sputtering chamber.

Figure 3 (Color online) Resistivities of Ag single layer (100 nm) and Ag (100 nm) films with various surface layers (5 nm) of Pd, Ni, W, Ti, and Nb as a function of annealing temperature.

Table 1 Properties of Ag, Pd, Ni, Ti, Nb, and W.

	Ag	Pd	Ni	Ti	Nb	W
Cohesive energy (kJ/mol)	248	376	428	468	730	859
Gibbs free energy of formation of oxide (kJ/mol)	-5.6 (AgO _{0.5})	-55.4 (PdO)	-211.7 (NiO)	-884.5 (TiO ₂)	-883.1 (NbO _{2.5})	-764.0 (WO ₃)
Maximum solid solubility in Ag (at.%)		100	0.3	5	0	0
Bulk resistivity at 293 K ($\mu\Omega$ cm)	1.59	10.8	6.84	42.0	12.5	5.65

Fig. 1

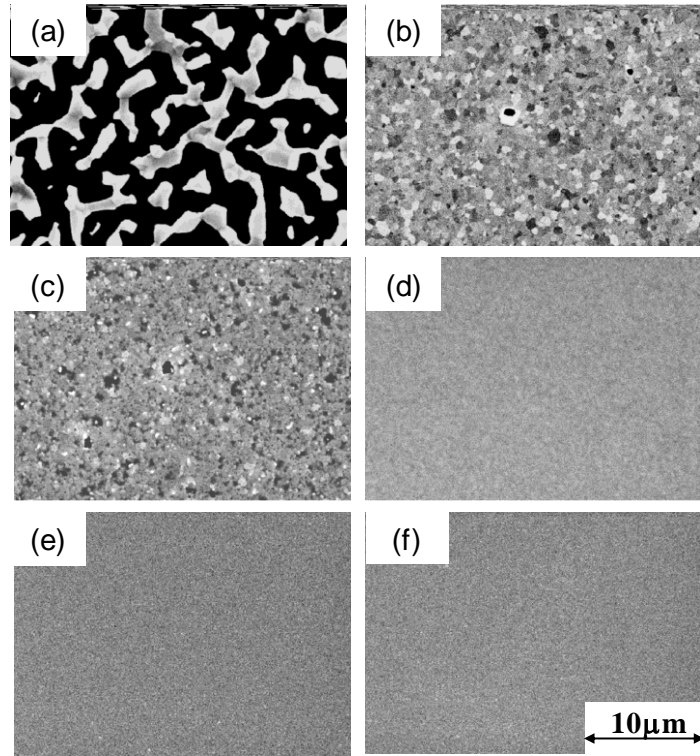


Fig. 2

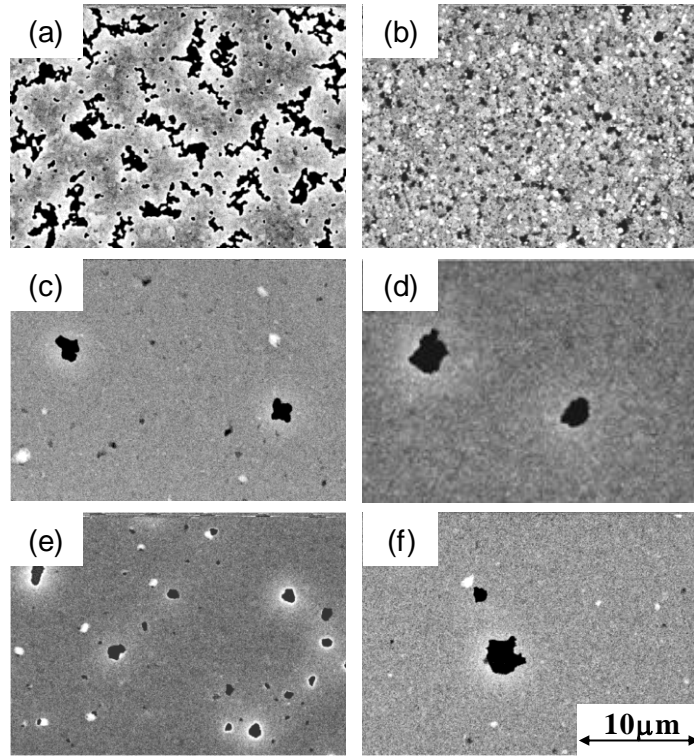


Fig. 3

