Effect of ZnO Film Thicknesses on the Adhesive Strength of Electroless Cu Deposits

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The effect of ZnO film thickness on the adhesive strength of electroless Cu deposited on ZnO-coated glass substrates was examined. An increase of adhesive strength of the Cu deposits with increasing ZnO film thickness was observed. Excellent adhesion was obtained on ZnO films thicker than 0.6 µm, which is considered to be associated with the formation of rougher, more porous structures. XPS data combined with SEM and AFM measurements showed that in addition to the surface area effect, the mechanical anchoring effect caused by Cu depositing deeply within the ZnO film may also play an important role in obtaining the excellent adhesion of the Cu deposits on thicker ZnO films.

The adhesion of electroless deposited metal films, especially noble metal films, to ceramic substrates is generally poor.[1-5] Improved adhesion is usually achieved by surface roughening of the substrate using a chemical or mechanical etching process. However, due to the inherent difficulty of controlling the etching process, inadequate surface roughness is usually obtained, which limits the adhesive strength of the metal deposits.

We have previously reported a new type of electroless metal deposition method that can overcome the above drawbacks by employing a ZnO thin film as an intermediate layer between the substrate and the deposited metal layer.[6] This method consists of three steps: 1) preparation of a ZnO thin film on an insulating substrate by spray pyrolysis; 2) catalyzation by immersing the ZnO-coated substrate in an acidic $PdCl_2$ solution; and 3) electroless metal deposition. Using this process, etching of the substrate is not necessary; nevertheless, more strongly adherent metal films are obtained than those obtained using the conventional method even on a smooth glass substrate.[6] Moreover, the adhesion of the electroless Cu deposits was found to be independent of the type of substrate (e.g., glass, Al_2O_3 and AlN),[7] indicating the versatility of this approach.

Recently we have been found that we can control and maximize the adhesive strength of electroless metal deposits by optimizing various experimental conditions. The most important factors was found to be the ZnO film thickness. The objective of the present work is to improve the understanding of this phenomenon.

ZnO films were prepared by spraying an acetate/ethanol solution onto a heated glass substrate (400 °C) at a constant rate of ~ 10 mL/min using the spray pyrolysis method, as described previously.[6] The thickness was adjusted by spray time, and an almost linear increase with spray time was observed under the above conditions. The growth rate was ~ 0.02 µm/min, as estimated from SEM images. After these ZnO-coated glass substrates were catalyzed in a 1.0 mM $PdCl_2$ solution for 2 min, they were subjected to electroless Cu deposition, first in a PB-503 bath (Ebara-Udylite Co.,) for 10 min at room temperature, and then in a ELC-SP bath (Uyemura & Co. Ltd.,) for 60 min at 60 °C. The Cu films prepared in this fashion have a thicknesses of ~2.0 µm. The results of the adhesive strength measurements of these Cu deposits are given in Table 1. It can be seen that the adhesive strength increases with increasing ZnO film thickness. For ZnO films thinner than 0.6 µm, electroless Cu deposits with high adhesive strengths were not obtained. However, those for the Cu deposits on ZnO films thicker than 0.8 µm were very high. They were so high that the substrates themselves were often broken in the pull test.

In order to understand the effect of ZnO film thickness on the adhesive strength of the Cu deposit, these films were examined using SEM, as shown in Figure 1. Due to the similarity of the surface textures, only two representative samples are shown here, with thickness of a) 0.8 and b) 1.6 µm. The surface morphologies of these films have similar aspects: all have a porous structure and are composed of small spherical particles. These particles have a greater tendency to form clusters or aggregates with increasing thickness. The diameters of these structures were in the 0.2 – 1.0 µm range. With increasing thickness, these aggregates became larger and more ball-like (Figure 1). As a consequence, the surface becomes increasingly

Table 1. Adhesive strength of electroless Cu deposited on ZnO films with various thicknesses

Thickness (µm)	Surface roughness (nm)	Adhesive strength (kg/mm^2)
0.2	-	weak[a]
0.4	68.6	1.3
0.6	-	2.2
0.8	93.8	>2.5[b]
1.0	-	>2.5
1.2	121.0	>2.5
1.4	-	>2.5
1.6	170.1	>2.5

[a] The Cu film was removable using adhesive tape;
[b] The glass substrate was often broken during the pull test.

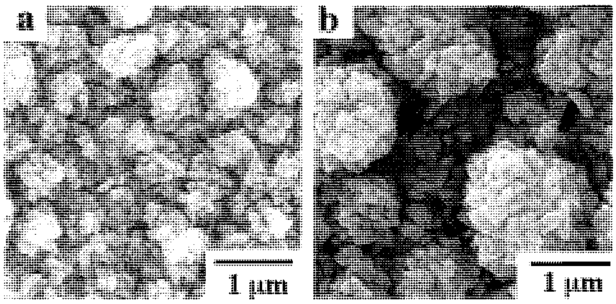

Figure 1. Two representative SEM images of ZnO thin films with different thicknesses. a) 0.8 µm and b) 1.6 µm.

rougher due to the formation of a more porous structure. This was confirmed by measuring the surface roughness from the AFM images (see data in Table 1).

Two possible explanations for the fact that the adhesive strength of the Cu deposits increases with increasing ZnO film thickness are 1) increased surface area with increasing thickness; and 2) a mechanical anchoring effect because of the Cu depositing deeply into the porous ZnO film. It is known that, in general, increasing the surface area upon which the van der Waals force acts is one of the key points in increasing the adhesion of metal deposits in electroless deposition. In the present work, the ZnO film surfaces become rougher and more porous with increasing film thicknesses as described above. Rougher surfaces generally possess larger surface areas. In addition, the formation of porous structure also increase the surface area greatly. Therefore, the increase of film thickness leads to larger surface area, which results in stronger interaction between ZnO and the Cu deposit when electroless deposition is performed on thicker ZnO films.

In order to evaluate the second explanation, i.e., the mechanical anchoring effect, XPS measurements coupled with depth profile analysis was carried out on Cu-deposited (0.4, 0.8, 1.2 and 1.6 µm thick) ZnO-coated glass substrates. The depths at which Cu was detected in the ZnO film showed that, the thicker the ZnO film is, i.e., the more porous and rougher the surface is, the more deeply the Cu particles can deposit into the film. The structures that form on the ZnO surfaces, as already described, are ball-like for the thicker films, as can be seen clearly in Figure 1b These structures can give rise to a "dovetail" or ball-and-socket joint effect. Thus, after electroless Cu deposition was carried out on such ZnO surfaces, due to the strong mechanical anchoring effect, as shown schematically in Figure 2, combined with the surface area effect, the adhesive strength of the Cu deposits was greatly improved.

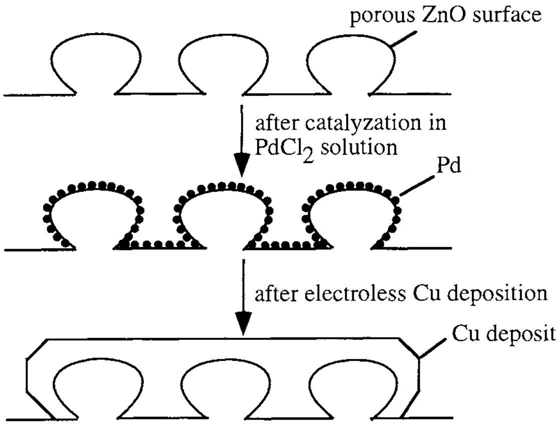

Figure 2. Schematic diagram of mechanical anchoring effect for Cu deposited on ball-like porous ZnO surfaces.

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