Resolution and Peel Adhesion Strength of Photoelectrochemically Plated Copper Layers onto a TiO_2-Adhered Alumina Substrate

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Synopsis. The resolution and peel adhesion strength of photoelectrochemically plated copper layers onto a TiO_2-adhered alumina substrate were investigated. The smallest line width was ca. 50 μm. The highest peel adhesion strength of the plated copper layer was attained with a heat-treatment on the TiO_2-adhered-alumina substrate before plating.

In the presence of ethylenediaminetetraacetic acid (EDTA), the photoelectrochemical deposition of copper onto TiO_2 particles was observed. Using this phenomenon, selective plating of copper onto irradiated parts of a TiO_2-sol-adhered alumina substrate was accomplished in an electroless copper-plating solution containing EDTA.[1] Compared to the conventional methods for producing printed-circuit boards, this method does not require any resist patterns, and copper lines are formed on the alumina substrate with simple processes.

This paper reports on the resolution and peel adhesion strength of photoelectrochemically plated copper layers onto a TiO_2-sol-adhered alumina substrate.

Experimental

Materials. The TiO_2 particles used in the experiment were purchased from Taki Chemical Co., Ltd. The crystal form was anatase. It is a sol-type TiO_2, and its diameter is ca. 80 Å. Degreased 96% alumina substrates (Kyocera) were etched in an aqueous hydrofluoric acid solution of 2.5 M ($M=mol\,dm^{-3}$). The etching amount was ca. $0.37\ mg\,cm^{-2}$. The alumina substrates were rinsed with ion-exchanged water, immersed in a TiO_2 solution of $10\ g\,dm^{-3}$, and dried at 85 °C. The amount of supported TiO_2 was ca. $3\times10^{-5}\ g\,cm^{-2}$. Some of the substrates were heated at between 300 and 900 °C for 1 h before plating. An electroless copper-plating solution containing EDTA of 0.3 M, copper(II) sulfate pentahydrate of 0.04 M, and formaldehyde of 0.1 M was employed. These reagents were purchased from Wako Pure Chemical Industries, Ltd. as guaranteed reagents. The pH value of the solution was 12.3. The temperature of the solution was ca. 60 °C.

Plating on an Alumina Substrate. The TiO_2-sol-adhered alumina substrate was set in the electroless copper-plating solution about 1 mm behind a mask (Melles Griot, USAF1951). A 250-W super-high-pressure mercury lamp (Ushio, USH250D) was used as the light source. Through an IR-cutting filter and the mask, light was applied to the alumina substrate for 5 s. After irradiation, the substrate was kept in an electroless copper-plating solution for 20 min. The thickness of the plated copper layers was ca. 2 μm.

Measurement of Peel Adhesion Strength. Using a mask with 4 mm^2 (2 mm×2 mm) windows, copper was plated onto the TiO_2-adhered-alumina substrate in the electroless copper-plating solution. In order to compare this photo-plating method with a conventional method, copper layers with the same shape were electroless-plated onto the alumina substrate with commercially available seeding solutions (Shipley, Cataprep 404, Cataposit 44, and accelerator 19) and a screen printing technique. The thickness of the plated copper layers was ca. 2 μm in both cases. In order to avoid the formation of intermetallic compounds with the plated copper and solder, nickel was plated onto the copper layers using a commercially available electroless nickel-plating solution (Nippon Kanigen, S754-1, S754-2). The thickness of the nickel layers was ca. 1 μm. A copper wire of 0.8 mm in diameter was laid on the nickel layer and then soldered. On terminal of the copper wire was connected to a tensile tester (Seishin Trading, SS-15KP) and the peel adhesion strength of the plated copper layer was measured.

Results and Discussion

Resolution of Plated Copper. Figure 1 shows the mask employed and the plated copper pattern onto the TiO_2-adhered-alumina substrate. A series of three copper lines was plated so closely that small pieces of copper tended to be broken from the deposited copper layers by hydrogen-gas evolution of the electroless copper-plating reaction and the solution-flow due to the hydrogen gas. They dropped onto the substrate near to the plated lines and acted as nuclei for the electroless copper-plating reaction. Therefore, line broadening occurred. Judging from the line separation of the pattern, two lines per milli-meter could be written on the TiO_2-adhered-alumina substrate. On the other hand, in the part where figures were plated, the amount of broken copper pieces appeared to be rather few; the smallest line width of ca. 50 μm was observed.

Peel Adhesion Strength of Plated Copper. Figure 2 shows the relationship between the peel adhesion strength of the plated-copper layers and the etching amount of the alumina substrate. In both cases, when the etching amount was below $0.2\ mg\,cm^{-2}$, the peel adhesion strength of the copper layers became higher with the etching amount due to an anchoring effect. When the etching amount was more than $0.3\ mg\,cm^{-2}$, the peel adhesion strength of the copper layers appeared to have a rather constant value. In this region, the peel adhesion strength of the copper layers plated by the photo-plating method was comparable to that plated by the conventional method.

Figure 3 shows the relationship between the peel adhesion strength of the plated-copper layers and the temperature of the heat treatment on the TiO_2-ad-

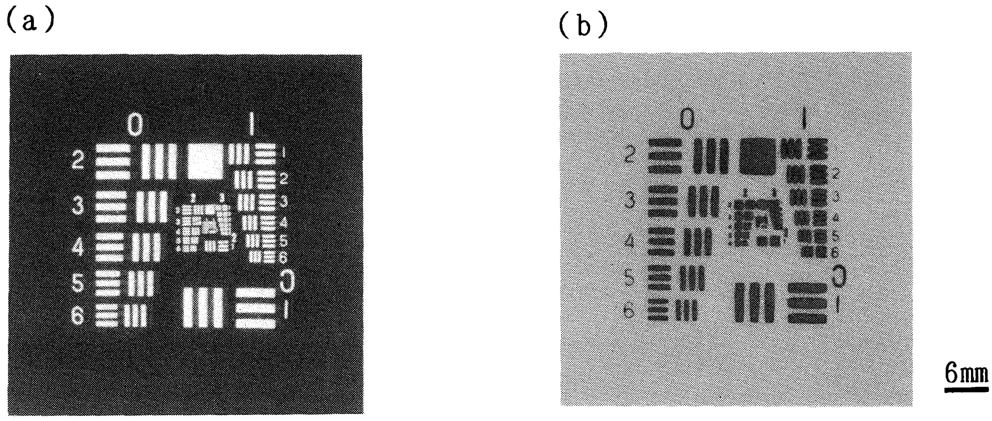

Fig. 1. (a) The mask. (b) Pattern of plated copper on the alumina substrate.

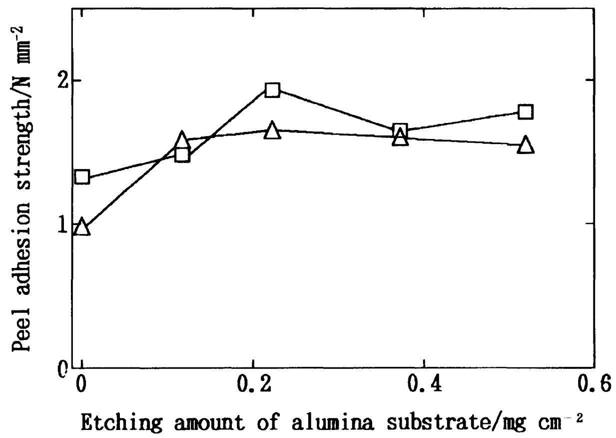

Fig. 2. Relationship between the peel adhesion strength of the copper layer on the alumina substrate and the etching amount of the alumina substrate: (□) plated on a TiO_2-adhered-alumina substrate without heat treatment before plating; (△) plated on an alumina substrate activated with commercially available seeding solutions.

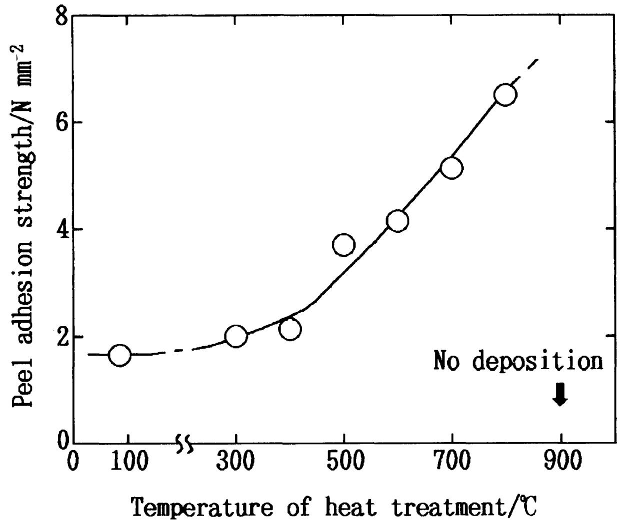

Fig. 3. Relationship between the peel adhesion strength of the copper layer on an alumina substrate and temperature of the heat treatment on an alumina substrate before plating.

hered-alumina substrate. The etching amount of the alumina substrate was ca. 0.37 $mg\,cm^{-2}$. The peel adhesion strength of the copper layers became higher with the temperature of the heat treatment. Especially, when the TiO_2-adhered-alumina substrate was heated at 800 °C for 1 h before plating, the peel adhesion strength became about four-times as much as that for the substrate treated by the conventional method. In this case, small flakes of the broken alumina substrate sometimes adhered to the back of the copper layers. This increase in the peel adhesion strength is thought to have been caused by the sintering of TiO_2 particles to the alumina substrate. When the temperature of the heat treatment was 900 °C, no deposition of copper was observed. This phenomenon is thought to occur due to the formation of an oxide compound between TiO_2 and Al_2O_3 of the alumina substrate.

Compared to the conventional plating method, the photo-plating method has the following characteristics:

1. It does not require any palladium colloids that act as nuclei for an electroless copper-plating reaction.

2. Copper patterns are formed with simple processes without resists.

It is very difficult to form resist patterns on a substrate that has steps or curved shapes at the surface. This method, therefore, is thought to be more effective for forming copper patterns on a substrate than the conventional method.

References

1) S. Morishita, *Chem. Lett.*, **1992**, 1979.