Copper Metallization on Photosensitive-Crystallizable Glass Surfaces

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Glass is popular as a basis material in the electronics field because of its excellent characteristics, including its ease of processing and its visible light permeability.[1,2] In particular, photosensitive-crystallizable glass (PC glass) is expected to be widely used in the electronics field because processing is easy, even on substrates with complex three-dimensional features. In general, conductive metal films on glass substrates are formed by dry processing. However, uniform film formation by such processing is difficult on glass substrates with complex three-dimensional features. Therefore, metallization on PC glass by wet processing is preferred. In this work, copper film formation by wet processing was performed and the adhesion strength between the copper films and the PC glass substrate was examined.

Experimental

Processing of PC glass

The processing sequence for PC glass is shown schematically in Fig. 1. As the first crystallization step, dispersed

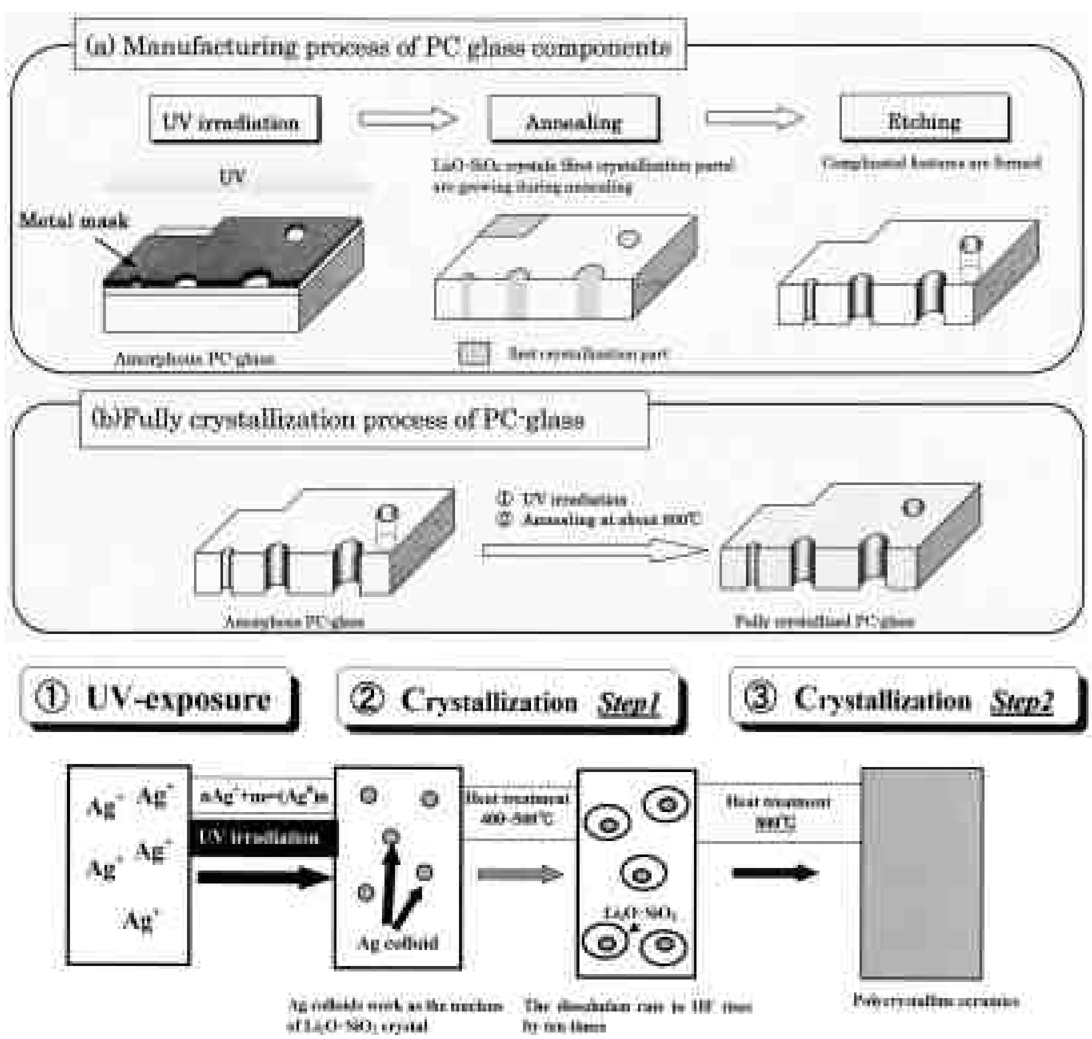

Fig. 1—Crystallization process for PC glass.

Table 1
Etching Bath Composition & Conditions

(a) Simple etchants	
i. Hydrofluoric acid (HF)	1 – 10 wt%
Temperature	Room temp
ii. Ammonium hydrogen fluoride (NH_4F/HF)	1 – 10 wt%
Temperature	Room temp
(b) Potassium-based etchant	
Ammonium hydrogen fluoride (NH_4F/HF)	5 – 20 wt%
Potassium fluoride (KF)	5 – 20 wt%
Temperature	70ºC (158ºF)

Table 2
Experimental Procedure

1. Alkaline degreasing
   (Rinse)
2. Etching
   (Rinse)
3. Conditioning (proprietary) 60ºC (140ºF); 5 min
   (Rinse)
4. Catalysis (Sn-Pd mixed catalyst) 40ºC (104ºF); 5 min
   (Rinse)
5. Activation ($PdCl_2$, 300 ppm) 25ºC (77ºF)
   (Rinse)
6. Electroless copper plating
   (Rinse and anneal)
7. Copper plating
   (Rinse and anneal)
8. Patterning
   (Rinse and dry)
9. Adhesion test

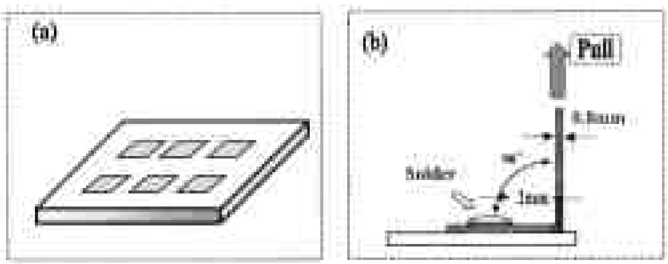

Fig. 2—Evaluation method of Adhesion test.
(a) sample image; (b) schematic diagram of adhesion test.

silver ions in the amorphous PC glass are converted to silver colloids by UV irradiation. Then, $Li_2O{\cdot}SiO_2$ crystals (first crystallization parts) are allowed to grow around the silver colloids during annealing. At this stage, the dissolution rate of the crystallized areas by hydrofluoric acid (HF) is ten times higher than the original amorphous PC glass substrate.[3] Accordingly, complex features can be formed on the glass substrate by selective exposure and HF etching, as shown in Fig.1(a). Finally, fully crystallized glass is obtained by UV irradiation and heat treatment at 800ºC (1472ºF), as shown in Fig.1(b). During the crystallization process, the silver colloids are surrounded by LiO_2 and SiO_2. Therefore the fixed silver colloids in the PC glass are not influenced by catalysis in the pretreatment process.

Experimental Procedure

Amorphous PC glass (non-exposed) and fully crystallized PC glass were used as test substrates. The etchant composition and etching conditions are shown in Table 1.[4] The metallization procedure is shown schematically in Table 2. After etching, a mixed tin-palladium catalyst was used, followed by activation with palladium chloride ($PdCl_2$). A 0.3 µm (11.8 µ-in.) thick copper film was formed by electroless copper plating. In a preliminary survey, electroless copper plating with hypophosphite as a reducing agent was found to improve the adhesion strength between deposited copper and non-conductive substrates.[5] Accordingly, a hypophosphite-type of electroless copper bath (weak alkaline type) was used in this work. In order to reduce the stress of the depositing copper films, a well-known stress inhibitor was added to the high-throwing copper electroplating bath.

The surface morphology and cross sections were observed with a scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDS) was used for elemental analysis.

After the copper was further electroplated to a thickness of 10 µm (0.4 mil), 2x2-mm pads were formed as shown in Fig. 2(a). Then, 20-µm (0.8-mil) diameter copper wire was soldered, as in Fig.2(b).[6] The adhesion strength was measured with a tensile tester using a cross-head speed of 5 mm/min (0.2 in./min).

Results & Discussion

Etching of the Glass Surface

Fluoride solution. Hydrogen fluoride (HF) or ammonium hydrogen fluoride (AHF) [Table (1a)] were used to etch the glass surface. Figure 3 shows the surface morphologies before and after etching. In the case of amorphous PC glass, the etching progressed uniformly. Therefore, anchor sites were not created. On the other hand, roughened surfaces were easily obtained on the fully crystallized PC glass by etching, since the $Li_2O \cdot SiO_2$ crystals in the glass surface were preferentially dissolved.

Mixed-fluoride solution. In order to roughen the amorphous glass surface, several other etchants were also evaluated [Table

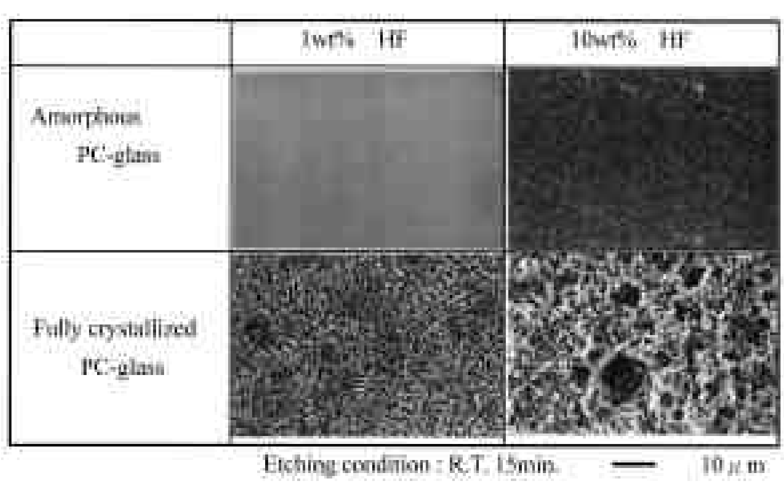

Fig. 3—SEM images of the PC glass surfaces.

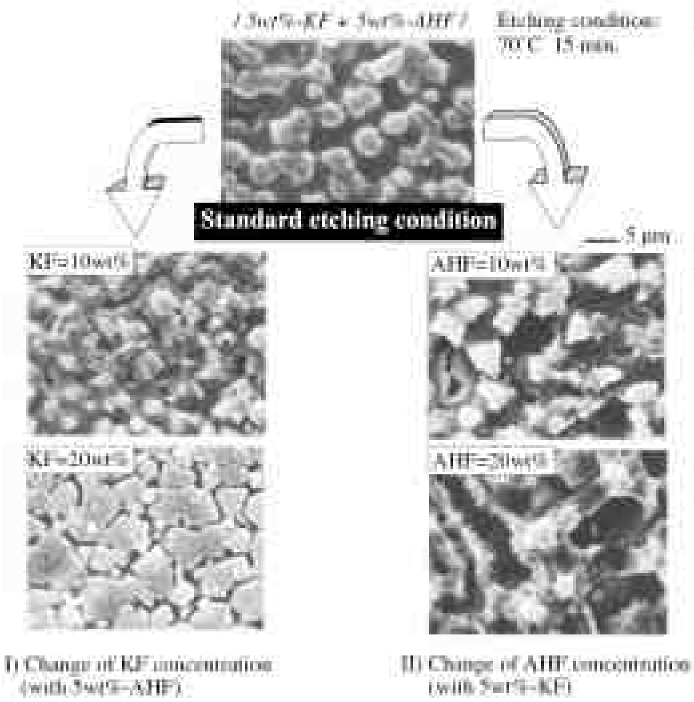

Fig. 4—Relationship between the etchant composition and the surface morphology on amorphous PC glass.

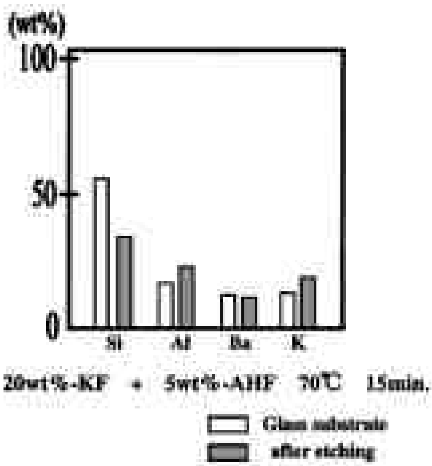

Fig. 5—EDS analysis results for the glass surfaces.

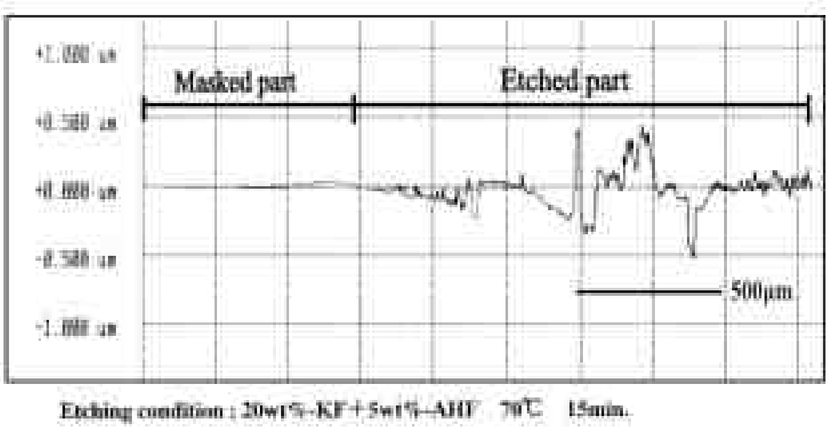

Fig. 6—Surface roughness measurements on amorphous PC glass after etching.

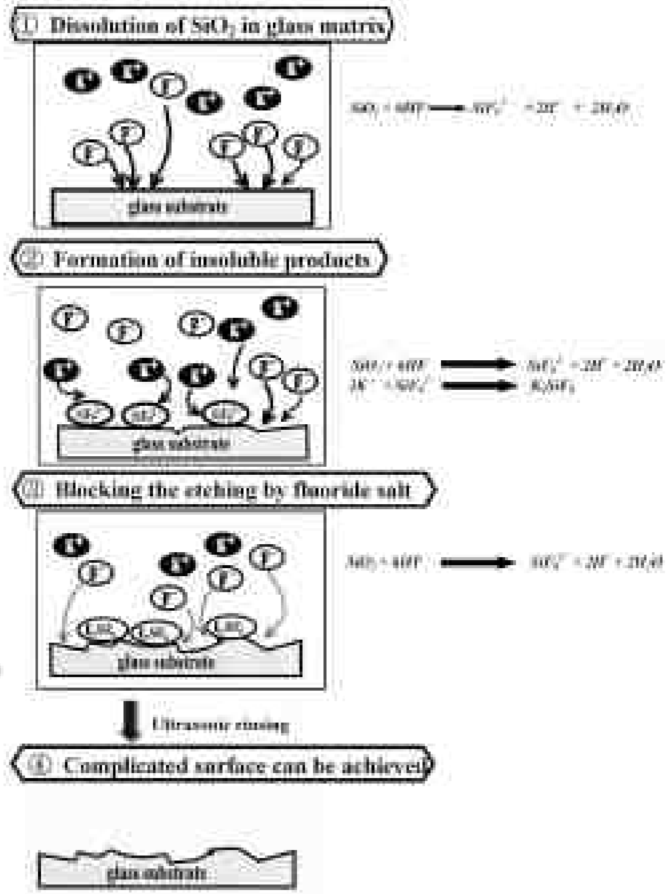

Fig. 7—Reaction mechanism of KF-AHF etching solution with amorphous PC glass.

1(b)]. Figure 4 shows the surface morphologies after etching. The glass surface was well-roughened and complex. We felt that such a surface might well provide anchor sites between the glass and copper films. Figure 5 shows the results of the elemental analysis of the etched glass surface. The amount of potassium on the surface increased after etching. From this result, it was assumed that a potassium-containing compound was formed on the glass surface during etching.

The roughness of the amorphous PC glass surface was measured and the results are shown in Fig. 6. Some loose particles even detached after etching. Presumably, insoluble compound layers were generated by dissolved ions from the glass surface during etching.

Figure 7 shows the etching model for the amorphous PC glass surface. First, the glass was uniformly etched by hydrogen fluoride to produce fluosilicate ions. Then, the fluoride and fluosilicate ions were precipitated as aluminum fluoride or potassium fluosilicate because the solubilities of these salts were very low. These insoluble products tended to stick on the glass surface, and shielded it from contact with the etchant. The selective etching still proceeded through the crevices of the insoluble product layer. Consequently, a complex glass surface was generated during etching. However, these insoluble products were not strongly adherent to the glass substrate. These surfaces may not have promoted good adhesion. Therefore, the poorly adherent reaction products on the etched

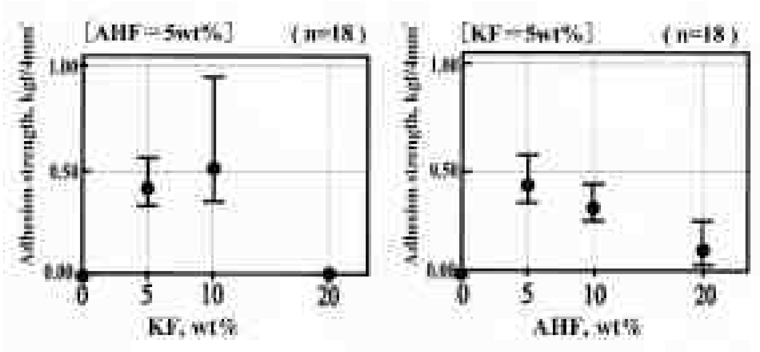

Fig. 8—Effect of each etching composition on adhesion strength on amorphous PC glass.

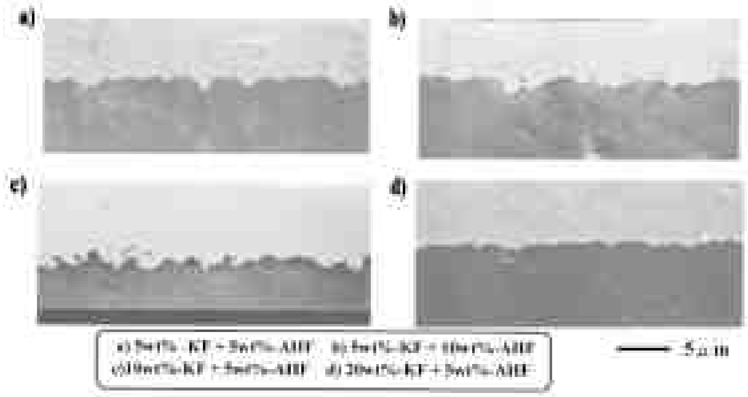

Fig. 9—SEM images of cross-sections for amorphous PC glass.

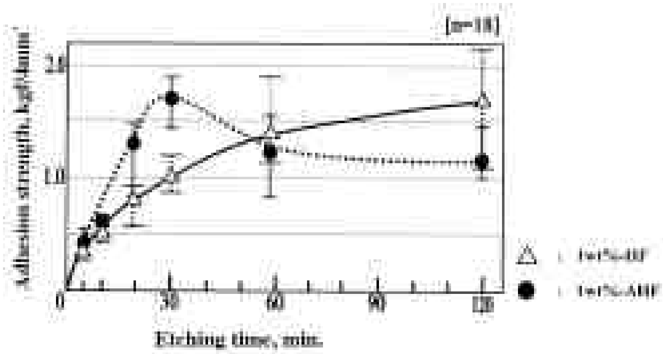

Fig. 10—Relationship between etching time and adhesion strength on fully crystallized PC glass.

surface had to be removed by ultrasonic cleaning.

Adhesion Strength

An electroless copper film of 0.3 µm (11.8 µm) was deposited on the etched glass by electroless plating. Subsequently, 10 µm (0.4 mil) of additional copper was formed by copper electroplating. The adhesion strength of deposited copper films on the etched glass was measured and the values for amorphous and fully crystallized glass were compared.

No adhesion on the amorphous glass was obtained with the etchant comprised of hydrofluoric acid or ammonium hydrogen fluoride solution. Because etching proceeded uniformly on the glass surface, anchoring sites were not created. Accordingly, the possibility of creating anchor sites using a potassium fluoride-containing KF-AHF mixed etchant was evaluated. These results are shown in Fig. 8. An adhesion strength of 0.12 kg/mm^2 (178 lb/in.^{2}) was obtained by an etchant comprised of 10 wt% KF and 5 wt% AHF. The resultant roughened, bumpy surface showed better adhesion than the shallow, low-profile surface after etching.

Next, the correlation between adhesion strength and the cross-sectional appearance was investigated. The results are shown in Fig. 9. In Figs. 9(a) and (c), the surface morphology indicated that the presence of anchor sites might provide good adhesion. However, appropriate adhesion strength was not achieved, even though the copper was embedded in the etched glass surface; the glass matrix itself was weakened and had become fragile by etching.

The adhesion strengths using fully crystallized glass are shown in Fig. 10. Adhesion strength increased with etching time when 1 wt% HF was used. The fully crystallized PC glass showed higher adhesion strength than did the amorphous PC glass. The maximum adhesion strength was obtained by etching for 30 minutes in 1 wt% AHF solution. This value is three times higher than that for the amorphous PC glass. Fig. 11 shows the cross-sectional views after plating. The copper films were completely embedded in the bottom of etched areas. However, the glass matrix was overetched and weakened with further etching time. From these results, the adhesion strength of copper films depended on the fragility of the glass after etching, even though copper was deposited into the bottom of the etched sites. Additionally, it is assumed that the surface anchor sites were generated without increasing the fragility, because the propagation of cracks stopped at the crystal grain boundaries. From this mechanism, higher adhesion strengths were obtained on crystalline surfaces versus amorphous ones.

Conclusions

The etching characteristics of PC glass and the factors determining the adhesion strength of the copper films were examined. The etching characteristics were different, depending on the crystallization conditions of the PC glass. For the crystalline state, selective dissolution of the glass surface led to form complex etching sites to create an anchoring effect. The complex etching sites were formed

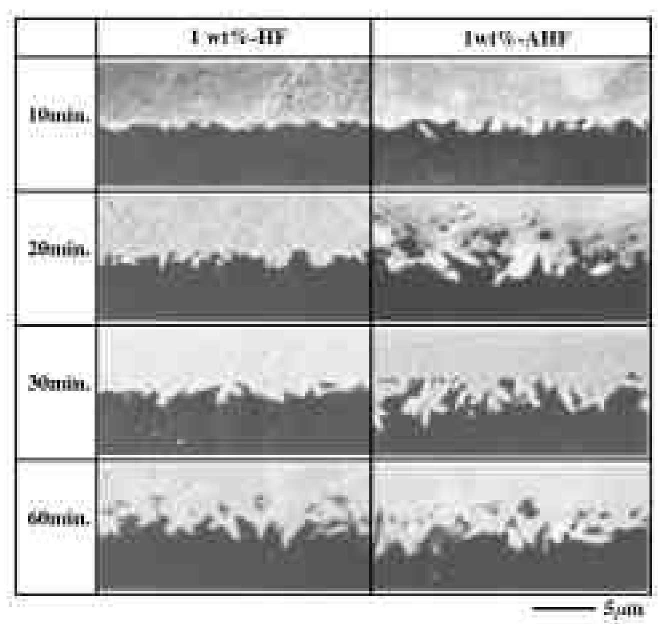

Fig. 11—SEM images of cross sections for fully crystallized PC glass.

by using the mixed-fluoride solution on amorphous PC glass.

As for the adhesion strength between etched glass and copper films, the maximum value was 0.12 kg/mm^2 (178 $lb/in.^2$) for amorphous glass, and 0.42 kg/mm^2 (605 $lb/in.^2$) for fully crystalline glass. Crystallized PC glass was fractured within the glass during the adhesion measurement.

References

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