Three substrates, Al₂O₃, AlN and glass, were directly metallized by copper electroplating using Al-doped ZnO (AZO) as an adhesive and conducting layer between these substrates and the electroplated copper layer. The AZO was synthesized in sol-gel solution, where the Al content in the AZO sol-gel was 2 at.%. Because the AZO is a conductor that can be etched by an acidic solution, copper patterns can be directly electroplated on these substrates coated with the patterned AZO. The AZO patterns went through dry film coating, pattern formation and dry film removal process steps. Two direct copper pattern electroplating processes were proposed in this work, where one process could protect the patterned AZO from being undercut because AZO layer was patterned first and then copper was directly electroplated on the patterned AZO; the other process could not do so because copper was electroplated on the AZO layer and then both the electroplated copper layer and the AZO layer were simultaneously patterned. The copper electroplating solution must be alkaline; otherwise the AZO coated on the substrates would be etched in an acidic copper electroplating solution.

Three-dimensional (3D) chip stacking packaging technology is dominating the state-of-the-art electronic products, especially portable electronic products. To stack up several chips, direct interconnection and through holes (THs) are formed in these substrates for vertical I/O interconnection among multi-chip stacking. For 2.5D chip packaging using an interposer, the architectural materials may be a silicon wafer, a glass wafer, an epoxy with glass fibers, depending on process integration, cost, and reliability, etc. Therefore, through-silicon vias (TSVs), through-glass vias (TGVs), and through holes (THs) are formed in these substrates for vertical I/O interconnection among multi-chip stacking. To stack for RDL fabrication, metallic lines have to be formed on these interposers with good adhesion. However, glass surface is extremely smooth and has few chemical function groups. Hence, glass surface is difficult to be metallized without surface pretreatment. Roughening glass surface by using chemical etching solution is a common approach to enhance the adhesion of a deposited metal layer due to an anchoring effect. A typical chemical etching solution is HF solution, which is too toxic to be widely accepted by industry. Alternatively, glass surface modification using self-assembly of silane molecules combining with Pd catalyst adsorption can metallize the glass surface through copper electroless deposition, where microcontact printing is a common example. However, the deposited metal layer usually exhibited weak adhesion on the glass surface. For LED packaging fabrication, both Al₂O₃ and AlN are good substrates for heat dissipation. The heat dissipation performance determines the luminance and lifetime of the LED. Therefore, the ceramic substrate is not only in charge of heat dissipation of LED but also shoulders the RDL of LED packaging. Unfortunately, the metallization of Al₂O₃ and AlN substrates with copper is hard because both Al₂O₃ and AlN are not conductors. Roughening their surfaces and then using electroless deposition was a common approach. Surface metallization, mask design, photoresistant coating, exposure, development, and then pattern etching are the standard operation process (SOP) for RDL formation on the ceramic substrates. The SOP takes a long time and is expensive, even high risk, because the process flow is long, the palladium used as the catalyst of the electroless deposition is expensive, and after baking the copper electroless deposition layer, copper blister may be formed on the substrates. Therefore, another approach, adhesive layer (i.e., chemical bonding) instead of anchor effect (physical bonding), was proposed. The promising adhesive layer that links the ceramic material and copper layer together is ZnO. However, although ZnO is a good adhesive layer, it is not a conductor. The copper RDL has to be formed on the ZnO layer by electroless deposition and subsequently copper electroplating is employed to increase the RDL thickness.

An adhesive layer (AdL) between the metal layer and the glass surface is necessary. The AdL plays a bridging material because it is capable of bonding the metal layer to the glass surface, even a ceramic surface. A basic bonding mechanism was explained by Fujishima et al., who employed a ZnO layer as an AdL to enhance the adhesion of a deposited copper layer on a glass surface. ZnO reacted with glass to form an intermediate oxide and provided anchoring effect to bond the deposited copper layer. However, ZnO is not a conductor, so the ZnO-coated glass substrate must be further metallized with copper electroless deposition and then electroplated with copper to increase the copper thickness on the glass substrate.

Herein, the physical property of ZnO is modified by doping alumina into the ZnO to form a conductive Al-doped ZnO (AZO) layer. The conducting mechanism of AZO is similar to that of indium tin oxide (ITO). Because an acidic solution can dissolve AZO, AZO layer can be patterned before and after copper metallization using an acidic etching solution. We demonstrate two metallization processes that can form copper patterns on the glass and ceramic substrates with good copper layer adhesion by means of the AZO coating process. One process is to deposit an AZO layer onto the glass or the ceramic substrate by dip coating and then copper film was directly electroplated onto the baked AZO layer. Finally, copper patterns were formed after an etching process. The other process is to deposit an AZO layer onto the glass or the ceramic substrate through a baking process and then AZO patterns were formed first by an etching process. Following that, copper was directly electroplated on the patterned AZO.

Experimental

The dimensions of the glass and ceramic substrates were 20 mm × 20 mm. Before the AZO coating process, these substrates were cleaned in a DI water bath and then transferred into an alcohol bath with ultrasonic auxiliary for 30 minutes. Following that, these substrates were transferred into a bath containing 1M NaOH solution for 5 minutes, and then transferred into a bath containing H₂SO₄/H₂O₂ solution with a volume ratio of 1:1 in order to remove any organic contamination. Finally, these substrates were cleaned with DI water again to remove any chemicals. The AZO sol-gel was prepared by mixing Zn(CH₃COO)₂·2H₂O with AlCl₃·6H₂O (Al/Zn = 2 at. %) in dehydrated alcohol at 70 °C, and slowly adding 2-aminoethanol (C₂H₅NO) in the solution. The molar ratio of Zn(CH₃COO)₂·2H₂O to 2-aminoethanol was 10:1. Following
that, the temperature of the solution was cooled down to 25°C and the solution was continuously agitated for 2 hours and, subsequently, stewing it at 25°C for 24 hours. Regarding the sol-gel synthesis method of AZO, many papers have reported in detail.49,50,54,61,62

After surface pretreatment of the substrate as mentioned above, the substrate was put in the AZO sol-gel to do dip coating for 5 minutes. Following that, the AZO-coated substrate was dried at 25°C and then transferred in a furnace whose temperature had been maintained at 350°C for 10 minutes. The dip coating process was repeated three times. After the dip coating process, the AZO-coated substrate was heated in the furnace at 500°C for one hour to form a layer of hybrid oxide between the AZO and the substrate and also made the substrate be conductive due to the AZO layer.

The cross-section and element distribution of the AZO-coated substrate was imaged and analyzed using scanning electron microscopy (SEM, JEOL, JSM-6010LA), backscattered electron imaging (BEI) and energy-dispersive X-ray spectroscopy (EDS), respectively. The resistivity of the AZO layer was measured by using a four-point probe instrument. The “E&ESC” logotype was adopted as the pattern of copper electroplating. The pattern of the “E&ESC” logotype on the substrates was formed through dry film coating, pattern formation of the dry film, acidic etching, and then copper electroplating. An alkaline copper electroplating solution was used for the direct copper electroplating on the patterned AZO. Its composition and formula was reported in previous works.63,64 Two organic additives, bis-(3-sulfopropyl) disulfide (SPS) and polyethyleneimine (PEI), were employed in the alkaline copper electroplating solution.63

Results and Discussion

Figure 1 illustrates two copper metallization processes of the glass and the ceramic substrates. Process (a) is a typical copper electroless deposition process, which Pd is employed as the catalyst to be physically adsorbed on the substrate surface. Following the catalyst adsorption, the Pd-coated substrate is transferred into a copper elec-

![Figure 1. Process schemes of copper metallization of substrates. (a) Electroless deposition process, (b) AZO dip coating process.](image)

![Figure 2. Resistivity measurements after AZO coating and was baked on glass substrates. The coating times were 1, 3 and 6. After each AZO coating, the AZO-coated glass substrate was baked at 350°C for 10 minutes in order to remove the solvent of the sol-gel and to bond the AZO layer to the glass substrate.](image)
Alternatively, a process (b) is proposed and illustrated in Fig. 1b. The cleaned substrate is dipped in the AZO sol-gel bath for 5 minutes and then slowly pulled out from the AZO sol-gel bath. Following the AZO sol-gel dip coating, the AZO-coated substrate is transferred in a furnace to be baked at 350°C for 10 minutes. The AZO coating process is repeated for three times in order to increase the AZO thickness and the roughness thereof. The AZO-coated substrate becomes conductive due to the AZO layer, so copper can be electrodeposited directly on the substrate in an alkaline electroplating solution.

The coating times of the AZO sol-gel on the substrate, such as a glass plate, either influence AZO resistivity or AZO transparency, as shown in Fig. 2. Obviously, when the AZO coating times were increased, the AZO resistivity was correspondingly decreased and its transparency was also lowered. Evidently, the resistivity of one-time AZO coating was high (i.e., $5.65 \times 10^{-2} \, \Omega \cdot \text{cm}$) because the AZO layer was too thin to be a good conducting layer.65 The AZO resistivity was decreased after three-time coating, which was very close to that of six-time coating (i.e., $3.5 \times 10^{-2} \, \Omega \cdot \text{cm}$). This result implies that there is a minimum coating times to increase the AZO thickness with the minimum resistivity, as shown in Fig. 2. To decrease the resistivity of AZO to 1.54 to $1.66 \times 10^{-2} \, \Omega \cdot \text{cm}$, even $2.0 \times 10^{-3} \, \Omega \cdot \text{cm}$, its thickness has to be increased.59,65,66 Herein, the thickness of the AZO coated on the substrate was 0.45 μm (see Fig. 4), which is much thinner than that reported in previous works.59,65,66 Therefore, all the results subsequently appearing in this work went through three-time AZO coating rather than six-time AZO coating in order to shorten the overall process time.

Figure 3 shows that AZO films not only could be coated on the glass substrate (see Figs. 3a, 3d) but also on ceramic substrates, including Al2O3 (see Figs. 3b, 3e) and AlN (see Figs. 3c, 3f) substrates. Surface etching process for roughening the substrate surface was not necessary. AZO films were tightly coated on these substrates. Because the AZO films were conductive, these AZO-coated substrates could be directly electroplated with copper in an alkaline electroplating solution, as shown in Figs. 3g, 3h, 3i. A Scotch tape (3 M, #610) could not peel off the electroplated copper film that had been made a cross-cut pattern on it. Because the AZO is a sol-gel solution rather than powder before drying, its adhesion strength depends on its dry thickness and coverage, that is, the sol-gel concentration coated on these substrates, especially the ZnO concentration in the sol-gel solution. The relationship between the ZnO concentration and the adhesion strength of the AZO layer is described in the supplemental material.

To understand the root cause of good adhesion, a typical SEM cross-section image of Cu/AZO/glass is shown in Fig. 4. Besides, element mapping detected by EDS was also carried out and shown in Fig. 4. Figures 4a and 4b show that the mean thickness of the AZO film is around 0.45 μm and the interface between the glass surface and the AZO surface is very flat, almost no roughness. This result indicates that the root cause of strong adhesion between the glass surface and the AZO surface does not rely on roughness (i.e., anchoring effect) but chemical bonding.42,43,46,47,50,67,68 Previous articles45,69 have confirmed that ZnO can react with glass at a high temperature to form a composite oxide (i.e., ZnSiO3), such that the two materials, glass and ZnO, merge together within a short range after being baked.

On the other hand, the mean copper thickness plated on the AZO was around 0.55 μm and the interface between the AZO surface and the electroplated copper surface was rough, as confirmed by Figs. 4a and 4b. Because copper atom easily diffuses into oxides, such as Al2O3 or ZnO,43,45,46,70,71 to form hybrid oxides, the electroplated copper film can be tightly attached on the AZO surface. The copper and zinc elements distribution was characterized by EDS mapping and shown in Figs. 4d and 4e, respectively, to make sure that the gray and white color images in Fig. 4c are copper and AZO, respectively. Both Al2O3 and AlN can react with ZnO to form ZnAl2O4 spinel72 and (AlN)1-x(ZnO)x compound.73 AlN also can be co-doped into ZnO to form covalent bond.42,43,47,50,67,68 Actually, another approach for spinel formation is also possible in the presence of H2O that is, 2AIN + 3H2O $\rightarrow$ Al2O3 + 2NH3 and then Al2O3 + ZnO $\rightarrow$ ZnAl2O4 (spinel).

Since AZO can be dissolved in an acidic solution, two processes can be employed to make copper patterns. Figure 5 illustrates one metallization process that the substrate is entirely coated with AZO
Figure 4. Cross-section of the AZO-coated glass substrate after copper plating shown in Fig. 3g and the element mapping thereof. (a, b, c) SEM images enlarged in ×10 K, ×20 K and 5 K, where the white layer is copper and gray layer is AZO, (c, d, e) copper and zinc elements distribution. The thickness of the copper and the AZO layer is about 0.55 μm and 0.45 μm, respectively.

film first, as illustrated in Fig. 5a and then directly transferred into a copper electroplating bath to electrodeposit copper on the AZO layer, as illustrated in Fig. 5b. Following these steps, the entire substrate is coated with a layer of copper film. Subsequently, a layer of dry film is attached on the copper surface and goes through a patterning process, as illustrated in Fig. 5c. The copper and AZO films except for the substrate can be etched by an acidic solution, and then conductive patterns are formed on the substrate, as illustrated in Fig. 5d. After the dry film is removed, the conducting circuits are obtained, as illustrated in Fig. 5e. The conducting lines are composed of two layers of materials. The upper layer is copper, the lower layer is AZO. Obviously, the sidewall of the patterned AZO shown in Fig. 5e is exposed in air, so an undercut of the AZO sidewall caused by the etching solution may occur if the etching parameter is not appropriately controlled. The etching solution has to simultaneously deal with two materials (i.e., copper and AZO) whose etching rate is different.

Figure 5. Process schemes of copper pattern formation through a panel copper plating on AZO-coated substrates. (a) AZO dip coating and being baked on substrates at 350°C for 10 minutes for three times, (b) electrochemical deposition of copper (ECD Cu) on the entire AZO-coated substrates, (c) dry film coating and the pattern formation thereof, (d) simultaneous etching of copper and AZO layers, (e) dry film removal. The electroplated copper films are bonded to the patterned AZO. The sidewalls of the patterned AZO are exposed in air.
Figure 6. Practical results of Fig. 5. The substrates are (a, d, g) glass, (b, e, h) Al$_2$O$_3$, (c, f, i) AlN. The copper pattern is the “E&ESC” logotype. DF means dry film. The dimension of these substrates are 50 mm × 50 mm.

The process steps proposed in Fig. 5 were carried out using “E&ESC” logotype as the pattern. Figures 6a–6c show bare glass, Al$_2$O$_3$ and AlN substrates, respectively, after a surface cleaning step. Following AZO coating process for three times, the surface color was somewhat different from the original one, as shown in Figs. 6d–6f. After dry film coating, pattern formation, copper electroplating, etching and dry film removal, the “E&ESC” logotypes of copper appeared on these substrates, as shown in Figs. 6g–6i. These logotypes could pass the peeling test by using the Scotch tape (3 M, #610).

Another process is proposed and illustrated in Fig. 7. Figure 7 illustrates that the substrate is entirely coated with AZO film first, as illustrated in Fig. 7a, and then followed dry film coating, pattern formation steps, as illustrated in Fig. 7b. Subsequently, the substrate is transferred into an etching solution to remove the AZO where is not covered by the dry film, as illustrated in Fig. 7c. After the patterned dry film is removed, the AZO film is also correspondingly patterned, as illustrated in Fig. 7d. The patterned AZO can be directly transferred into an alkaline copper electroplating bath to electrodeposit copper on the patterned AZO, as illustrated in Fig. 7e. Obviously, the sidewalls of the patterned AZO are covered by the electroplated copper films.
The etching solution used in Fig. 7c only needs to deal with one electroplated copper because the patterned AZO lines are conductive. Al₂O₃ and AlN substrates were coated with AZO films and had the case shown in Fig. 5d. The undercut issue at the sidewalls of the patterned AZO lines shown in Fig. 7e are entirely covered by the materials (i.e., AZO). Therefore, the undercut issue at the sidewalls of the AZO lines shown in Fig. 7c is easily controlled compared with the case shown in Fig. 5d.

The process steps proposed in Fig. 7 were also carried out using the “E&ESC” logotype as a pattern. Figures 8a–8c show that the glass, Al₂O₃ and AlN substrates were coated with AZO films and had the “E&ESC” pattern of dry films, respectively. Figures 8d–8f show that the “E&ESC” patterns were formed on these substrates after the AZO layers where were not covered by the dry film was etched by an acidic solution and then the patterned dry films were removed. The “E&ESC” logotype could only be clearly seen on the glass substrate, as shown in Fig. 8d, because glass is transparent. Subsequently, these substrates with the “E&ESC” logotypes were directly electroplated with copper in the alkaline copper electroplating solution to metallize the logotypes with copper, as shown in Figs. 8g–8i. Figures 8g show that the glass substrate where was not covered by the patterned AZO and copper was not employed. Instead, a cheap AZO sol-gel coating process exhibits needs expensive palladium catalyst and is not environment-friendly is not employed. Instead, a cheap AZO sol-gel coating process exhibits a promising approach for direct copper pattern electroplating on these ceramic and glass substrates.

Conclusions

The surface metallization of ceramic and glass substrates with copper patterns are achieved using AZO as a conducting layer. The AZO layer plays three roles in the copper metallization process. The first one is to act as an adhesive layer to interlock the substrates and the electroplated copper layer. The second one is to act as a conducting layer for copper electroplating on it, although the resistivity of the AZO is 3.5 × 10⁻² Ω·cm. The third one is to provide an approach for direct copper pattern electroplating because AZO can be etched by an acidic solution. In this work, the electroless copper deposition process that needs expensive palladium catalyst and is not environment-friendly is not employed. Instead, a cheap AZO sol-gel coating process exhibits a promising approach for direct copper pattern electroplating on these ceramic and glass substrates.

Acknowledgments

This work is supported by the Ministry of Science and Technology of Taiwan with a contract number of NSC 103-2622-E-005-002.

References

1. L. W. Schaper, S. L. Burkett, S. Spieszhoefer, G. V. Vangara, Z. Rahman, and S. Polanreddy, *IEEE Trans. Adv. Packag.*, 28, 356 (2005).
2. S. W. R. Lee and R. Hon, *MRS Online Proc. Lib.*, 970 (2006).
3. C.-W. Lin, H.-A. Yang, W. C. Wang, and W. Fang, *J. Micromech. Microeng.*, 17, 1200 (2007).
4. R. Beica, P. Siblerud, C. Sharbono, and M. Bernt, in *Electronics Packaging Technology Conference*, p. 212, IEEE (2008).
5. B. Dang, S. L. Wright, P. S. Andry, E. J. Sprogis, C. K. Tsang, M. J. Interrante, B. C. Webb, R. J. Polastre, R. R. Horton, C. S. Patel, A. Sharma, J. Zheng, K. Sakuma, and J. L. Knickerbocker, *IBM J. Res. Dev.*, 52, 599 (2008).
6. J. Inouzhi, R. G. Southwick, V. N. Johnson, W. B. Knowlton, and A. J. Moll, *IEEE Trans. Adv. Packag.*, 31, 4 (2008).
7. J. L. Knickerbocker, P. S. Andry, B. Dang, R. R. Horton, C. S. Patel, R. J. Polastre, K. Sakuma, E. S. Sprogis, C. K. Tsang, B. C. Webb, and S. L. Wright, in *Electronic Components and Technology Conference*, p. 538, IEEE (2008).
8. K. Kumagai, T. Yoneda, H. Izumino, H. Shimojo, M. Sunohara, T. Kurihara, M. Higashi, and Y. Mabuchi, in *Electronic Components and Technology Conference*, p. 571 IEEE (2008).
9. O. Seong Joon, K. Chunho, and D. F. Baldwin, *IEEE Trans. Adv. Packag.*, 26, 302 (2003).
10. L. S. Burkett, X. Qiao, D. Temple, B. Stoner, and G. McGuire, *J. Vac. Sci. Technol. B: Microelectron. Nanometer Struct.–Process., Meas., Phenom.*, 22, 248 (2004).
11. A. Klumpp, R. Merkel, P. Ramm, J. Weber, and R. Wieland, *Jpn. J. Appl. Phys.*, 43, L829 (2004).
12. P. Benkart, A. Kaiser, A. Munding, M. Bischor, H. J. Pfleiderer, E. Kohn, A. Heitmann, H. Huebner, and U. Ramacher, *IEEE Des. Test. Comp.*, 22, 512 (2005).
13. C. Ilicciu, J. Jing, F. E. H. Tay, J. Miao, and T. Sun, *Surf. Coat. Technol.*, 198, 314 (2005).
14. T. Karakuzu, B. M. Maoz, G. Lando, A. Vaskevich, and I. Rubinstein, *ACS Appl. Mater. Interfaces*, 3, 978 (2011).
15. G. A. Shafeev, J. M. Themlin, L. Bellard, W. Marine, and A. Crous, *J. Vac. Sci. Technol. A: Vac. Surf. Films*, 14, 319 (1996).
16. Y. F. Chen, E. T. Kang, K. G. Neoh, and W. Huang, *Langmuir*, 17, 7425 (2001).
17. E. Delamarine, M. Geissler, R. H. Magnussen, H. Schmidt, and B. Michel, *Langmuir*, 19, 5892 (2003).
18. E. Delamarine, M. Geissler, J. Vichiconti, W. S. Graham, P. A. Andry, J. C. Flade, P. M. Fryer, R. W. Nunes, B. Michel, E. J. O’Sullivan, H. Schmidt, H. Wolf, and R. L. Wisnieff, *Langmuir*, 19, 5923 (2003).
19. E. Delamarine, J. Vichiconti, S. A. Hall, M. Geissler, W. Graham, B. Michel, and R. Nunes, *Langmuir*, 19, 6367 (2003).
20. M. Geissler, H. Kind, P. Schmidt-Winkel, B. Michel, and E. Delamarine, *Langmuir*, 19, 6283 (2003).
