CO_2 Laser-Induced Metal Deposition On Epoxy Resin Boards from Aqueous Solution

by C. Chen,* J. Zheng, J. Liu, Z. Xu, H. Liu, & W. Huang

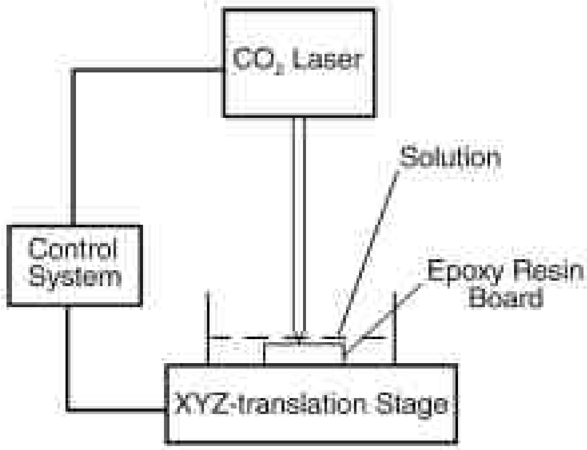

Fig. 1—Setup for CO_2 laser-induced deposition from aqueous solution.

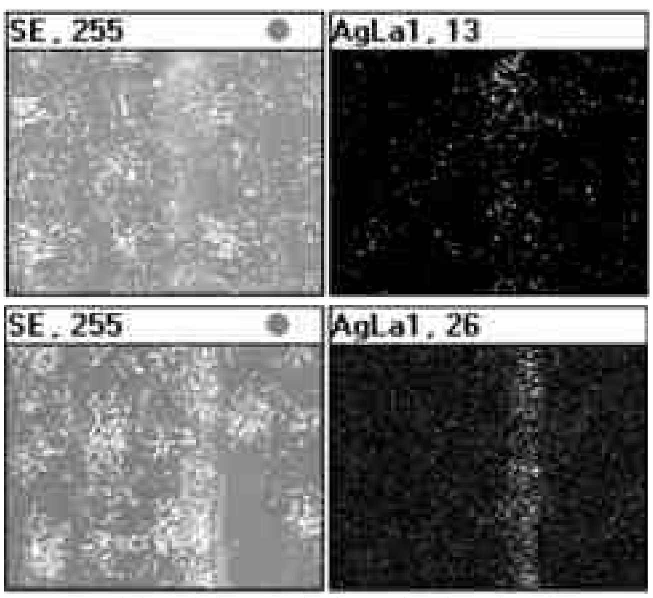

Fig. 2—Morphology of silver granules deposited on the surface of epoxy resin with 3.0 W laser power in (a) 0.1M and (b) 0.5M silver nitrate solutions.

Nuts & Bolts: What This Paper Means to You

This work describes the first use of CO_2 lasers for laser-induced metal deposition from aqueous solution. A silver line was deposited on an epoxy resin board. The researchers cover the effects of operating conditions, including solution concentration, laser power, scanning velocity, etc. When compared with other laser-based techniques, this process is simple, convenient, low cost and easy to handle.

A carbon dioxide (CO_2) laser was used for laser-induced metal deposition from aqueous solutions for the first time. In this work, a silver layer/line was deposited on an epoxy resin board by using a CO_2 laser. The effects of operating conditions, including solution concentration, laser power, scanning velocity and the thickness of water film on the substrate were studied as they influenced deposit thickness, width and density. Analysis of the silver deposit by electron probe micro-analysis (EPMA) and dynamic force microscopy (DFM) indicated that a transitional layer developed in the subsurface of the substrate. The silver can serve as an active seed layer for subsequent electroless copper plating. When compared with other techniques such as laser-induced forward transfer (LIFT), pulsed-laser deposition and laser-assisted chemical vapor-phase deposition (LCVD), this process is simple, convenient, low cost and easy to handle.[1]

Laser-induced deposition allows the localized metallization of polymeric materials such as epoxy resin, polyimide (PI) and Mylar. The laser beam is characterized by spatial and temporal coherence, and directionality, and thus the processes can be controlled and monitored with spatial resolution on the order of a micrometer or in the submicrometer range.[1] In microelectronics industry, especially in the manufacture of PCBs, the wire line on a polymeric substrate must be narrow and homogeneous. The conventional method used to produce such a metal layer/line involves electroless- and electro-plating. The entire process includes a long series of processes, including pretreatment (activation and sensitization), metallization of the substrate, image-transfer and etching. Such a complicated process involves high cost and low productivity. Recently, several methods using lasers to locally deposit such metal layer/lines on polymers have been reported,[2] including laser-induced forward transfer (LIFT), pulsed-laser deposition and laser-assisted chemical vapor-phase deposition (LCVD). These techniques cover a wide range of deposit/substrate combinations, but they have disadvantages, including the need to use vacuum and gas systems and the use of harmful compounds.[1,5,7,9,10]

Because of its simplicity, ease of handling and non-toxicity, laser-induced liquid-phase deposition on polymers

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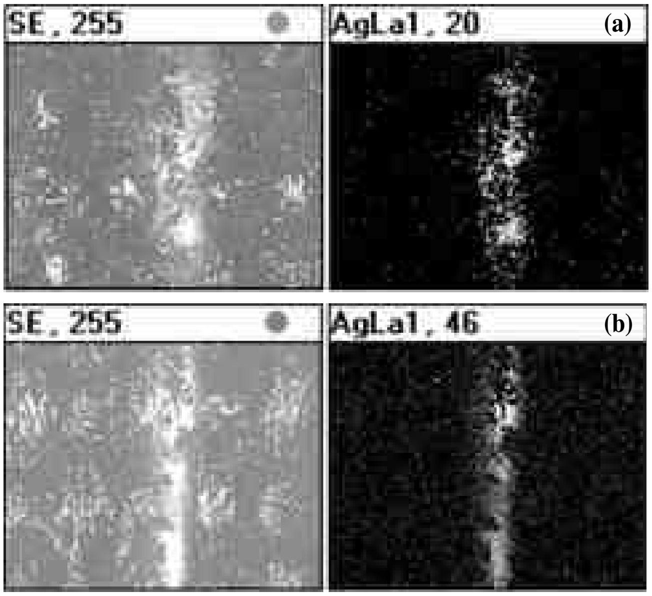

Fig. 3—Morphology of the silver layer deposited on the surface of epoxy resin at (a) 2.5 W and (b) 3.5 W laser power.

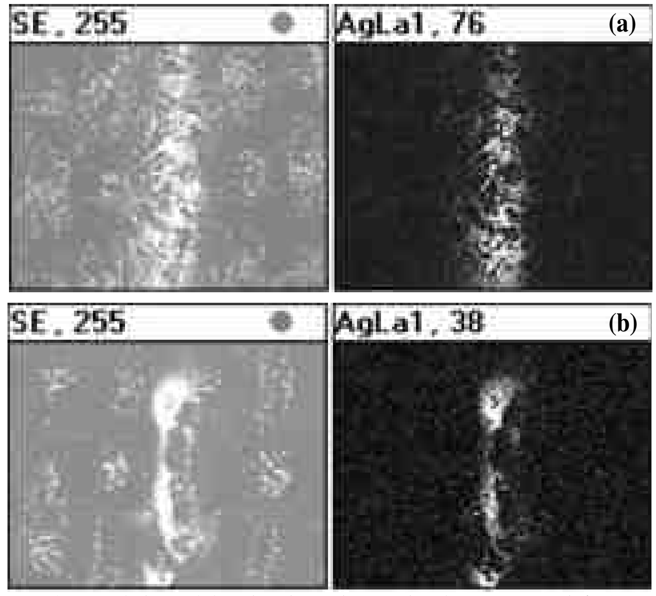

Fig. 4—Morphology of the silver layer deposited with (a) 1 mm and (b) 2 mm thickness of liquid film on the epoxy resin board.

is attracting more and more attention.[11,16] There are two types of such processes. One is laser-induced chemical liquid-phase deposition (LCLD), and the other is seeding and subsequently plating or electroless plating.[10] In the latter case, the surface of substrate is only activated with a laser pretreatment or receives a thin metal layer or metal seed from liquid precursors.[14,15] Generally, the lasers used with these techniques are among the following: XeCl, KrF, Nd:YAG. or Ar^+. The advantage of these types is that their energy can be selectively absorbed by the metal ions in liquid-phase. The wavelength of the laser is appropriate to strong absorption of metal ions, but not of the solvent itself. This can reduce energy losses. However, the disadvantage of these lasers, especially the excimer-type lasers, is their high cost. Even if this technology is successful, the costs limit its application in the microelectronics industry.

Using a carbon dioxide (CO_2) laser may be cheaper. An inexpensive low power CO_2 laser is useful for metal deposition in aqueous solutions. In the deposition process, energy absorption by water is stronger than that by the dissolved metal ions at the wavelength of a CO_2 laser, namely, $\lambda \approx 10.6\ \mu m$. Apparently, the metal deposition will be influenced to some extent, but the metal ions in solution can be deposited onto the surface of the substrate in the form of crystallites by controlling appropriate conditions, and more partial metal crystallites will diffuse into subsurface of the substrate. The metal crystallites are also seed crystals (such as Pd, Cu, Ni or Ag),[2,6] with which the surface of polymers (such as epoxy resin) can be activated. The copper layer/line can be subsequently deposited on the crystallites, and the result is a copper line of good conductivity and adhesion. In this work, we mainly studied CO_2 laser-induced deposition of silver from aqueous solution on epoxy resin boards. A finished copper layer was ultimately formed on the silver by electroless plating.

Experimental

The experimental setup was quite simple, as shown in Fig. 1. The solution was a solution of $AgNO_3$ and NH_4OH, whose concentration was varied from 0.1 to 1.0M. The laser used was a medical type built by HuaZhong University of Science and Technology. The focal spot size was controlled in the range of 0.1 to 1.0 mm (3.9 to 39.4 mils). The setup was computer-controlled. The beam was focused by moving the laser in the direction of the Z-axis. Its scanning velocity was controlled between 0.1 and 3.0 m/min (4 to

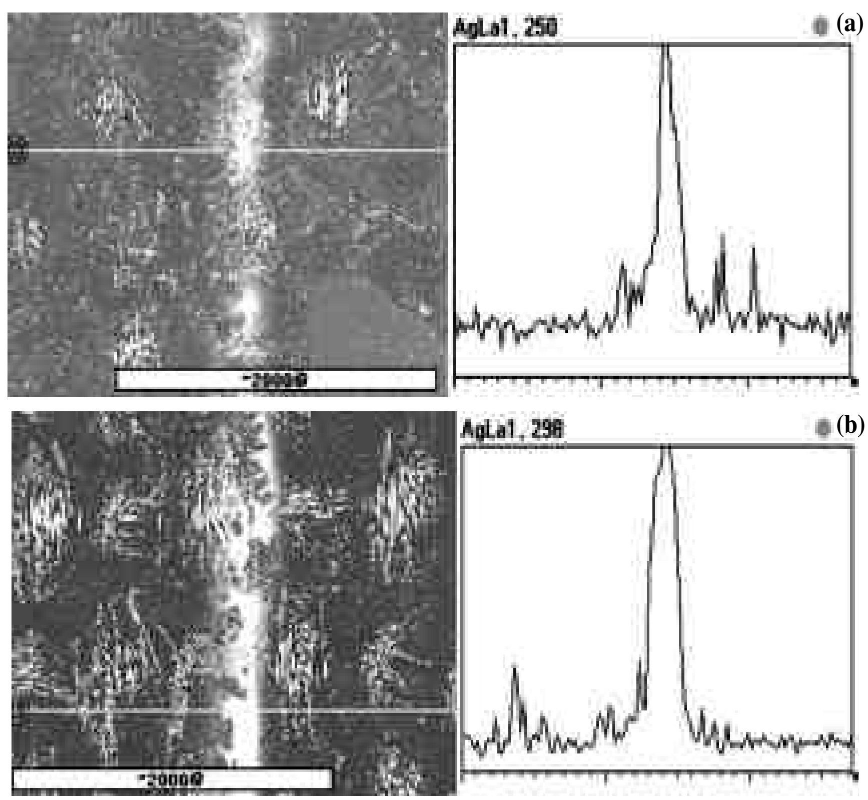

Fig. 5—Line analysis of EPMA for silver layers deposited on the substrate with different laser power levels:
(a) 2.5 W; length, 2.696 mm; width, 0.25 mm.
(b) 3.5 W; length, 2.717 mm; width, 0.35 mm.

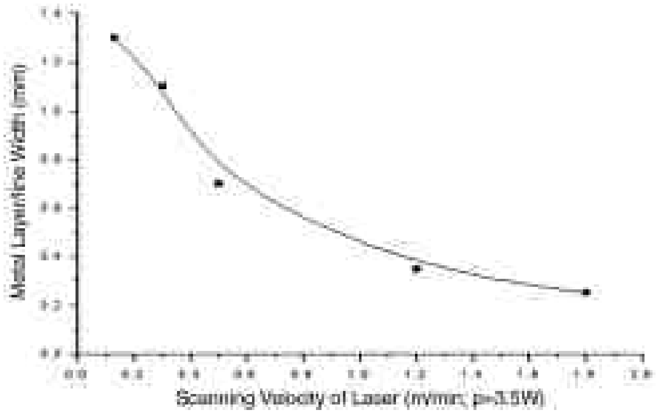

Fig. 6—Influence of scanning velocity of laser on the width of the metal layer.

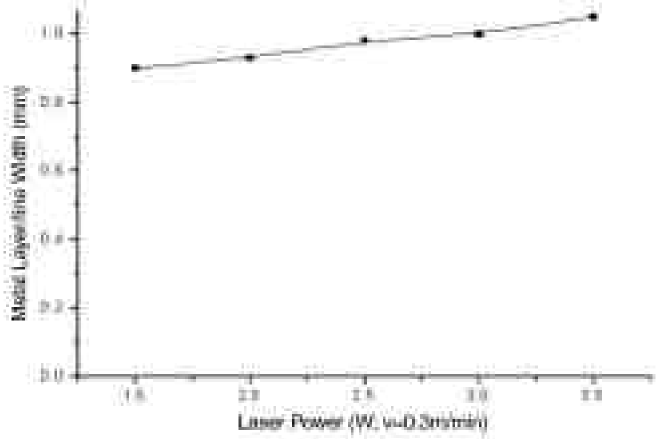

Fig. 7—Influence of the laser power on the width of the metal layer/line.

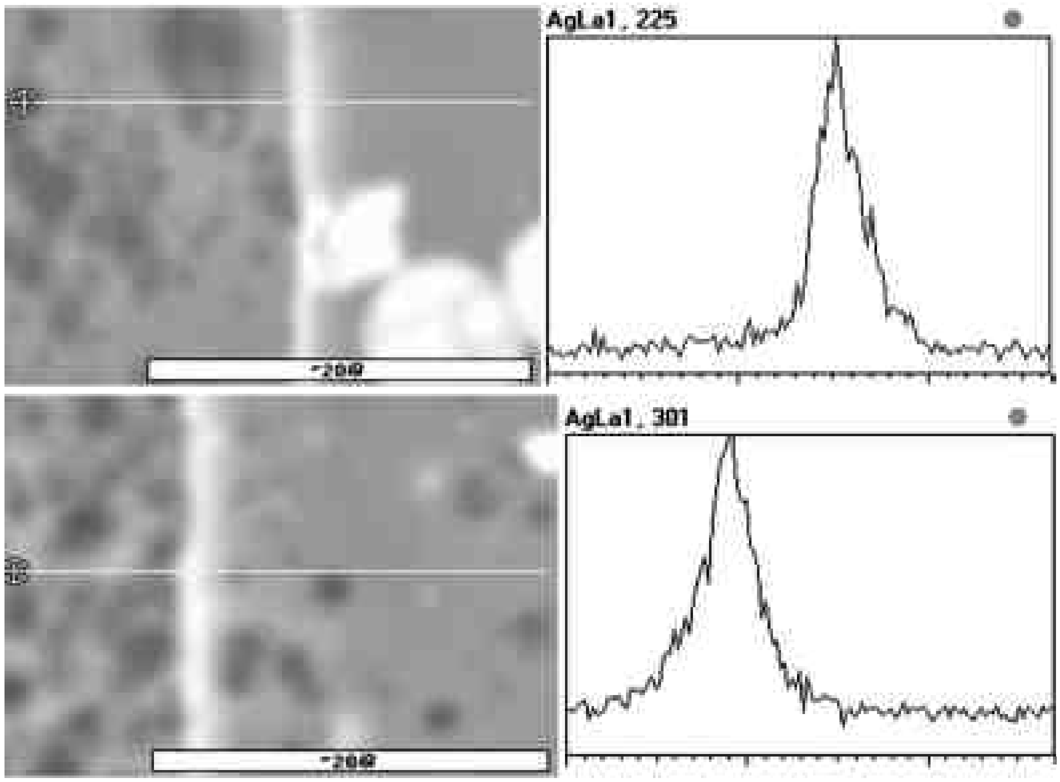

Fig. 8—Transverse section line analysis of EPMA of metal layer thicknesses at different laser power levels:
(a) 3.0 W; length, 26.96 µm; thickness, 5 µm. (b) 4.0 W; length, 26.96 µm; thickness, 7 µm.

118 in./min). The substrate was an epoxy resin board, measuring 40 x 20 x 1 mm (1.57 x 0.79 x 0.4 in.). The operating temperature was 25°C (77°F). After washing with distilled water, the substrate was dipped into solution. The immersion depth was determined by the scanning velocity and laser power.

In the process of laser-induced deposition, the chemical reaction was one of thermal decomposition:

$$Ag^+ + 2NH_4OH \rightarrow Ag(NH_3)_2^+ + 2H_2O \quad (1)$$

$$Ag(NH_3)_2^+ + NO_3^- \rightarrow Ag + 2NH_3 + NO_2 + O_2 \quad (2)$$

In reaction (1), ammonia is a ligand, the electric potential $E_{Ag+/Ag}$ decreased and the stability of the silver ion was enhanced. In reaction (2), with the laser irradiating and ammonia volatilizing, the electric potential $E_{Ag+/Ag}$ increased and the redox reaction (2) was accelerated. In a sense, NH_4OH acts as a catalyst in the process of metal deposition. After that, metallic silver remained on the surface of substrate, and silver crystallites were formed.

The physical properties of the silver metal layer such as surface profile, width and thickness were analyzed with by electron probe microanalysis (EPMA) and dynamic force microscopy (DFM).

Results & Discussion

Surface Profile Analysis Of the Deposited Metal Layer/Line

The silver layers obtained varied with the deposition conditions, particularly as to density and line width. The major influencing factors were solution concentration, laser power, scanning velocity and liquid film thickness. Figure 2 shows the results of EPMA analysis for silver layers deposited at different concentrations. In each set of photos, the left shows surface morphology, and the right shows surface distribution analysis. It can be seen that the deposited metal seeds or layers varied with solution concentration. The

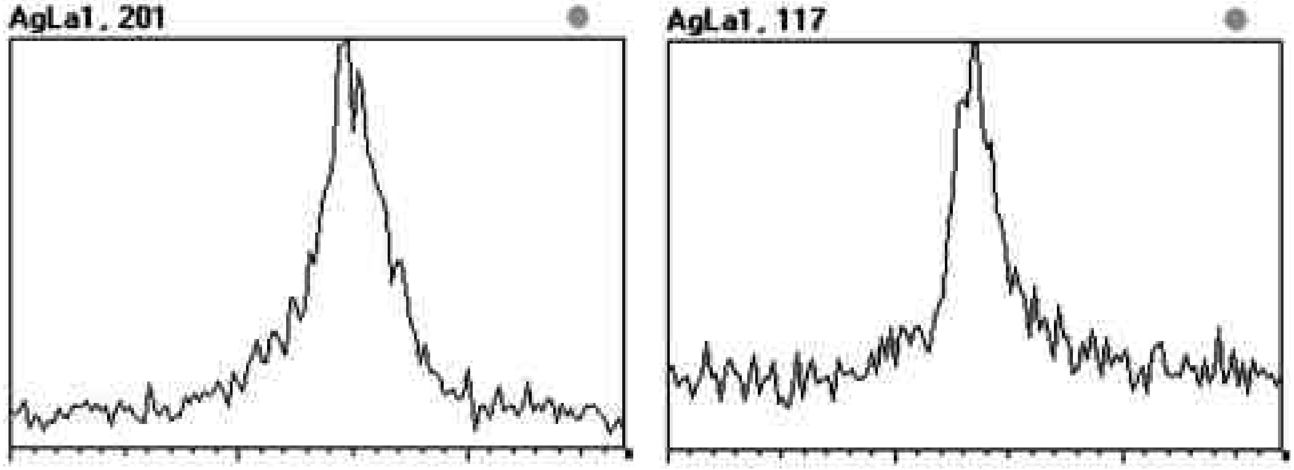

Fig. 9—Transverse section line analysis of EPMA of metal layer thicknesses at different scanning speeds (Power = 3.0 W):
(a) 0.13 m/min; length, 26.85 µm; thickness, 6 µm. *(b) 0.30 m/min; length, 26.96 µm; thickness, 3 µm.*

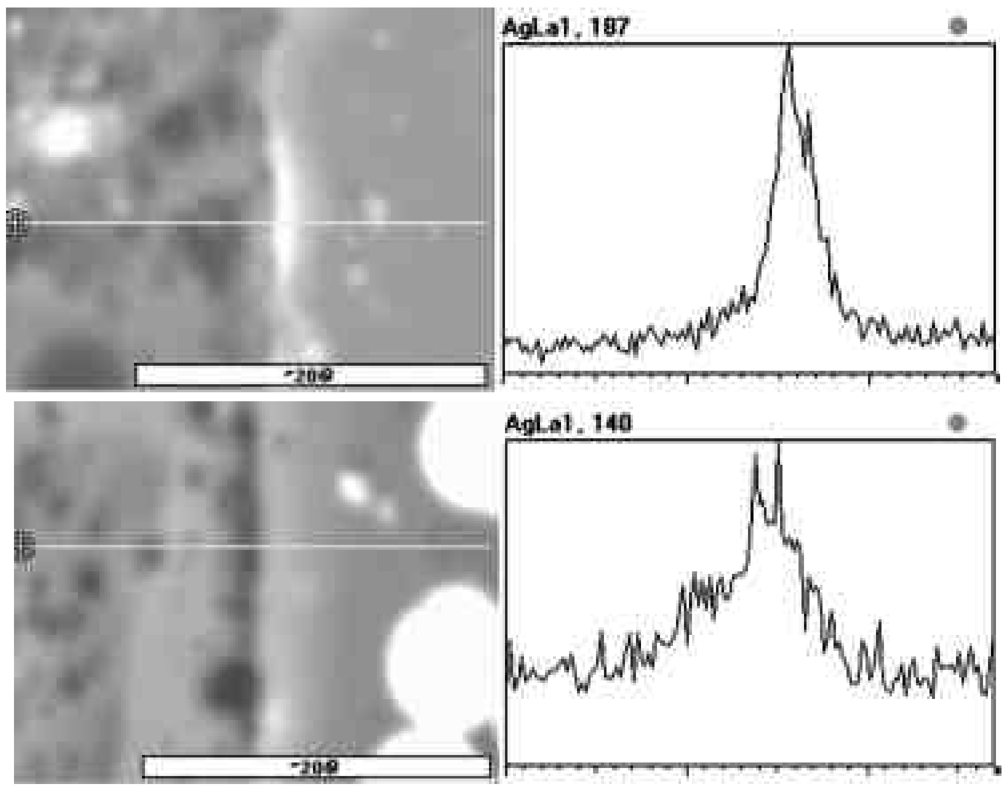

Fig. 10—Thickness of metal layers deposited on epoxy resin board at different solution concentrations:
(a) 0.1M; length, 26.74 µm; thickness, 4 µm. *(b) 0.5M; length, 26.85 µm; thickness, 8 µm.*

silver metal granules on the substrate were sparse at low concentrations, but dense and linear at higher concentrations.

Figure 3 illustrates the EPMA results for silver layers deposited at different laser power levels. With increasing laser power, the silver metal layer became denser and more continuous. Because of the rapid decomposition of $AgNO_3$ and other compounds, the line was better defined. The linearization of the metal layer is quite clear. The higher the laser power, the easier the linearization of the metal layer. Figure 4 shows the effect of liquid film thickness on the substrate on the morphology of the deposited metal layer. The energy absorption of the water caused a partial loss of energy. This energy loss was enhanced with increasing liquid film thickness, which in turn caused a decline in the continuity of the metal layer. Thus, selecting the appropriate liquid film thickness on the substrate is important for CO_2 laser-induced metal deposition from aqueous solution.

Line Width of the Silver Metal Layer

The line width of the silver metal layer is an average value of the data measured by line analysis of the EPMA results (Fig. 5). The primary factors influencing line width were scanning velocity (V) and laser power (W). The relationship between the width and V or W is shown in Figs. 6 and 7. It can be interpreted that the absorbed energy in the localized area of the liquid film and epoxy-resin board was influenced by irradiation time of the laser beam and the laser power. At higher scanning speeds and lower power, the absorbed energy was reduced, and the rate of diffusion in the vertical direction of the beam track was slower. This led to slower deposition and diffusion of the silver granules on the surface of substrate. Thus, a narrow and linear silver layer could be deposited on the substrate.

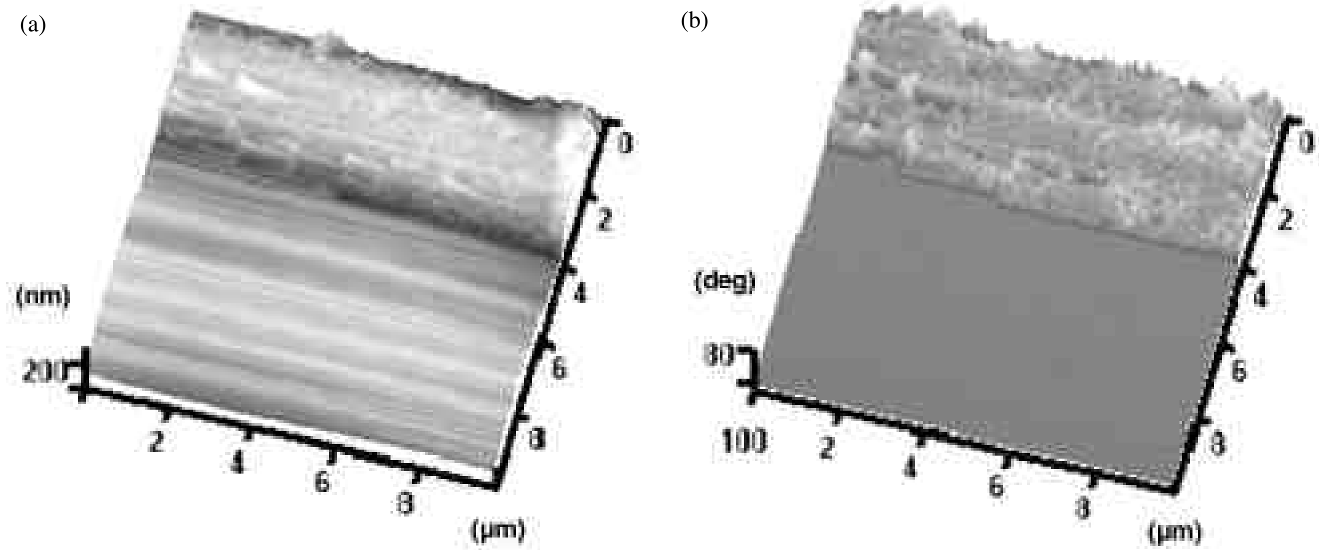

Fig. 11—DFM three-dimensional images of the silver layer: (a) surface morphology images; (b) phase images. The laser power was 4.0 W and the scanning velocity was 0.4 m/min.

Thickness of the Metal Deposits

After the cross sections of the specimens were polished, the deposit thickness was determined by EPMA line analysis. The corresponding curves are given in Figs. 8, 9 and 10. It can be seen in Fig. 8 that the thickness of the metal layer was 5 μm and 7 μm, when the laser power was 3 W and 4 W, respectively. The thickness increased with laser power. Fig. 9 shows the effect of scanning velocity (V). The thickness decreased with increasing scanning velocity. The relationship between thickness and solution concentration is shown in Fig. 10. The metal layers deposited from the solutions of higher concentration are clearly thicker. Silver metal granules that diffused into the surface of the epoxy resin board are somewhat deep, but not dense. A special subsurface layer, called the transitional layer, was found to form by such silver granules. The transitional layer became thicker and less defined in higher concentration solutions.

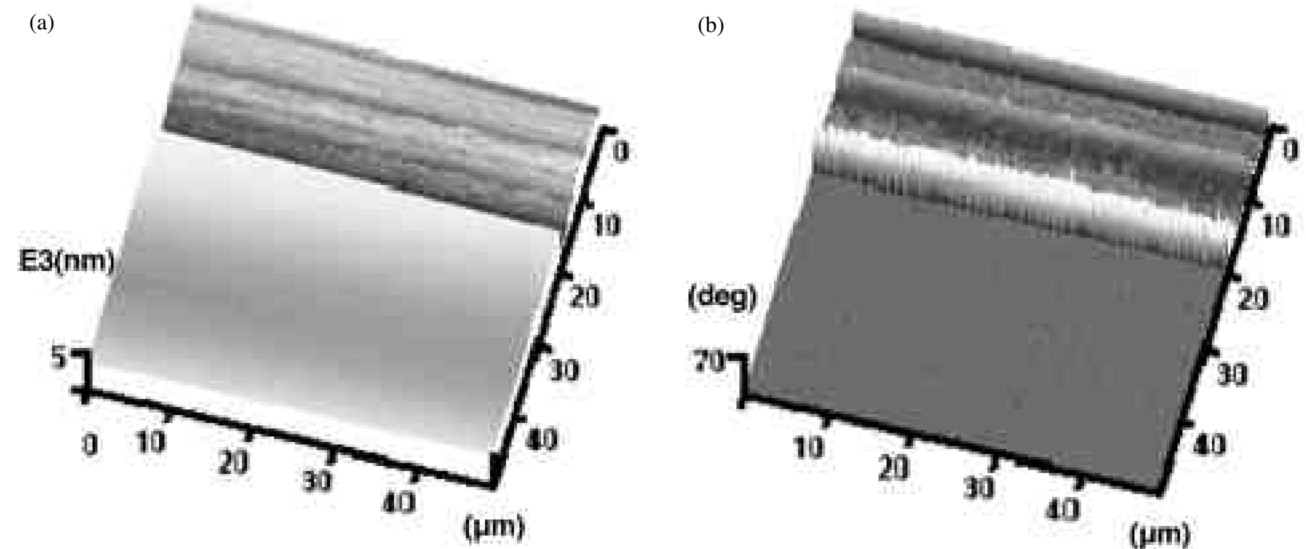

Fig. 12—DFM three-dimensional images of copper layer on the silver layer: (a) surface morphology images; (b) phase images. The copper layer was deposited on silver by electroless plating. The solution composition was 0.1M $CuSO_4$, 0.2M NaK-tartrate, 0.1M NaOH and 6M HCOH.

Copper Deposition on the Silver Layer

Autocatalytic electroless copper deposition is well known and has been used for a long time. If the substrate is non-conductive, as with epoxy resins, polyimides or ceramics, such electroless plating is virtually impossible because of the lack of catalytic sites on the substrate.[8] Hence, an area-selective palladium-, copper-, or nickel-seeding needs to be carried out by laser treatment. Further, its thickness directly affects the deposition of the copper layer. Of course, the silver metal layer on an epoxy resin board surface is an important kind of seed crystal. Silver and copper layers on silver were investigated by analyzing three-dimensional photographs obtained by dynamic force microscopy. Figure 11 illustrates the morphology of the silver layer deposited on an epoxy resin board. Its surface is very wavy, but dense and continuous. The copper layer deposited on silver by electroless plating is also dense and continuous, as shown in Fig. 12, but its surface is not as wavy as the silver layer surface.

Conclusion

Silver metal layers/lines have been directly deposited on epoxy resin boards from aqueous solutions using a CO_2 laser. The EPMA and DFM results show that the thickness, line width and continuity of the silver metal deposits were influenced by solution concentration, laser power, scanning velocity and the thickness of the liquid film on the substrate. A transitional layer formed by silver was found in the subsurface of the substrate, followed by bulk deposition of silver. Both the deposit thickness and density increased with increasing laser power and solution concentration. However, the metal layer/line became discontinuous when the liquid film on the substrate was too thick. Thus, selecting an appropriate liquid film thickness is very important. It was also found that the width of the metal layer/line varied with the scanning speed.

Although the deposition parameters have not been fully optimized, the deposits were more continuous and uniform. On the silver deposit, we found that a subsequent electroless copper layer could be formed, which was found to be dense, continuous, conductive and very adherent to the substrate.

References

1. K. Kordas, *et al*., *J. Appl. Surf. Sci*., **172**, 178 (2001).
2. T.J. Hirsch, R.F. Miraky & C.Lin, *Appl. Phys. Let*., **57** (13), 1357 (1990).
3. A. Bauer, *et al*., *Applied Surface Science*, **46**, 113 (1990).
4. T.L. Rose, D.H. Longendorfer & R.D. Rauh, *Appl. Phys. Let*., **42** (2), 193 (1983).
5. I.P. Herman, *Chem. Rev*., **89**, 1323 (1989).
6. J. Zahavi, S. Tamir & M. Halliwell, *Plating and Surface Finishing*, **73**, 57 (February 1986).
7. K.W. Beeson & N.S. Clements, Appl. Phys. Lett., **53** (7), 547 (1988).
8. S. Fähler, S. Kahl, M. Weisheit, K. Sturm & H.U. Krebs, *Appl. Surf. Sci.,* **154-155**, 419 (2000).
9. E. Hilmar, R. Seeböck, M. Charbonnier & M. Romand, *Surface and Coating Technology*, **125**, 19 (2000).
10. G.A. Shafeev and P. Hoffmann, *Appl. Surf. Sci*., **138-139**, 455 (1999).
11. Z. Geretovszky & I.W. Boyd, *Appl. Surf. Sci*., **138-139**, 401 (1999).
12. K. Révész, B. Hopp & Z. Bor, *Appl. Surf. Sci*., **109-110,** 222 (1997).
13. S.I. Dolgaev, A.A. Lyalin, A.V. Simakin, V.V. Voronov & G.A. Shafeev, *Appl. Surf. Sci*., **109-110,** 201 (1997).
14. H. Horm, S. Beil, D.A. Wesner, R. Weichenhain & E.W. Kreutz, *Nuclear Instruments and Methods in Physics Research B*, **151**, 279 (1999).
15. K. Kordás, *et al*., *Thin Solid Films*, **384**, 185 (2001).
16. A.G. Schrott, B. Braren, E.J.M. O Sullivan, R.F. Saraf, P. Bailey & J. Roldan, *J. Electrochem. Soc*., **142**, 944 (1995).
17. K. Kordás, *et al*., *Appl. Surf. Sci*., **154-155**, 399 (2000).
18. D. Bimberg, *et al*., *Laser in Industrie und Technik*, Lexika-Verlag, Grafenau / Württemberg, Germany, 1977.
19. M. Cao, *et al*., *Heat Processing of Lasers*, **6**, 98 (1995).

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