The Effect of Ultrasonic Agitation On Copper Plating in an Acid Bath

By M.C. Hsiao and C.C. Wan

Although stronger than mechanical agitation obtained by magnetic stirring, ultrasonic agitation is dependent on the location of the transducer in the plating tank. This dependency of position affected the crystal orientation of copper deposited in an acid sulfate bath. Ultrasonic agitation can lower the surface activation potential. However, deposit distribution in drilled holes In a printed circuit board was not Improved when ultrasonic agitation was compared with mechanical agitation.

Sufficient, uniform mechanical agitation is an essential process control variable in many plating systems. Mechanical stirring or continuous pumping are the usual methods of agitation, but have proven to be insufficient for plating multi-layer printed circuit boards with drilled holes or integrated circuit lead frames. Because of its ability to induce cavitation and acoustic streaming in fluids, ultrasonic agitation appeared to be a candidate for the supply of high-intensity agitation. Several researchers’-’ have studied the effect of ultrasonic agitation on the microhardness, porosity and grain size of electrodeposits. Although results have shown some improvements, practical applications of ultrasonic agitation are still limited to surface cleaning processes. This paper describes a systematic study of the performance and kinetics of copper plating with ultrasonic agitation, which was undertaken to provide an objective evaluation of the incorporation of ultrasonic agitation in an acid copper sulfate bath.

Experimental Procedure

A cylindrical, stainless steel tank, 10.5 cm in diameter and 5 cm deep, was selected for experiments with a 20-watt, 30 kHz ultrasonic agitator. * A rotating disk electrode system coupled with a potentiostat was used to measure the diffusion layer thickness. In this case, the plating bath was a 0.1 M H_2SO_4 solution containing 0.05 M $CuS0_4$.

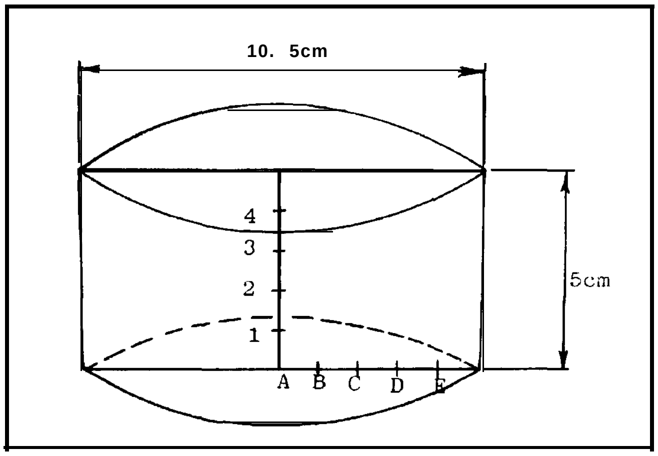

Fig. 1-Cathode locations in plating tank over a transducer in the center below the bottom of the tank.

To study kinetics and potential transient response, rectangular untreated printed circuit board segments covered with the original copper foil were used as cathodes in a Solution containing 0.75 M $CuS0_4$ and 0.76 M H_2SO_4. The area surrounding the 4-cm^2 plated area was covered with epoxy resin. Another type of cathode used in this solution was a segment of printed circuit board with a hole that varied in diameter from 0.5 to 2.4 mm, which had previously been plated with electroless copper. The anode faced the cathode at a distance of 3.5 cm. The ultrasonic transducer was located under the bottom of the tank.

Deposit thickness was measured by examining cross sections. Crystal orientation was determined by X-ray diffraction. The position of the cathode inside the plating tank was changed as shown in Fig. 1.

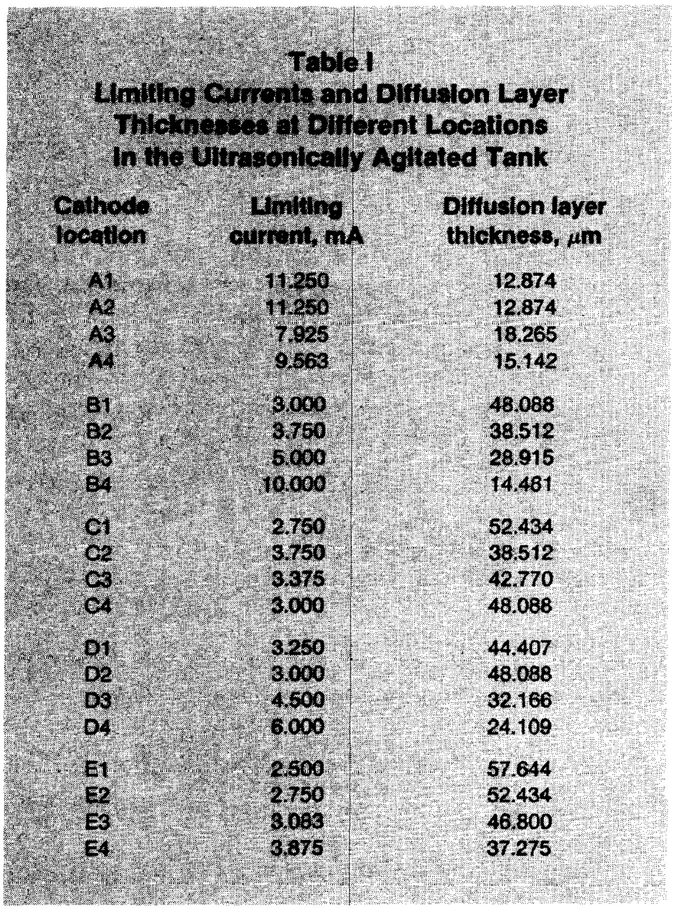

Table I
Limiting Currents and Diffusion Layer Thicknesses at Different Locations In the Ultrasonically Agitated Tank

Cathode location	Limiting current, mA	Diffusion layer thickness, μm
A1	11.250	12.874
A2	11.250	12.874
A3	7.925	18.265
A4	9.563	15.142
B1	3.000	48.088
B2	3.750	38.512
B3	5.000	28.915
B4	10.000	14.461
C1	2.750	52.434
C2	3.750	38.512
C3	3.375	42.770
C4	3.000	48.088
D1	3.250	44.407
D2	3.000	48.088
D3	4.500	32.166
D4	6.000	24.109
E1	2.500	57.644
E2	2.750	52.434
E3	3.083	46.800
E4	3.875	37.275

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*Seishin UA50/SK Disperser.

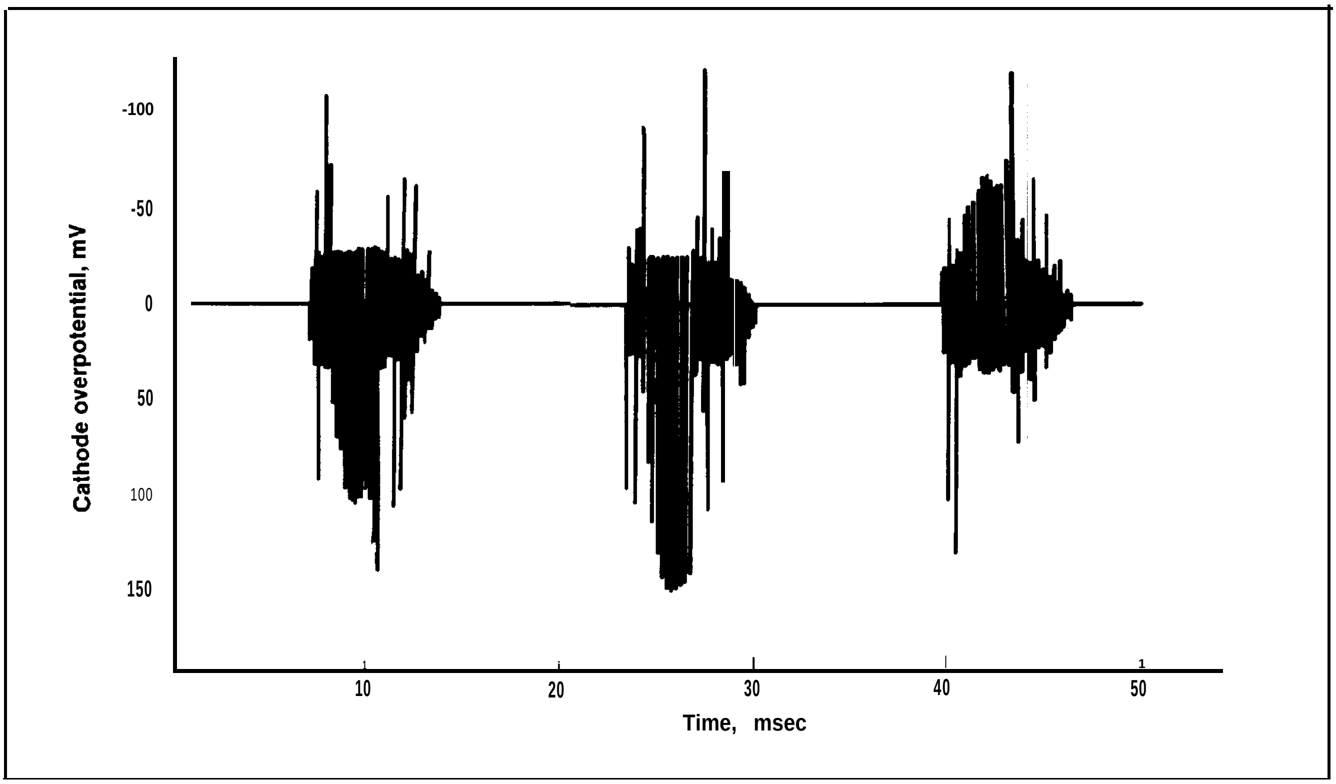

Fig. 2—A profile of electrode potentials as a function of time with ultrasonic agitation and no externally applied voltage.

Results and Discussion

With no externally applied current, the electrode potential of copper pulsated with time when the solution was ultrasonically agitated, as Fig. 2 shows. The time between pulses was about 9.5 msec. The potential oscillated violently during the pulses. Several other ultrasonic instruments that were tested produced similar results.

Figure 3 shows cathode overpotentials with an externally applied current, equivalent to 100 mA/cm^2, while the bath was ultrasonically agitated. Large potential oscillations, like those in Fig. 2, again were observed. However, the potential was a straight, horizontal line (line1) at about - 130 mV vs. a saturated calomel reference electrode when the ultrasonic agitation was turned off.

The intensity of ultrasonic agitation differed from one location in the tank to another. Cathode positions A2 and E2 in Fig. 1 were selected for a comparison study. Cathode overpotentials for A2 and E2 are shown in Figs. 4 and 5, respectively. The overpotentials at A2 are about 10 mV lower than those at E2. The agitation intensity apparently was greater at position A2 in the center of the tank.

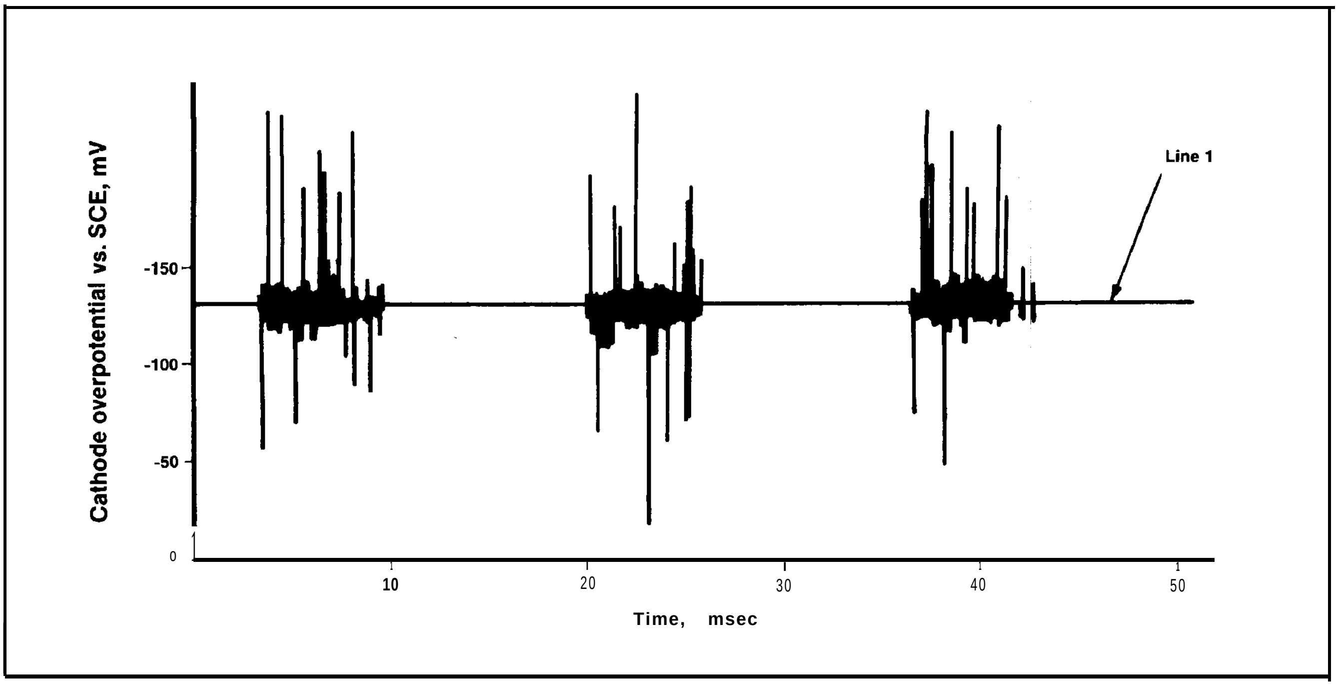

Fig. 3—Cathode potential vs. SCE as a function of time with an applied current density of 150 mA/cm^2 in an ultrasonically agitated acid copper bath.

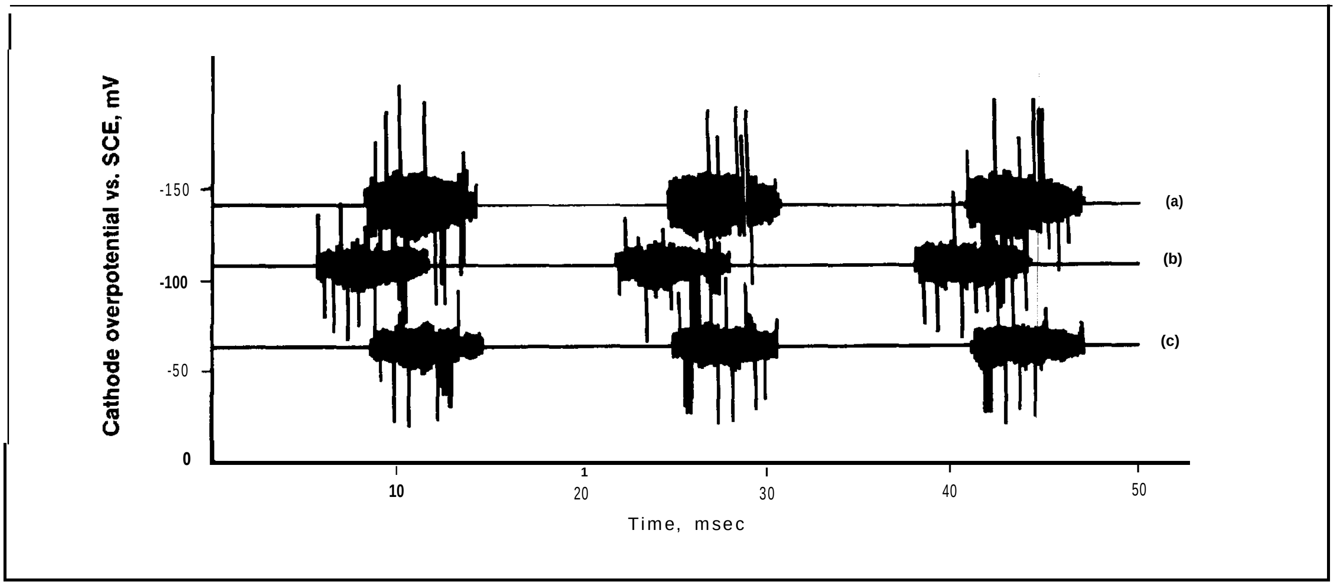

Fig. 4—Cathode potential vs. SCE as a function of time at position A2 with applied current densities of (a) 50, (b) 100 and (c) 150 mA/cm^2.

Two crystal orientations were observed during the X-ray diffraction studies. The ratio (RI) of diffraction intensities for the <111> and <220> crystal planes is an indication of the dominant plane and the preferred orientation. Figure 6 shows that the ratio was dependent on the thickness of the copper and the current density when the solution was agitated mechanically by magnetic stirring. The <111> plane was dominant at thickness levels of 12 to 38 µm (0.0005 to 0.0015 in.). R1 was 4 and nearly 12 in 25-µm-thick copper deposited at 150 and 200 mA/cm^2, respectively. By comparison <220> was the dominant plane in thicker deposits (>37.5 µm or 0.0015 in.). The influence of current density was especially noteworthy when the current density was raised from 100 to 200 mA/cm^2, to deposit 25 µm (0.001 in.) of copper.

Figure 7 shows that R1 ratios obtained with ultrasonic agitation when the cathode was located at position E2 were similar to those determined on cathodes produced with mechanical agitation (Fig. 6). However, the RI ratios were greatly different when” the cathode was located at position A2 where the agitation intensity was greater. In this case, <220> was the dominant crystal plane in all deposits thicker than 12.5 µm (0.0005 in.). The authors attribute the hardening effect of ultrasonic agitation, which was reported by Walker,[5] to a change in the crystal orientation,

The diffusion layer thickness is considered an important index of the effectiveness of agitation. It was measured during our study by rotating disk experiments governed by the following equation:

$$d = DNFC_b/I_1 \qquad (1)$$

where d is the diffusion layer thickness, I_l is the limiting current density measured from the electrode and D is the diffusion coefficient of copper ions, equal to 7.66 x 10-’ cm^2/sec.

The measured limiting currents and diffusion layer thicknesses calculated from equation (1) are given in Table 1. Agitation was more effective in the Al to A4 locations (the central region) than in the other (B, C, D or E) zones. According to the calculated, diffusion layer thicknesses,

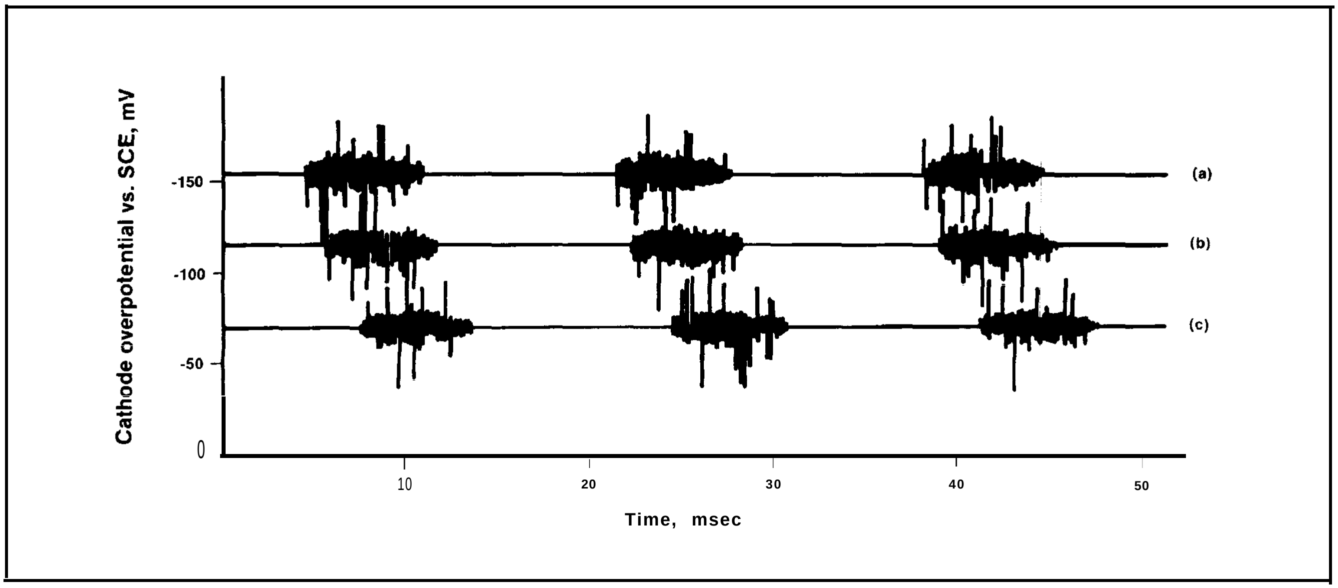

Fig. 5—Cathode potential vs. SCE as a function of time at position E2 with applied current densities of (a) 50, (b) 100 and (c) 150 mA/cm^2.

positions A1 and A2 immediately above the ultrasonic transducer had more agitation than A3 and A4 in the upper part of the tank.

Polarization data (overpotential vs. log of current density) for the copper sulfate solution are given in Fig. 9. The exchange current density calculated from the curve and Tafel equation was 2.65 x 10-3 A/cm*, which is about 50 percent greater than that obtained without ultrasonic agitation. Hence the intense ultrasonic agitation tended to increase the reversibility of the deposition reaction.

During experiments conducted to determine the effectiveness of ultrasonic agitation for improving the deposit distribution on the walls of holes drilled in a printed circuit board, thickness was measured at three points, E_b, H and E_f, inside the hole and two points, S_b and S_f, outside the hole, as shown in Fig. 10. In the representative photomicrograph in Fig. 11, the outer layer of copper was electrodeposited over the 15-µm-thick, electroless inner layer. Thickness data for deposits obtained with mechanical and ultrasonic agitation are given in Tables 2 and 3, respectively. In both cases, an increase in aspect ratio obtained by decreasing the diameter of the hole reduced the uniformity of the electrodeposited copper. The ultrasonically agitated

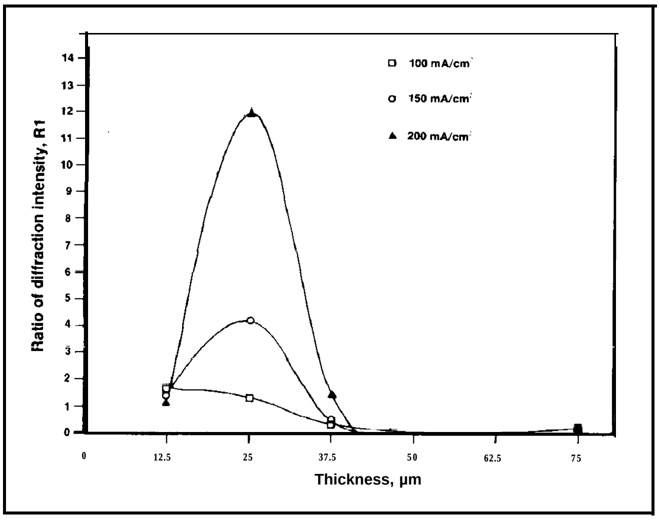

Fig. 6—Ratio (R1) of the intensities of <111> and <220> crystal planes as a function of the thickness of copper deposited in a mechanically agitated bath.

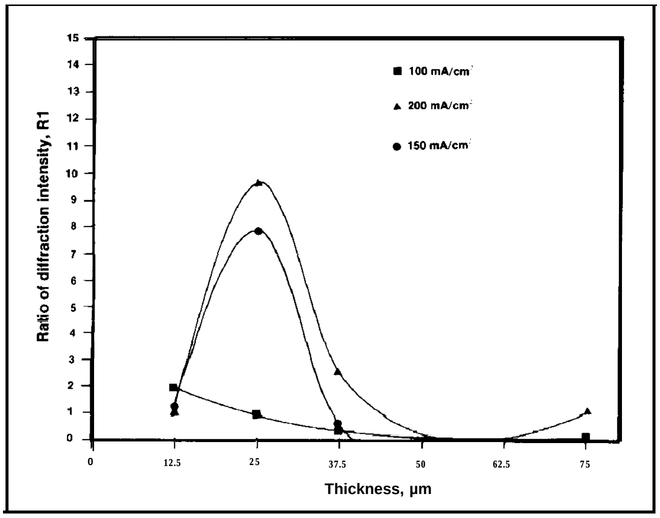

Fig. 7—Ratio (R1) of the intensities of <111> and <220> crystal planes as a function of the thickness of the copper deposited at position E2 in the ultrasonically agitated bath.

Table 2
Copper Thickness Ratios With Magnetic Stirring

Hole size, mm	Thickness ratio at 100 mA/cm^2		
	S_f:H	E_f:H:E_b	S_b:H
2.4	2.15	1.6:1:1.2	1.62
1.2	3.00	2.0:1:1.4	2.00
0.8	3.73	2.1:1:1.7	2.09
0.6	4.38	2.5:1:1.7	2.18
0.5	5.20	2.5:1:2.8	3.33

Table 3
Copper Thickness Ratios With Ultrasonic Agitation

Hole size, mm	Thickness ratio at 100 mA/cm^2		
	S_f:H	E_f:H:E_b	S_b:H
2.4	3.71	2.1:1:1.8	2.44
1.2	3.93	2.7:1:1.9	2.93
0.8	5.60	3.6:1:2.5	3.87
0.6	5.84	3.6:1:2.6	4.81
0.5	10.31	3.8:1:3.2	9.19

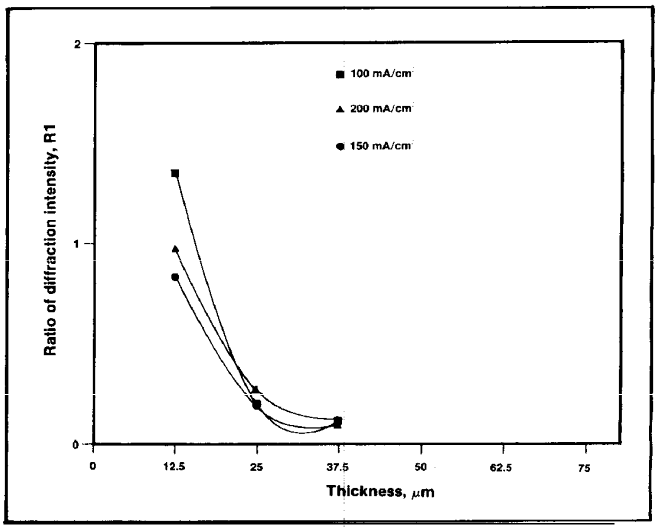

Fig. 8—Ratio (R1) of the intensifies of <111> and <220> crystal planes as a function of the thickness of the copper deposited at position A2 in the ultrasonically agitated bath.

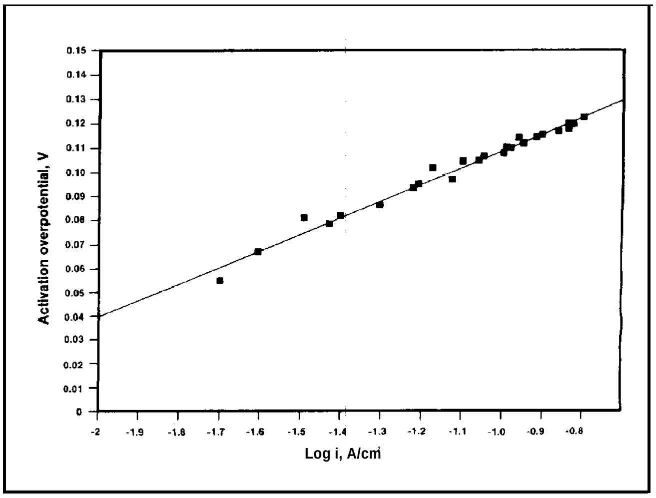

Fig. 9—The cathodic activation overpotential as a function of the log of the current density in the ultrasonically agitated copper bath.

Table 4
Potential Difference Between Two Platinum Electrodes

Current density, mA/cm^2	Ultrasonic agitation potential difference, mV			Mechanical agitation potential difference, mV		
	Exp. 1	Exp. 2	Avg.	Exp. 1	Exp. 2	Avg.
50	62	71	66.5	60	53	56.5
100	70	79	74.5	70	66	68.0
150	92	100	96.0	81	80	80.5

system resulted in less uniform copper distribution, compared to the mechanically agitated bath for the same aspect ratio.

Two platinum wires used as reference electrodes were positioned outside and inside the holes to measure potential differences. The potential difference between the two platinum indicator electrodes was larger when the bath was agitated ultrasonically, compared with the difference observed in the case of the mechanically agitated solution (Table 4). Ultrasonic waves moving up vertically from the bottom of the tank evidently had little effect on thickness distribution in the horizontal hole, which confirms the importance of the location of the ultrasonic transducer. Similar results regarding the orientation of electrodes and transducer have been observed by Hickman.'

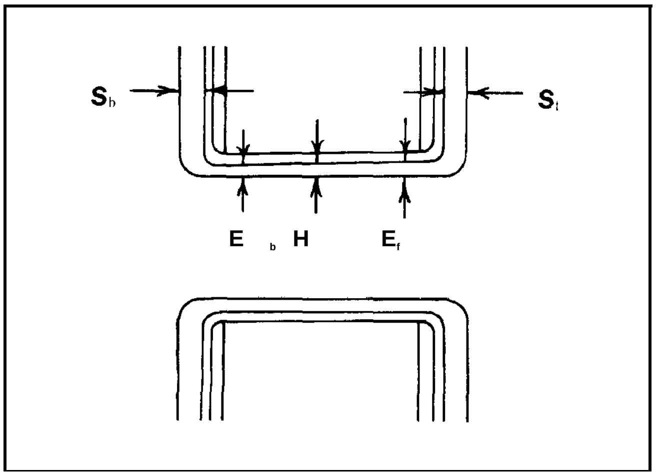

Fig. 10—A schematic diagram of a drilled hole in a printed circuit board showing five positions where the thickness of copper was measured.

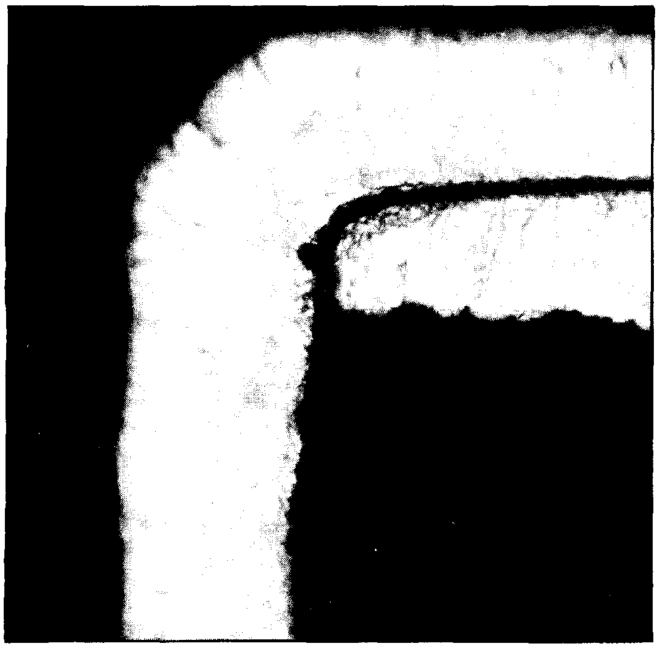

Fig. 11—Cross section of the copper deposited in a drilled hole in a printed circuit board.

Conclusions

Ultrasonic agitation was found to be a pulsed process with oscillations in the millisecond range. The intensity of agitation is strongly dependent on the location of the transducer, relative to the cathode. These effects result in an uneven thickness distribution and a nonuniform crystal orientation. in the case of copper deposited in an acid sulfate bath, a <220> orientation was dominant. Although rarely used for electroplating, ultrasonic agitation appears useful for increasing the mass transfer rate and exchange current density.

Acknowledgment

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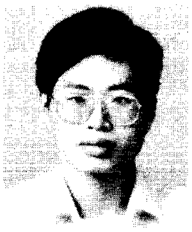

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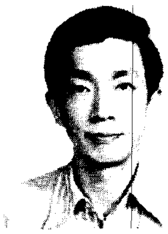

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