Pulsed Deposition of Ultra-thin Copper Foils

by Chein-Ho Huang,[a]* Wen-Yung Shu,[b] Hsien-Ming Wu,[b] and Chin-Ho Lee[c]

Ultra-thin 5-µm (197-µ-in.) copper foil was prepared by pulse plating onto stainless steel from an acid copper electrolyte which contained 2 ppm of a gelatin having a molecular weight (MW) below 50,000. In addition to the advantage of being pinhole-free, the copper foil obtained was also free of internal stress. Moreover, these copper foils had high tensile strength to provide desired handleability.

Copper foil has become widely used in a variety of electronic and electrical component technologies. Owing to the recent miniaturization and densification of electronic equipment, the need for ultra-thin copper foil has intensified. Therefore, the preparation of ultra-thin 5-µm (197-µ-in.) copper foil having pinhole-free and stress-free properties was investigated in this work. When a copper deposit exhibits a large grain size, pinholes are easily produced in ultra-thin copper foils and cause serious problems in practical use. With DC currents, in order to reduce the grain size of the deposits, a relatively high current density is required. As a consequence, however, the internal stress in these deposits is inevitably enhanced.[1] Although internal stresses in copper deposits are typically less than those in nickel deposits, the tendency of a 5-µm (197-µ-in.) copper foil to curl is detectable when its internal stress is greater than 345 kPa (50 lb/in^2). Thus, it is generally believed that it is difficult to produce ultra thin, pinhole-free and stress-free copper foils by DC-plating.

In order to improve the quality of ultra-thin copper foil, the influence of pulse current parameters on the properties of copper deposits obtained from acid copper electrolytes was studied.[2,3] In addition to the advantage of being able to use a higher peak pulse current density to reduce the grain size, it also reduces the stress buildup in the deposits by allowing the impurities to diffuse away during the off-time.[4,5] Pulse plating has these advantages over DC plating, and therefore we undertook this study to see whether or not stress-free and pinhole-free foils could be obtained by pulse plating.

Physical property studies of copper deposits from baths employing additives are available, but relatively few of them deal with internal stress.[6] It is known that gelatin is a grain refiner and a surface-active compound.[7] Moreover, according to our previous work,[8] different molecular weights (MW) of an additive added to the electrolyte will yield different microstructures and, consequently, the stress of the copper deposit. Accordingly, the influence of the molecular weights of gelatins on the preparation of ultra-thin copper foils was examined here.

Experimental procedure

Ultra-thin copper foils were prepared from an acid copper electrolyte containing 20 g/L (2.7 oz/gal) of copper (as $CuSO_4 \cdot 5H_2O$) and 80 g/L (10.7 oz/gal) of sulfuric acid. Regular gelatin was characterized by a primary electrophoresis experiment[9] to be a heterogeneous mixture of water-soluble proteins with molecular weights in the range from 5,000 to 250,000. A low molecular weight gelatin having a molecular weight below 50,000 was obtained by performing dialysis of regular gelatin solution at room temperature. Three other protein reagents were also studied in the acid copper electrolyte in order to understand the effect of protein molecular weight on the deposit stress. Their molecular weights were 6,000, 12,000 and 29,000, respectively. The concentration of the gelatin and that of the three proteins was 2 ppm (0.0002%).

As in our previous work,[10] cyclic voltammetric stripping (CVS) experiments of these protein-containing electrolytes were performed. Electroforming was conducted in a 2-L beaker mechanically stirred at 300 rpm. The cathodes were flat, bright, stainless-steel specimens (3.5 × 14 cm; 1.4 × 5.5 in.), which was polished with 1200-grit emery paper prior to plating. The anode was a flat, platinum sheet.

Pulse plating experiments were carried out over a range of peak pulse current densities, 4.0 to 20 A/dm^2 (37 to 186 A/ft^2); duty cycles, 5.0 to 87.5%; and pulse times, 0.5 to 350 msec. The off-time current density for all pulse plating was zero. The deposition times of both DC- and pulse

Nuts & Bolts: What This Paper Means to You

The miniaturization and increasing density to the level of nanoscales in electronic circuitry has cried out for ultra-thin electroformed copper foil that is both pinhole and stress-free Ð a rather tall order. This work deals with just that, and shows a bit of promise in meeting this critical need.

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plating runs were adjusted in order to obtain a deposit thickness of 5 μm (197 μ-in.), which was measured with an accuracy of ±0.5 μm (±19.7 μ-in.) using a high-precision mechanical gauge. Internal stress was determined by using a spiral contractometer. Tensile strength was determined with a strain speed of 1.67 × 10^{-2} mm/sec (0.657 mil/sec).

The copper foil surface in direct contact with the cathode (back side of the deposit) is a replica of the cathode surface, which is smoother than the front side. The back side is generally called the shiny side and the front side is called the matte side.[11] Since the thickness of the foil is only 5 μm (197 μ-in.), the grain size of the deposit can be observed by examining the shiny side with a scanning electron microscope (SEM).

Results & discussion

DC plating

DC plated copper deposits obtained from acid copper electrolytes with no addition agents always have high tensile stresses. Figure 1(a) shows that the internal stress is increased at higher current densities. Although lowering current density can lower stress, the grain size of the deposits increases accordingly because lower deposition rates tend to favor crystal growth over nucleation. For instance, the average grain size of the shiny side of the deposit is greater than 2 μm (79 μ-in.) in diameter when the current density is decreased to 0.5 A/dm^2 (4.64 A/ft^2) as indicated in Fig. 2(a). At this grain size pinholes are easily visible in an ultra-thin foil, as indicated in the figure. Thus, lowering stress will end up with larger grain size, resulting in serious pinhole problems when plating ultra-thin copper foil from an additive-free electrolyte by DC plating.

In an attempt to reduce grain size and minimize pinholes, regular gelatin was added to the acid copper electrolyte. The test results, shown in Fig. 3, show that the grain size was substantially reduced from about 0.4 μm (15.7 μ-in.) to less than 0.1 μm (3.9 μ-in.) when regular gelatin was added to the electrolyte. In addition to lowering grain size, the addition of gelatin also lowered the internal stress as shown in Fig. 1(b). However, the DC-plated ultra-thin copper foils were still heavily stressed and were difficult to handle.

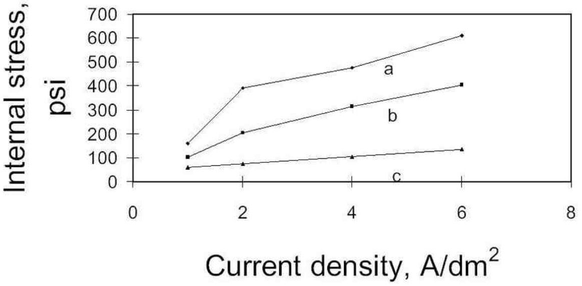

Figure 1—Dependence of internal stress on current density of copper deposits by DC plating from acid copper electrolytes containing (a) no additive, (b) regular gelatin and (c) a low molecular weight (MW) gelatin.

Our previous work[8] showed that the interfacial activity of acid copper electrolyte and the properties of the resultant copper deposits were influenced by the molecular weight of the organic additives. Because gelatin is a heterogeneous mixture of water-soluble protein of high molecular weight, the molecular weight of protein would be expected to play a fundamental role in determining the stress in the ultra-thin copper foils. Thus both CVS and stress experiments were conducted to investigate the effect of the molecular weight of the protein reagents on internal stress. The CVS results, shown in Fig. 4, show that the relative rate parameter (A_r/A_s) decreased with increasing concentration and molecular weight of protein in the electrolyte. Moreover the work of Ye, *et al.*[12] indicates that the addition of a high molecular weight protein to the electrolyte caused an increase of cathodic overpotential, resulting in copper deposits with different physicomechanical properties. This work implies that the molecular weight of proteins added to the electrolyte may influence the internal stress of copper

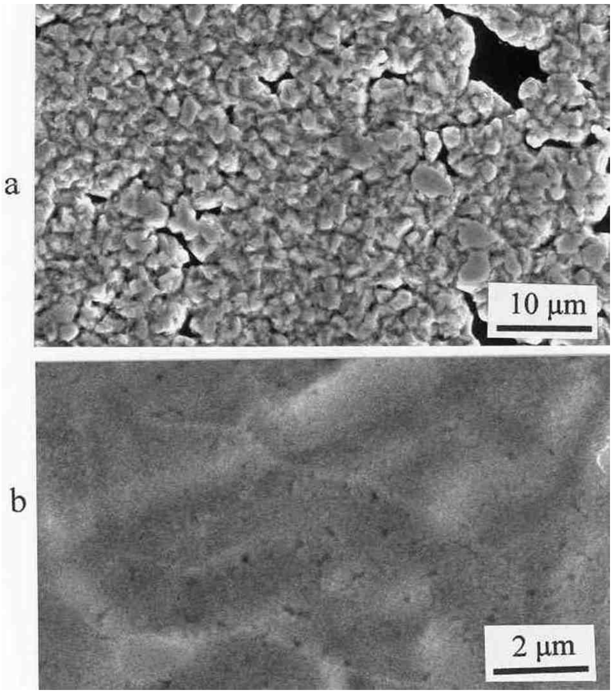

Figure 2—SEM photographs of the shiny side of ultra-thin copper foils obtained from an acid copper electrolyte by (a) DC plating at 0.5 A/dm^2 (4.65 A/ft^2) and (b) pulse plating under Condition A (average pulse current density 0.5 A/dm^2 (4.65 A/ft^2), pulse time 0.5 msec, and duty cycle 12.5% from an additive-free electrolyte).

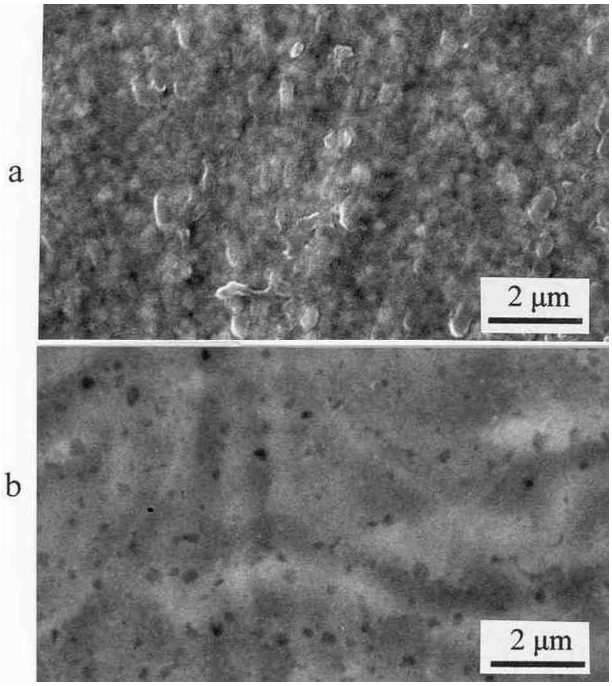

Figure 3—SEM photographs of the shiny side of ultra-thin copper foils obtained by DC plating at 2.0 A/dm^2 (18.6 A/ft^2) from an acid copper electrolyte containing (a) no additive and (b) regular gelatin.

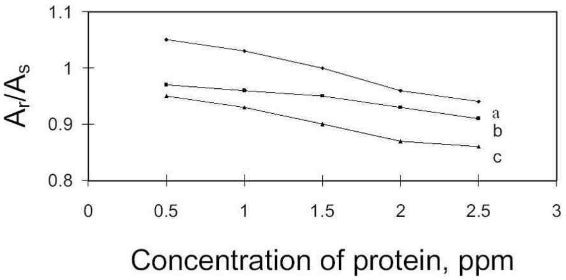

Figure 4—Variation of A_r/A_s (CVS relative rate parameter) values with concentration of protein added to acid copper electrolyte. Protein MW: (a) 6,000, (b) 12,000 and (c) 29,000.

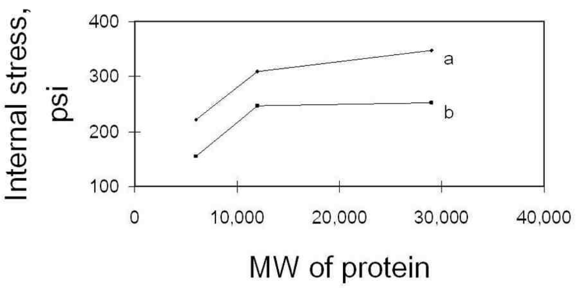

Figure 5—Variation of internal stress with the molecular weight of protein for copper deposits obtained from acid copper electrolyte by DC plating at (a) 4.0 A/dm^2 (37.2 A/ft^2) and (b) 2.0 A/dm^2 (18.6 A/ft^2).

deposits. Our stress results, shown in Fig. 5, indeed show that the internal stress tended to decrease with decreasing molecular weight of the proteins added.

These results predict that the addition of a lower molecular weight gelatin to the electrolytes might lower the stress of copper deposits. This prediction is supported by the results shown in Figs 1(b) and 1(c), which indicate that the stress was lower in the deposits obtained from the electrolyte containing a low molecular weight gelatin (MW <50,000), and higher in deposits obtained from an electrolyte containing regular gelatin. Even though adding a lower molecular weight gelatin to the electrolyte can considerably reduce the stress, the foils prepared by DC-plating were still stressed. Thus further study to eliminate the residual stress was needed.

Pulse plating

It has been reported that pulse current is able to refine the grain size and reduce the internal stress in copper alloy deposits.[5] Figure 2 compares the SEM results for the shiny side of foils DC-plated at 0.5 A/dm^2 (4.65 A/ft^2) [Fig. 2(a)] versus those plated with pulse current at the same average current density [Fig. 2(b)]. The results clearly indicate that pulse current was effective in refining grain size and eliminating pinholes. Pulse plating was also effective in lowering internal stress, as indicated in the first run of Table 1 under Condition A, *i.e.*, an average pulse current density of 0.5 A/dm^2 (4.65 A/ft^2), a pulse time of 0.5 msec and a duty cycle of 12.5% from an additive-free electrolyte.

Table 1 summarizes the effects of changing pulse parameters on the internal stress of copper deposited from additive-free electrolytes. It shows that:

1. Internal stress remained negligibly low when the average pulse current density was varied between 0.2 and 0.5 A/dm^2 (1.87 and 4.65 A/ft^2) and the duty cycle was varied between 5.0 and 12.5%, while fixing peak pulse current density at 4.0 A/dm^2 (37.2 A/ft^2) and the pulse time at 0.5 msec,
2. Internal stress tended to increase with increasing average pulse current density above 0.5 A/dm^2 (4.65 A/ft^2), and
3. Internal stress tended to increase with pulse times greater than 0.5 msec or duty cycles greater than 12.5%.

The highest pulse parameters that did not cause excessive internal stress were:

- Average pulse current density, 0.5 A/dm^2 (4.65 A/ft^2),
- Pulse time, 0.5 msec and
- Duty cycle, 12.5% (Condition A).

Table 1
Internal Stress of Copper Deposits Obtained from an Additive-free, Acid Copper Electrolyte by Pulse Plating

Average pulse current density, A/dm^2 (A/ft^2)	Peak pulse current density, A/dm^2 (A/ft^2)	Pulse on-time, msec	Duty cycle %	Internal stress, MPa (lb/in^2)
0.50 (4.65)	4.0 (37.2)	0.5	12.5	0 (0)
0.32 (2.97)	4.0 (37.2)	0.5	8.0	0 (0)
0.28 (2.60)	4.0 (37.2)	0.5	7.0	0 (0)
0.24 (2.23)	4.0 (37.2)	0.5	6.0	0 (0)
0.20 (1.86)	4.0 (37.2)	0.5	5.0	0 (0)
2.0 (18.6)	4.0 (37.2)	2.0	50	1.30 (189)
2.0 (18.6)	4.0 (37.2)	20	50	1.49 (216)
2.0 (18.6)	4.0 (37.2)	200	50	1.73 (251)
3.5 (32.5)	4.0 (37.2)	3.5	87.5	1.77 (257)
3.5 (32.5)	4.0 (37.2)	35	87.5	1.83 (265)
3.5 (32.5)	4.0 (37.2)	350	87.5	1.94 (282)
0.75 (6.97)	6.0 (55.7)	0.5	12.5	1.32 (192)

These parameters were considered low from the standpoint of practical application.

The synergistic effect of pulse plating and the molecular weight of gelatin

In an attempt to enhance the pulse parameters, regular gelatin was added to the electrolyte. As shown in Fig. 6, because of the presence of regular gelatin, a compact morphology was still observed on the shiny side even when the average pulse current density of Condition A was decreased to 0.25 A/dm^2 (2.32 A/ft^2). The addition of gelatin however, showed no beneficial effect on internal stress, and the pulse parameters (Table 2) in the presence of regular gelatin remained the same as for the additive-free conditions (Table 1). The highest pulse parameters that did not cause excessive internal stress remained:

- Average pulse current density, 0.5 A/dm^2 (4.65 A/ft^2),
- Pulse time, 0.5 msec and
- Duty cycle, 12.5% (Condition A).

Finally, a low molecular weight gelatin was added to the electrolyte and ultra-thin copper foils were deposited by pulse plating. The results showed a remarkable improvement in overall performance. The resultant foil was both pinhole- and stress-free and the highest average pulse current density was measurably improved. Table 3 shows the effect of changing the pulse parameters on the internal stress and tensile strength for the ultra-thin copper foil prepared from the electrolyte containing the low molecular weight gelatin. Internal stress remained undetectable when the average pulse current density was raised from 0.5 A/dm^2 (4.65 A/ft^2) to 2.5 A/dm^2 (23.2 A/ft^2), a five-fold improvement over the best conditions established earlier. Table 3 also shows that the tensile strength of the ultra-thin copper foil tended to increase with increasing average pulse current density. The levels of tensile strength demonstrated are in line with average high strength electrodeposited copper. The tests were repeated with two lower molecular weight gelatins (MW <25,000 and <12,000) instead of the <50,000 molecular weight gelatin used earlier. The results were about the same, showing pinhole- and stress-free deposits with high tensile strength.

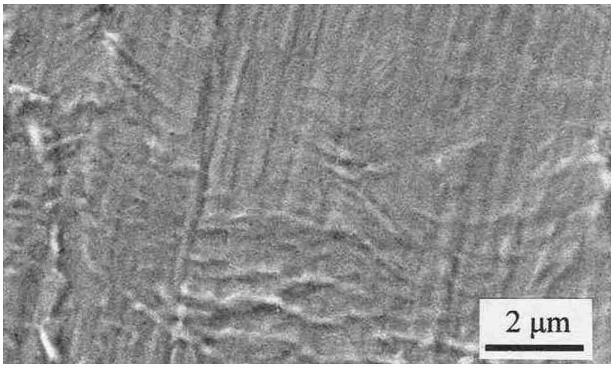

Figure 6—SEM photograph of the shiny side of ultra-thin copper foil obtained from an acid copper electrolyte containing regular gelatin by pulse plating (average pulse current density 0.25 A/dm^2 (2.3 A/ft^2), pulse time 0.5 msec, and duty cycle 12.5%).

Conclusion

Pinhole-free and stress-free, ultra-thin (5 μm; 197 μ-in.) copper foils with tensile strengths on the order of 372 to 483 MPa (54,000 to 70,000 lb/in^2.) were prepared by pulse plating from an acid

Table 2
Internal Stress of Copper Deposits Obtained from an Acid Copper Electrolyte Containing Regular Gelatin by Pulse Plating

Average pulse current density, A/dm^2 (A/ft^2)	Peak pulse current density, A/dm^2 (A/ft^2)	Pulse on-time, msec	Duty cycle %	Internal stress, MPa (lb/in^2)
0.50 (4.65)	4.0 (37.2)	0.5	12.5	0 (0)
0.75 (6.97)	6.0 (55.7)	0.5	12.5	1.00 (145)
1.25 (11.6)	10.0 (92.9)	0.5	12.5	1.42 (206)

Table 3
Internal Stress and Tensile Strength of Copper Deposits Obtained from an Acid Copper Electrolyte Containing a Low Molecular Weight Gelatin by Pulse Plating

Average pulse current density, A/dm^2 (A/ft^2)	Peak pulse current density, A/dm^2 (A/ft^2)	Pulse on-time, msec	Duty cycle %	Internal stress, MPa (lb/in^2)	Tensile Strength MPa (lb/in^2)
0.50 (4.65)	4.0 (37.2)	0.5	12.5	0 (0)	370 (53636)
0.75 (6.97)	6.0 (55.7)	0.5	12.5	0 (0)	406 (58934)
1.00 (9.29)	8.0 (74.4)	0.5	12.5	0 (0)	451 (65374)
1.25 (11.6)	10.0 (92.9)	0.5	12.5	0 (0)	471 (68330)
2.50 (23.2)	20.0 (185.8)	0.5	12.5	0 (0)	480 (69558)

copper electrolyte containing a low molecular weight gelatin (MW < 50,000). The highest average pulse current density was 2.5 A/dm^2 (23.2 A/ft^2), and the longest pulse time and duty cycle were 0.5 msec and 12.5%, respectively. The deposits tended to be stressed when higher average pulse current densities, longer pulse times or longer duty cycles were used.

The highest average pulse current density that did not cause excessive internal stress was only 0.5 A/dm^2 (4.65 A/ft^2) when a low molecular weight gelatin was replaced by regular gelatin (MW 5,000-250,000) or was eliminated from the electrolyte.

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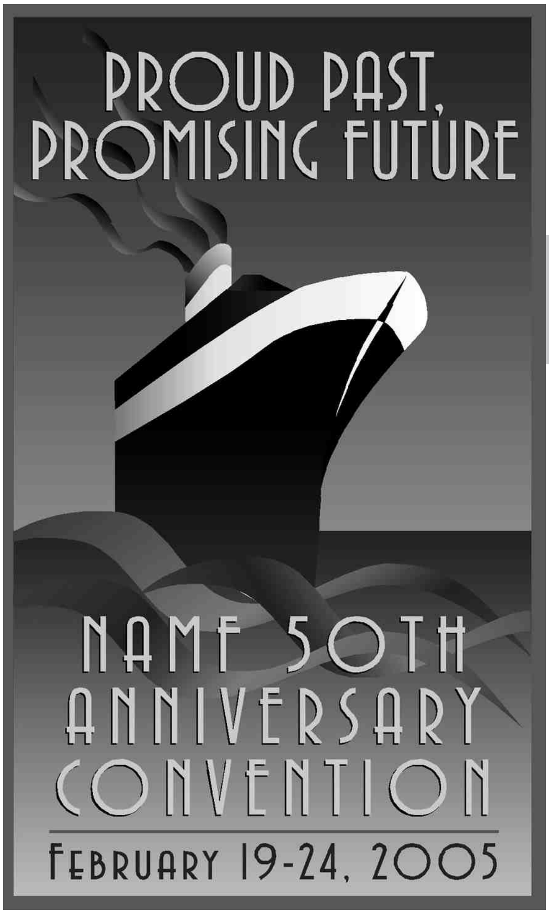

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