Orientation and Property of Gold Plating in the Presence of Organic Additives

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ABSTRACT

The addition of sodium laurylsulfate, decylamine, and dodecylamine to the cyanide gold plating bath was found to suppress the growth of the (111) facet. Similar trends were observed for deposits obtained at higher current densities and lower temperatures. The decylamine and dodecylamine enhance the growth of (220) and (311) facets and result in lowering of the microhardness of the deposits. A shell-like morphology was obtained when the growth of (220) and (311) facets was enhanced. An increase in the concentration of sodium laurylsulfate tends to produce flake platings.

Gold plating has been developed chiefly for electronics applications. Pure gold deposits, however, are relatively soft and subject to poor wear resistance when used for sliding contacts. The wear resistance of gold deposits can be improved by the codeposition of alloying elements such as nickel and cobalt (1, 2) to enhance the hardness of the deposit. The manufacturing of devices such as tape-automated bonding (TAB) packages (3, 4) has the further requirement of thin, pore-free, and fine-grained deposits. Efforts to achieve these qualities require modification of the microstructure of deposits. In this regard, the application of additives and alternative plating parameters has been a major objective in the past few decades.

As far as additives are concerned, both organic and inorganic agents have been investigated. Thallium, lead, and arsenic (5, 6) were generally added in low concentrations to the plating bath for grain refining. These inorganic additives also significantly affect the strength of thermocompression wire bonds (5, 6). The microstructure of the gold deposit was also affected, such that lead and thallium favor the (311) plane, while the (111) plane is predominant in the presence of arsenic or in the absence of any additive (6). Organic additives such as nylon and melamine (7, 8) were reported to affect the epitaxial growth and hence the continuity of the gold deposit at the initial stage of deposition. The effect of surfactant-type additives on the electro-

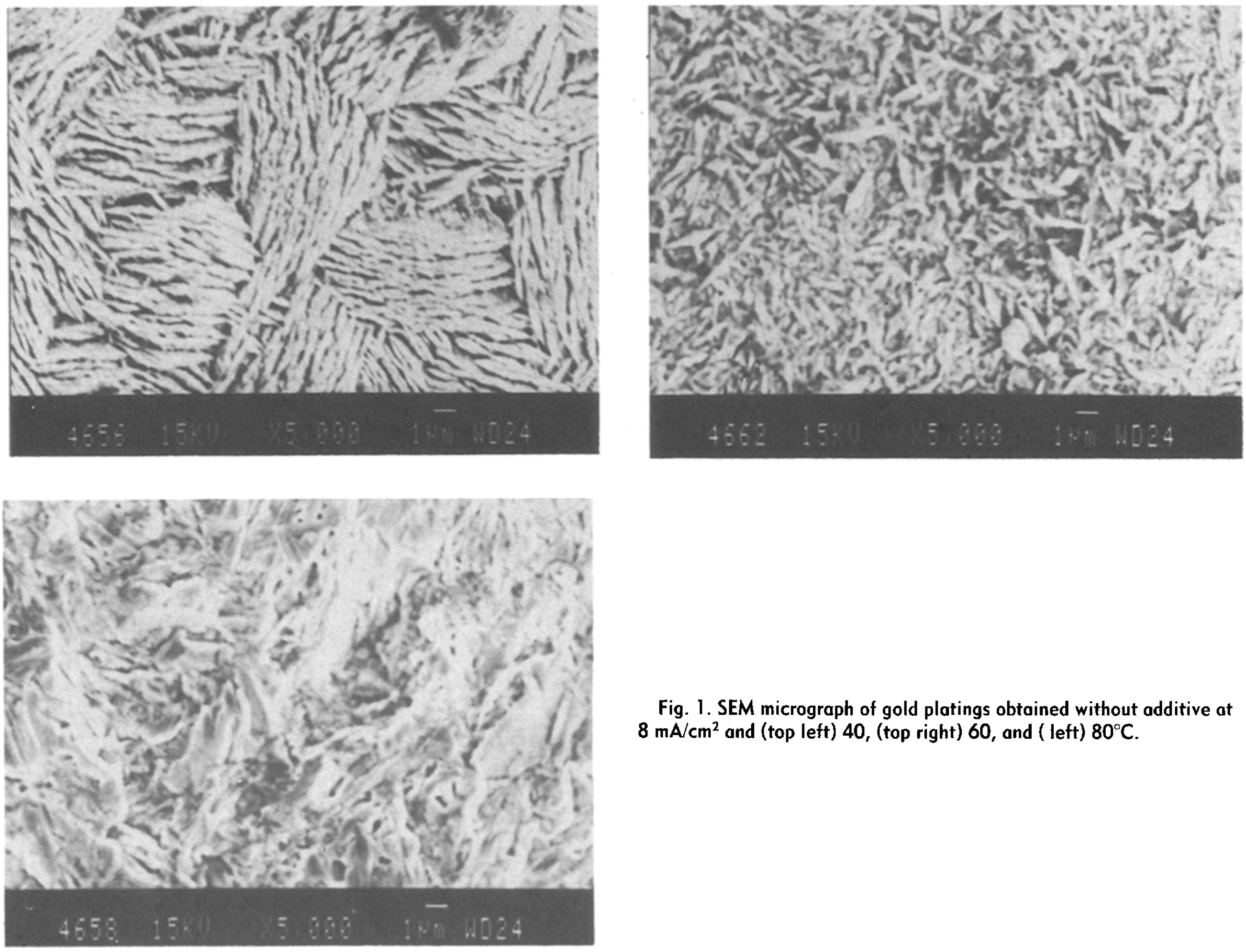

Fig. 1. SEM micrograph of gold platings obtained without additive at 8 mA/cm^2 and (top left) 40, (top right) 60, and (left) 80°C.

crystallization of deposits mainly results from the inhibition of the growth of certain planes due to surface adsorption, which induces higher overpotential for the electroreduction reaction. The differences in the surface energy of the structural planes give rise to variations in the electrochemical properties of the deposit surface which might result in the preferred orientations of electrodeposits (10). The present work attempted to investigate the influences of surfactants including decylamine, dodecylamine, and sodium laurylsulfate on the morphology, preferred facet plane, and functional properties of gold deposits. The property variations are explained from the point of view of electrocrystallization behavior.

Experimental

In order to simulate the real situation of TAB manufacturing (3, 4), gold plating was performed on a piece of electrolytic copper pre-sputtered with ~300 Å of gold. The 2.8 × 1.6 × 0.1-cm electrolytic copper, mounted with epoxy to reveal one face only, was polished with No. 220, No. 500, and No. 1000 sandpaper and ultrasonically cleaned in acetone prior to sputtering. Electrodeposition was performed in a 300-ml cyanide solution consisting of 20 g/l $KAu(CN)_2$, 21 g/l citric acid, and 76 g/l tri-potassium citrate at pH 5, with or without additives. The temperature was controlled with a water bath. Platinum-plated titanium wire net was used as the anode. The distance between the anode and the cathode was maintained at 1 cm.

Electroplating without additives was performed at current densities of 4 to 12 mA/cm^2 at temperatures of 40-60°C, while electroplating with additives was performed at 60°C within the same current density range. Additive concentrations ranged from 0.05 to 0.30 weight percent (w/o) of sodium laurylsulfate, decylamine, and dodecylamine. A Hokuto HA-310 potentiostat/galvanostat was used as the power supply for direct current (dc) plating. The plating bath was stirred during electroplating using a magnetic stir bar. Surface morphology of the deposits was investigated with a Joel JSM-840 scanning electron microscope. The crystallization structure was investigated with a Rigaku x-ray diffractometer, at a speed of 4 degrees per minute, by applying copper K_α as the target and nickel as the filter. The Vickers microhardness of the deposits was measured with an Akashi MVK-E Vicker's tester at a load of 10 gf.

Results and Discussion

DC plating without additives.—The results of x-ray diffraction indicate that the fcc gold deposits obtained grew mainly as (111) planes. The growth of the (111) plane was found to be enhanced at lower temperatures and greater current densities. The next major plane is (311), the growth of which was suppressed by increasing current density. The surface morphology of the platings is affected by both bath temperature and current density in the present work. Figure 1 presents the SEM micrograph of the platings obtained at 8 mA/cm^2 and various temperatures of 40, 60, and 80°C. An increase in bath temperature tends to produce a block structure instead of the flake structure which appears at lower temperature. The appreciable effect of temperature on plating morphology may be ascribed to the enhancement in long-range surface diffusion of the adatoms at higher temperatures. It is also known that increased temperature lowers the overpotential and hence allows the plating to grow uniaxially to produce block structure. An increase in current density, on the other hand, does not allow enough time for long-range diffusion to take place, as it increases the deposition rate. Accordingly, a finer morphology was observed, as shown in Fig. 2 and Fig. 1(a).

Effect of sodium laurylsulfate.—The anionic surfactant sodium laurylsulfate exhibits marked influence on the morphology of gold electrodeposits. Figure 3 indicates that increasing the concentration of sodium laurylsulfate from 0.08 to 0.3 (w/o) enhances the formation of the flake structure. A comparison between Fig. 1 and Fig. 3 seems to indicate that the plating behavior at a greater concentration of sodium laurylsulfate is similar to that at lower temperature without additive, except that the laurylsulfate enhances the grain growth of the deposit. Furthermore, it also seems to indicate that the laurylsulfate tends to be adsorbed on the surface, rather than the edge, of grains, and thus gives rise to flake-like structure at higher w/o of sodium laurylsulfate. The (111) facets were also found to be the major facets of the deposits obtained in the presence of laurylsulfate.

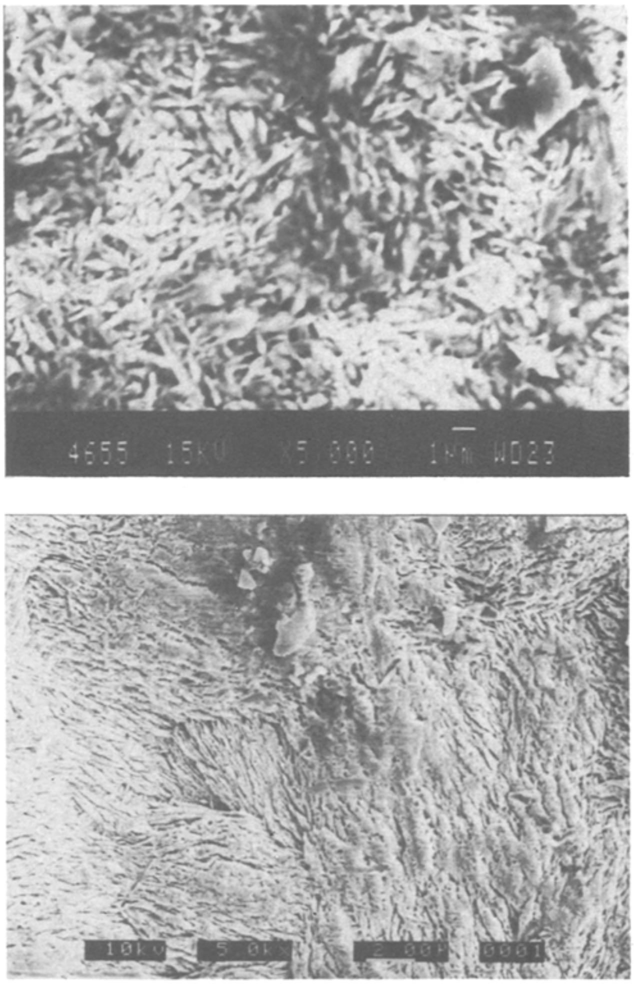

Fig. 2. SEM micrograph of gold platings obtained without additive at 40°C and (top) 4 and (bottom) 12 mA/cm^2.

Effect of decylamine and dodecylamine.—The presence of amine-type surfactants, decylamine and dodecylamine, produces shell-like platings within the concentration range 0.05 to 0.26 w/o. The plating structure becomes more densely compact with increasing current density, as shown in Fig. 4. An increase in concentration of the surfactant within the experimental conditions of the present work did not show an observable effect on the deposit morphology. It is apparent from the morphologies shown in Fig. 3 and 4 that the effects on deposit morphology and hence the adsorption behavior of the sodium laurylsulfate and the amines are quite different.

Table I presents the relative diffraction intensity of the various planes for the gold deposits obtained in the presence of 0.26 w/o dodecylamine. The amine-type surfactant tends to enhance the growth of the planes other than (111),

Table I. Orientations of gold platings at various current densities and 60°C in the presence of 0.26 w/o dodecylamine.

(hkl) I mA/cm^2	(111)	(200)	(220)	(311)	(222)
12	100	0	0	79.7	0
8	100	3.6	2.1	27.0	4.9
4	93.1	5.6	100	36.9	3.8

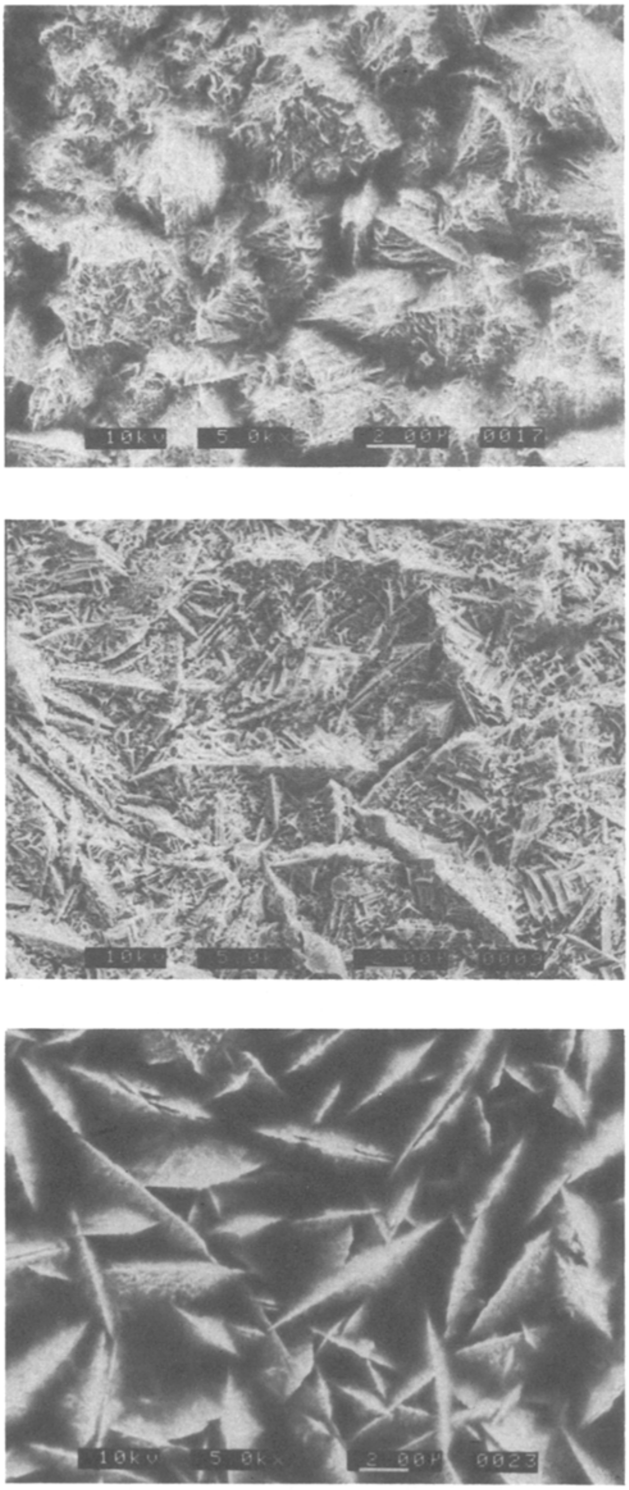

Fig. 3. SEM micrograph of gold platings obtained at 8 mA/cm^2 and 60°C, and in the presence of (top) 0.08, (middle) 0.15, and (bottom) 0.3 w/o sodium laurylsulfate.

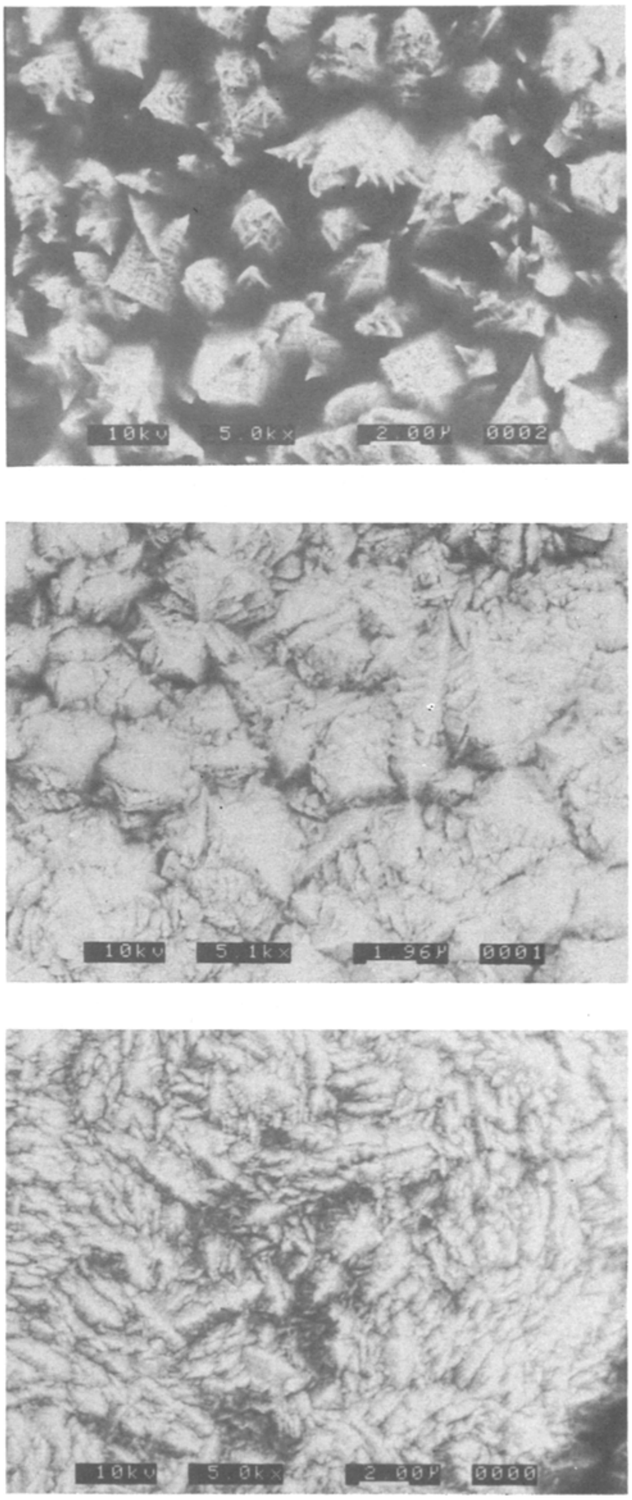

Fig. 4. SEM micrograph of gold platings obtained at 60°C with the addition of 0.26 w/o dodecylamine and (top) 4, (middle) 8, and (bottom) 12 mA/cm^2.

especially the (220) and (311) planes. Current density further mediates the effect of surfactant. The (220) plane, rather than (111), exhibits the greatest intensity among all planes at 4 mA/cm^2, while a higher current density enhances the growth of (311) and suppresses planes other than (311) and (111). The significant intensity of (220) or (311), coexisting with (111), greatly affects the plating morphology. The shell-like morphology of Fig. 4 is thus ascribed to the simultaneous growth of various planes, as shown in Table I.

Microhardness of the platings.—The microhardness of the deposits depends on the morphology, dislocation, defects, and plane orientation of the platings. From the plane orientation point of view, a plating with the (111) plane, the plane with the greatest atomic density, as the major orientation, would be expected to exhibit greater microhardness. It was mentioned earlier that lower temperatures and higher current densities tend to enhance the growth of the (111) plane. The parallel enhancement in microhardness [shown in Fig. 5 in Vickers (Hv)] of the platings is observed. On the other hand, the presence of the amines significantly lowers the microhardness of the plating, Fig. 6, especially at lower current densities. The lowering in the microhardness may be, in addition to other pos-

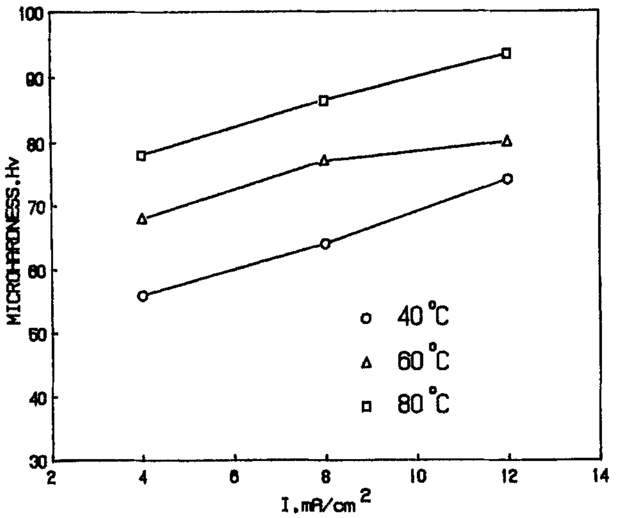

Fig. 5. Microhardness of gold platings obtained without additive at 40 to 80°C and 4 to 12 mA/cm².

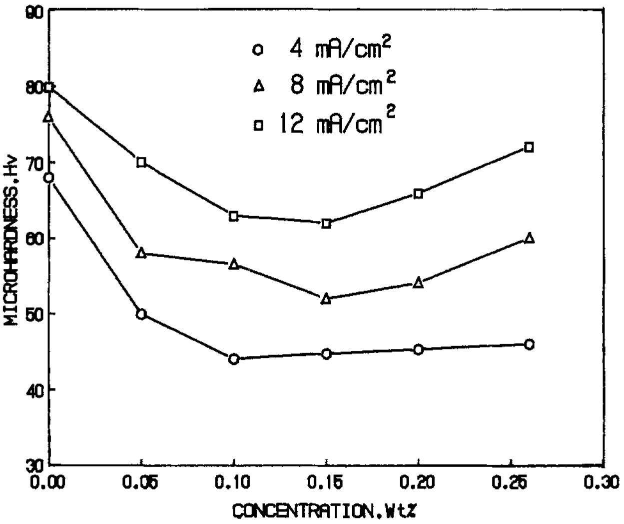

Fig. 6. Microhardness of gold platings obtained at 60°C, 4 to 12 mA/cm², and various additions of dodecylamine.

sible factors, ascribed to the enhanced growth of the (220) or (311) planes, Table I, and to the formation of a loose structure, as for 4 mA/cm², Fig. 4(a), in addition to other possible factors.

Conclusions

The growth of the (111) facet in gold plating is predominant at lower temperatures and greater current densities. An increase in sodium laurylsulfate as additive gives rise to a flake-like morphology of the deposit. Decylamine and dodecylamine enhance the growth of (220) and (311) facets of gold plating. Amine-type surfactants give rise to dense shell-like platings with lower microhardness.

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