Nucleation and Initial Growth of Pulse-Plated Gold on Crystalline and Amorphous Substrates

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ABSTRACT

In the electronics industry, there is a demand for dense gold films both as contact material and as corrosion-protective films. Pulse plating is a promising technique that could provide such fine-grained films with lower porosity than those obtained by conventional dc plating if the right deposition conditions are identified. In this study, gold was deposited both by pulse plating (rectangular pulses) and dc plating onto various crystalline copper and amorphous electroless nickel substrates. The current characteristics were varied to study the influence of overpotential and adion concentration on the nucleation and initial growth of these films. The growth morphology was examined by electron microscopy and x-ray diffraction to reveal the topography, internal defect structure, and preferential orientation. The growth of Au on crystalline Cu-substrates is initially strongly substrate-dependent both under pulse and dc plating conditions. When the deposit has reached a thickness of 50-100 nm, the growth gradually turns from substrate-controlled to transport-controlled growth resulting in a morphological change. This change appears earlier when the substrate grain size is small. On amorphous Ni/P-substrates, the initial growth of gold is polycrystalline both by pulse and dc plating. At high pulse current density, the grain size is small. At low current density the grain size distribution is bimodal. Large grains comparable in size to the film thickness develop along with a small grain morphology.

Today, the major application of electroplated gold is as electrical contacts. To obtain low resistivity and good corrosion protection of these contacts, it is important that the gold is dense and has low porosity. New growth morphologies can be obtained for this purpose by using pulse plating (1-14). Fine-grained structures with low porosity can be obtained under proper deposition conditions. It has been proposed that the grain refinement is due to an increased nucleation rate caused by an increased overpotential (6, 9). However, there is a lack of basic understanding of the pulse plating process. The first step to increase the knowledge in how the growth is affected by pulsating current on alloyed gold systems, is to study the characteristics of the gold system without the alloying elements.

The influence of adion concentration and overpotential on the nucleation rate has been studied by, amongst others, Bockris and Damjanovic (15). They found that the rate of homogeneous nucleation increases when the adion concentration is increased. When the current density is increased, the adion concentration is decreased (16), and consequently, the nucleation rate is decreased. For pulse plating, the adion concentration at the beginning of a pulse is higher than that of dc plating (16), and furthermore, the adatom concentration is higher due to the high deposition rate. Consequently, pulse plating results in more fine-grained deposits than dc plating, as long as the nuclei do not coalesce.

In this study, we compare the nucleation and initial growth of pulse- *vs.* dc-plated gold prepared under otherwise equivalent conditions. The internal microstructure was studied with electron microscopy. Coarse-grained, fine-grained, and amorphous substrates were used. The nucleation and initial growth is discussed in terms of surface diffusion, homogeneous, and heterogeneous nucleation considerations.

Experimental Procedure

Pure gold was deposited onto the following three types of substrates: electroformed pure PC-board copper, exhibiting a columnar structure having an average of 3 μm grain size and a weak [011] texture; coarse-grained oxygen-free high conductivity (OFHC) copper of grain size 50-200 μm with a [001] texture; and amorphous electroless nickel with a phosphorous content of approximately 12 weight percent (w/o) as determined by energy-dispersive x-ray spectroscopy. The amorphous structure was confirmed by transmission electron microscopy and both electron and x-ray diffraction.

The copper substrates were cleaned by anodic electrolytic degreasing in a metasilicate alkaline solution for 1 min at room temperature and a current density of 20 mA/cm^2. To obtain a smoothness which would not affect the topography and to further improve the cleanliness of the film, the cleaning was followed by electropolishing in a mixture of 775 mliter/liter orthophosphoric acid and 225 mliter/liter propylene glycol for 1 min at room temperature and a current density of 350 mA/cm^2. The substrates were activated in 10% sulfamic acid for 30s at room temperature.

Copper was also used as substrate for the electroless nickel deposits. It was degreased as described above and activated for 30s in 20% sulfuric acid. The substrates were rinsed and subsequently transferred to the electroless nickel bath where 10 μm amorphous Ni/P was deposited. The Ni/P was dipped in 20% sulfuric acid, rinsed, and immediately transferred to the gold bath.

Pure gold was deposited from a citrate-buffered gold bath in a flow channel with nonturbulent electrolyte flow passing the electrodes (5). The bath containing 10 g/liter gold (added as $KAu(CN)_2$) and 115 g/liter citric acid was operated at pH 4.7 (adjusted with KOH) and at a temperature of 40°C. Gold was plated by a rectangular cathodic pulsating current at an average current density of 5 mA/cm^2 and by a dc current at a current density of 5 mA/cm^2, respectively. The pulse duration time was 4 ms, the pause time 16 ms, and the peak current density 25 mA/cm^2. The same pulse shape was used when gold was plated onto both types of copper substrates. When gold was plated onto the electroless nickel substrates, the off time was kept constant and the other pulse parameters were changed as listed in Table I. The final thickness of the pure gold deposits was within the range of 10 nm to several micrometers.

The film surface topography was examined by scanning electron microscopy (SEM) using a Cambridge Steroscan 250 Mk 3. To reveal characteristic features of the internal defect structure and preferred growth relationships, trans-

Table I. Pulse parameters for gold deposition onto amorphous electroless nickel substrates. The pause time is kept constant and the current density is varied both with constant current shape (pulse time constant, peak and average current density changed) and with constant average current density (pulse time and peak current density varied)

Pulse current density (mA/cm^2)	Pulse time (ms)	Pause time (ms)	Average current density (mA/cm^2)
5	10	40	1
25	10	40	5
125	10	40	25
10	40	40	5
25	10	40	5
50	4.4	40	5
100	2.1	40	5
500	0.4	40	5

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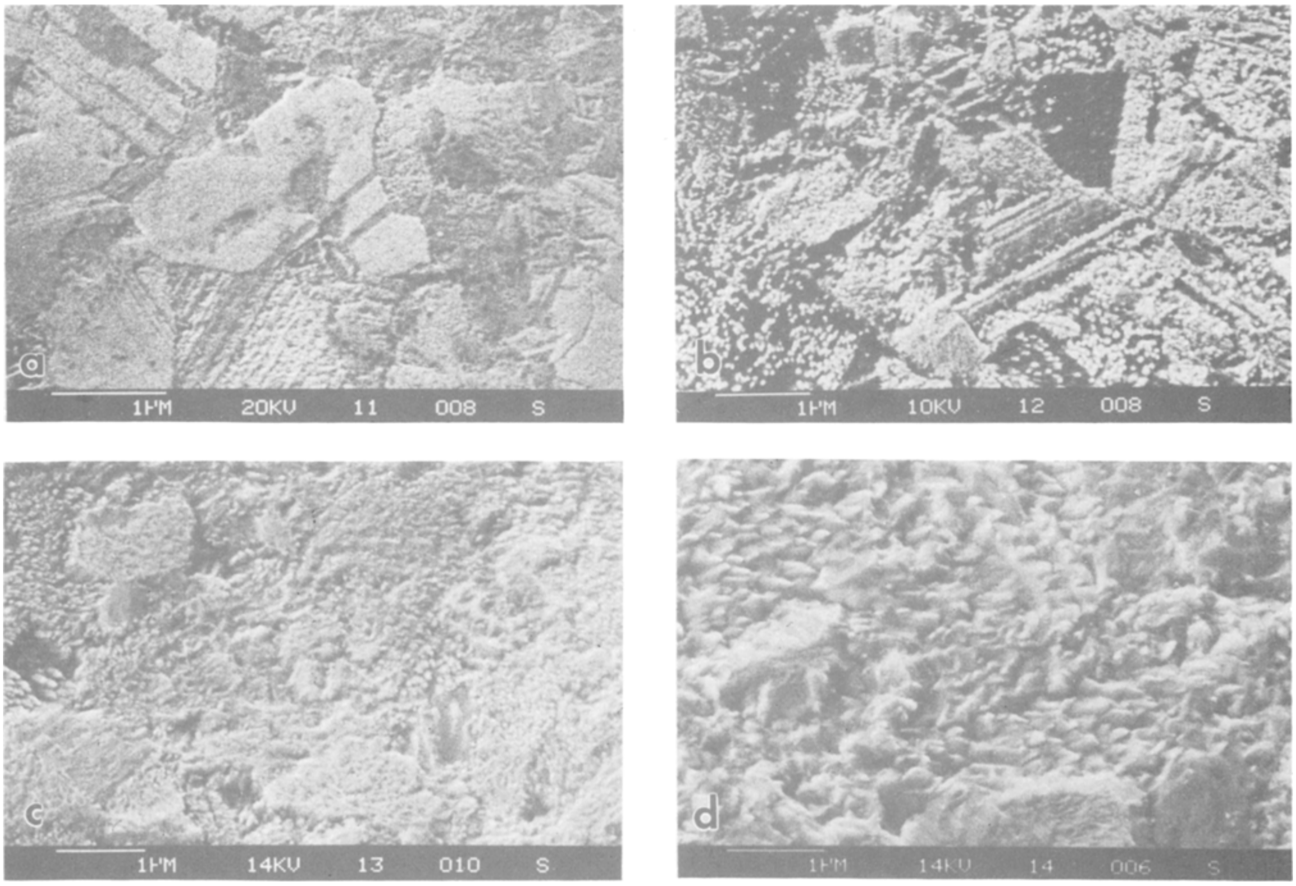

Fig. 1. Development of a gold film deposited under pulse plating conditions onto an electroformed copper substrate at gold thicknesses of (a) 10 nm, (b) 40 nm, (c) 150 nm, and (d) 500 nm.

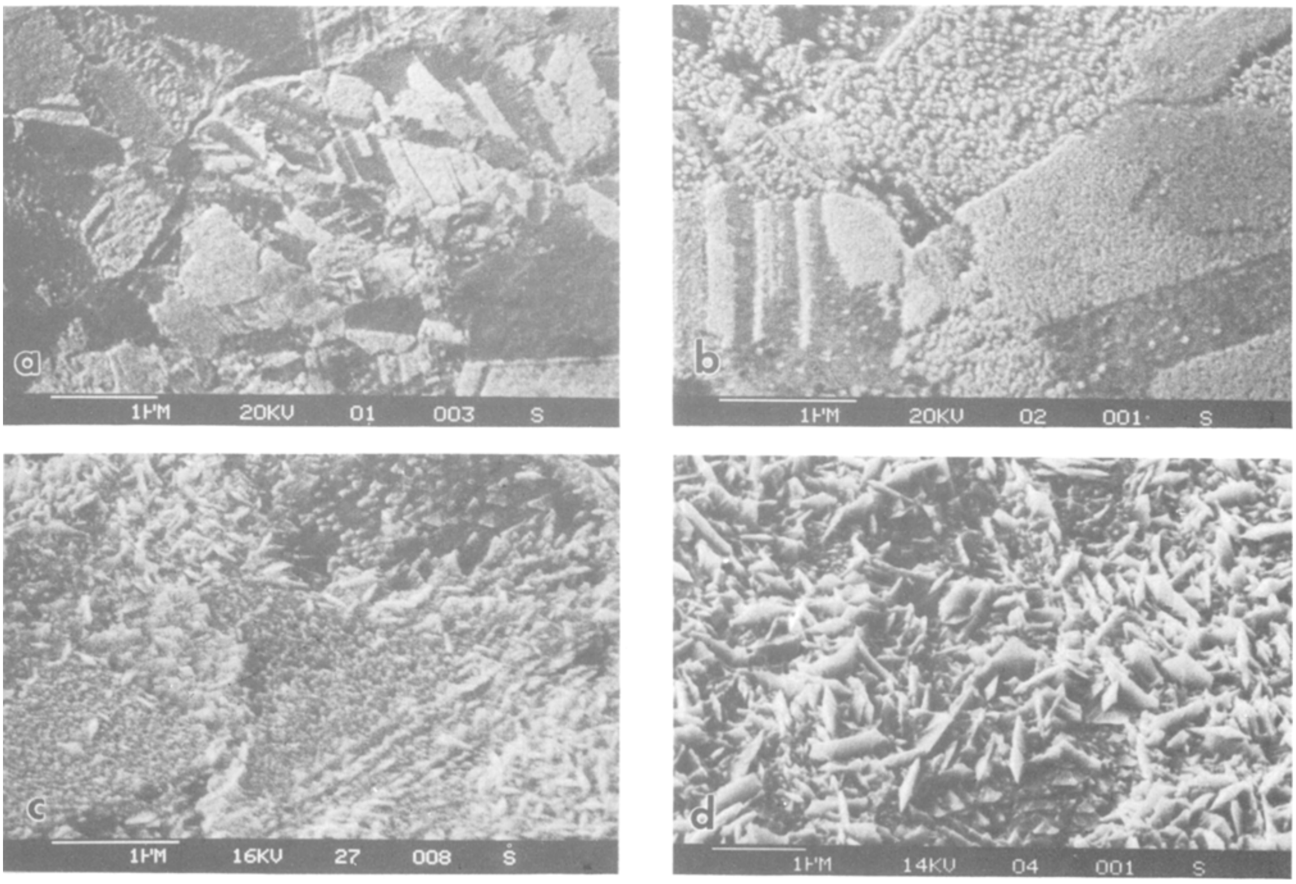

Fig. 2. Development of a gold film deposited under dc conditions onto an electroformed copper substrate at gold thicknesses of (a) 10 nm, (b) 50 nm, (c) 150 nm, and (d) 500 nm. A transition from epitaxial conditions to bath property–controlled conditions has started at a thickness of about 150 nm.

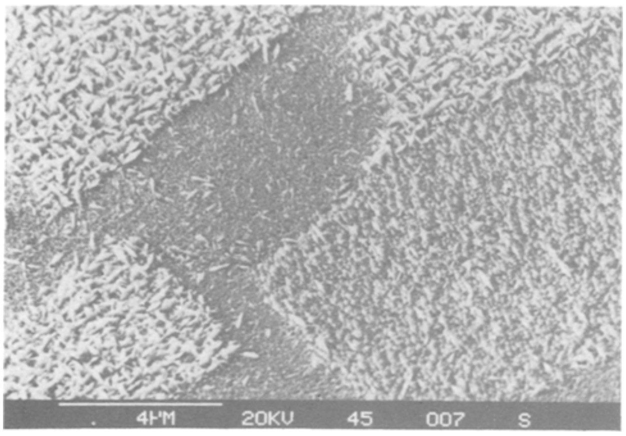

Fig. 3. A 500 nm thick dc-plated gold film deposited onto coarse-grained OFHC-Cu illustrating the difference in the transition substrate–controlled to bath–controlled growth compared with gold deposited onto fine-grained copper [Fig. 2(d)].

mission electron microscopy (TEM) using a Philips EM400T microscope operated at 120 kV was employed. The TEM samples were prepared from 10 to 50 nm thick Au films which were electron transparent after dissolving the substrates in 25% nitric acid. X-ray diffraction was used to reveal preferred crystal orientations of the copper substrates. The carbon content in films grown on OFHC-Cu substrates was measured by coulometric detection (17).

Results

Growth of gold on crystalline copper substrates.—The initial growth of gold on copper substrates is strongly influenced by the structure of the substrate surface. However, as the film morphology develops, the growth is eventually turned into a form which is determined by the bath properties. SEM micrographs of the initial growth stages of pulse-plated gold on electroformed copper (referred to as Cu-epoxy) is shown in Fig. 1. At a thickness of 10 nm, the gold film is dense and uniform on one set of the substrate grains, while it is more open on other grains. The nucleation density varies with the Cu grain orientation. This is still the case at 150 nm where the grain structure of the substrate still can be revealed. At 500 nm, the surface morphology has become more uniform and the underlaying substrate grain structure is vaguely observed.

The initial growth of dc-plated gold on Cu-epoxy is shown in Fig. 2. No obvious morphological differences are observed between dc- and pulse-plated deposits up to about 50 nm. The gold films are dense and uniform in the interior of some of the grains, while others are more open. Eventually, at about 150 nm, flake-like grains start to develop at grain boundaries. At 500 nm up to at least 5 μm, these flakes entirely dominate the topography of the film structure. This structure is referred to as the bath-controlled growth morphology of dc deposits. It is found in thick films on various types of substrates. This morphology is further discussed in Ref. (5).

The change from substrate-controlled to bath-controlled growth is gradual and sensitive to the grain structure of the substrate. It starts earlier when the substrate grain size is small. The two substrates used, Cu-epoxy and OFHC-Cu, exhibit large difference in grain size—the Cu-epoxy having grains 3 μm diam and the OFHC-Cu having grain sizes ranging from 50 to 200 μm. Gold films grown on Cu-epoxy exhibit an almost uniform topography independently of the orientation of the substrate grains at film thicknesses from 500 nm. Gold films on OFHC-Cu exhibit topographies influenced by the substrate even up to 2 μm (Fig. 3).

The grain structure of the gold reproduces the structure of the substrate. On each substrate grain, all gold nuclei have one common growth axis. The direction of their growth axis is parallel to either the [001] Au, the [011] Au, or the [112] Au direction. The orientation relationship between substrate and film has not been identified in detail, but it has been observed that the Cu-epoxy shows a weak [011] Cu texture while the OFHC-Cu shows a very strong [001] Cu texture, as shown in Fig. 4. In spite of the variations in preferred orientation of the substrates, no differences in the growth orientations of the Au is observed. By pulse plating, single-crystalline growth is observed for [001] Au and [011] Au oriented grains even up to thicknesses of 50 nm [Fig. 5(a), (b)]. Polycrystalline growth is observed in [112] Au oriented grains [Fig. 5(c), (d)]. Within the grain boundaries of one substrate crystal, the diffraction pattern is single crystalline from [001] Au and [011] Au oriented grains while from [112] Au oriented grains, three superimposed diffraction patterns are found mutually rotated 120° with respect to each other (Fig. 6). This indicates that gold nucleates in three equivalent lateral directions around the main [112] growth axis [Fig. 5(d)].

By dc plating, textured polycrystalline growth is observed in the initial growth stages. In [001] Au and in [011] Au oriented grains, single-crystalline diffraction patterns are obtained, but the grains exhibit cell or grain boundaries. In [112] Au oriented grains, the preferential polycrystalline growth by dc and pulse plating is the same.

During pulse plating, the nuclei forming [001] and [011] oriented grains coalesce when they come in contact with each other which leads to single-crystalline grain growth. For the formation of large grains, the growing nuclei must in some way obtain equal orientation (18). This has been observed only for pulse-plated Au and is probably due to desorption of impurities during the relaxation time between two successive pulses. Coalesence is more likely to occur if the growing surfaces are clean. If not, impurities are pushed in front of the growing surface and prevent two adjacent grains from coalescing, resulting in the formation of a grain boundary. By pulse plating, the impurity content is lower than by dc plating, *e.g.*, the carbon content in the pulse-plated deposits is half of that of dc-plated deposits

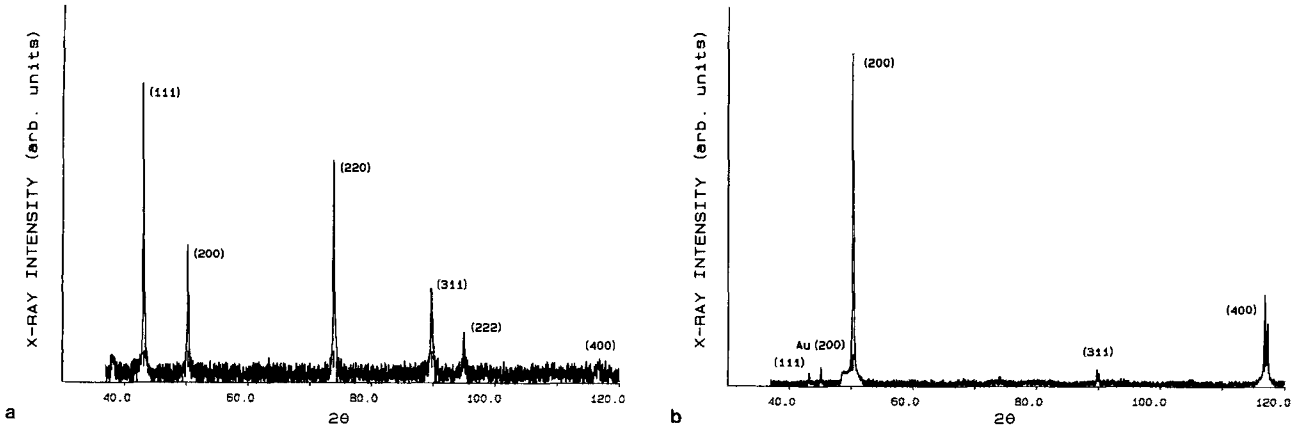

Fig. 4. X-ray diffractograms from Cu substrates. In (a) a diffractogram from electroformed Cu (Cu-epoxy) is shown. It exhibits a slightly increased intensity of the (220) reflection indicating a weak [110] texture. In (b) a diffractogram from OFHC-Cu is shown. The (200) reflection dominates completely indicating a strong [100] texture. The (400) and (311) reflections are also revealed.

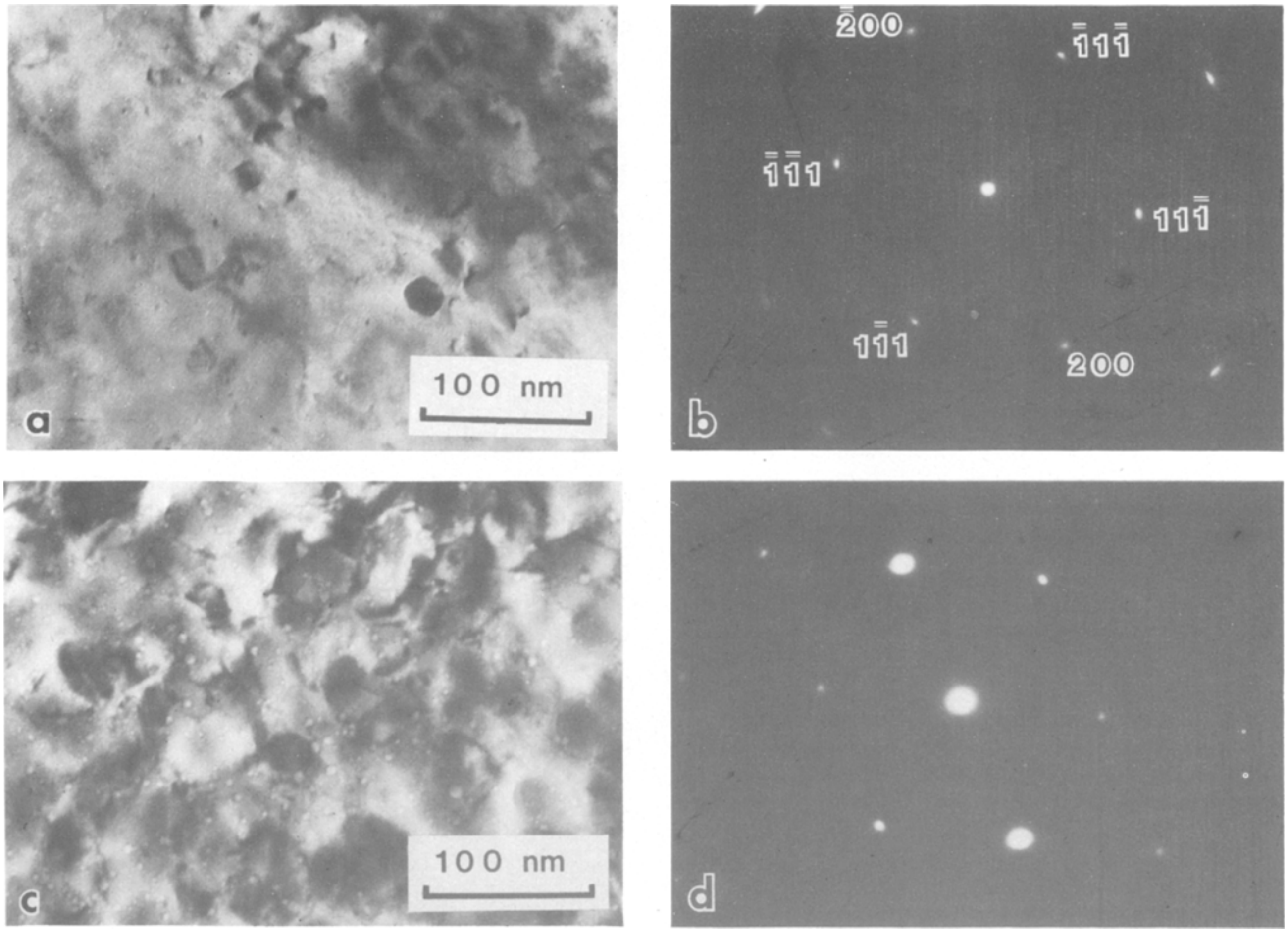

Fig. 5. TEM pictures and electron diffraction patterns showing the main growth orientations observed in 50 nm gold films. In (a) and (b) the single-crystalline structure of an epitaxial grain with [011] Au orientation is shown. In (c) and (d) a polycrystalline grain structure of [112] Au orientation is shown.

(175 and 340 ppm, respectively). This explains why the coalescence of [001] and [011] Au oriented grains is more likely to occur by pulse plating than by dc plating.

Growth of gold on amorphous electroless nickel substrates.—No texture was observed for gold deposited onto amorphous electroless nickel as can be seen from the diffraction pattern in Fig. 7(a). The internal microstructure of 50 nm thick gold films is illustrated in Fig. 7(b) and (c). Dislocations are rare, but twins are present in most grains. The grain structure is bimodal with a mixture of small and large grains. The smaller grains are of the order of 10-25 nm for all types of deposits. No significant difference in size between high- and low-current density deposits is de-

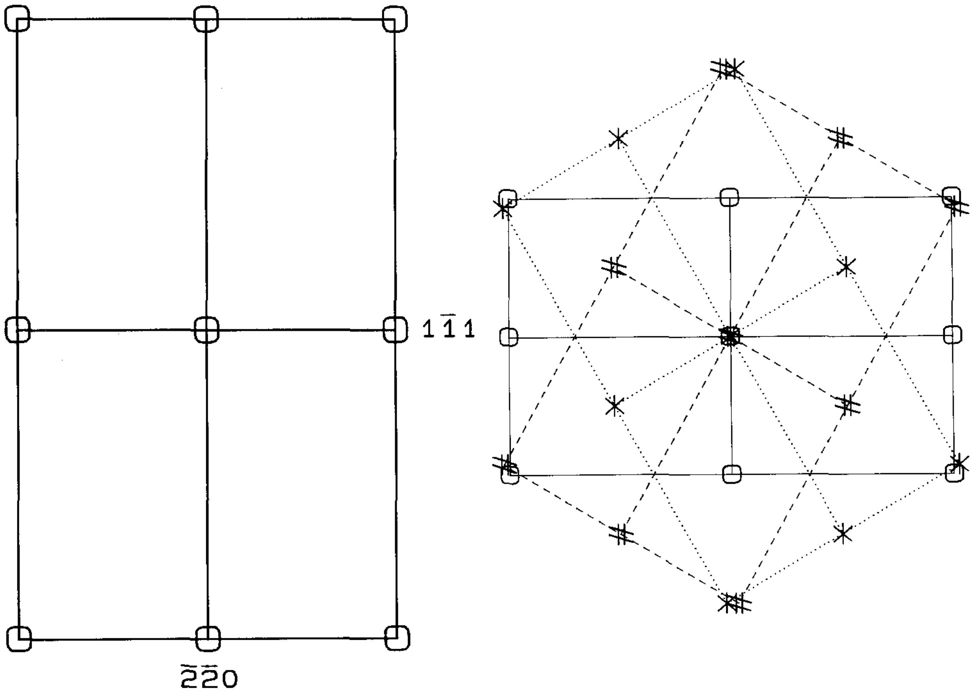

Fig. 6. In (a, left) a standard diffraction pattern from fcc, B = [$\bar{1}12$] is shown and, (b, right) illustrates three overlapping patterns identical with (a), mutually rotated 120° with respect to each other. This is how Fig. 4 (d) is built.

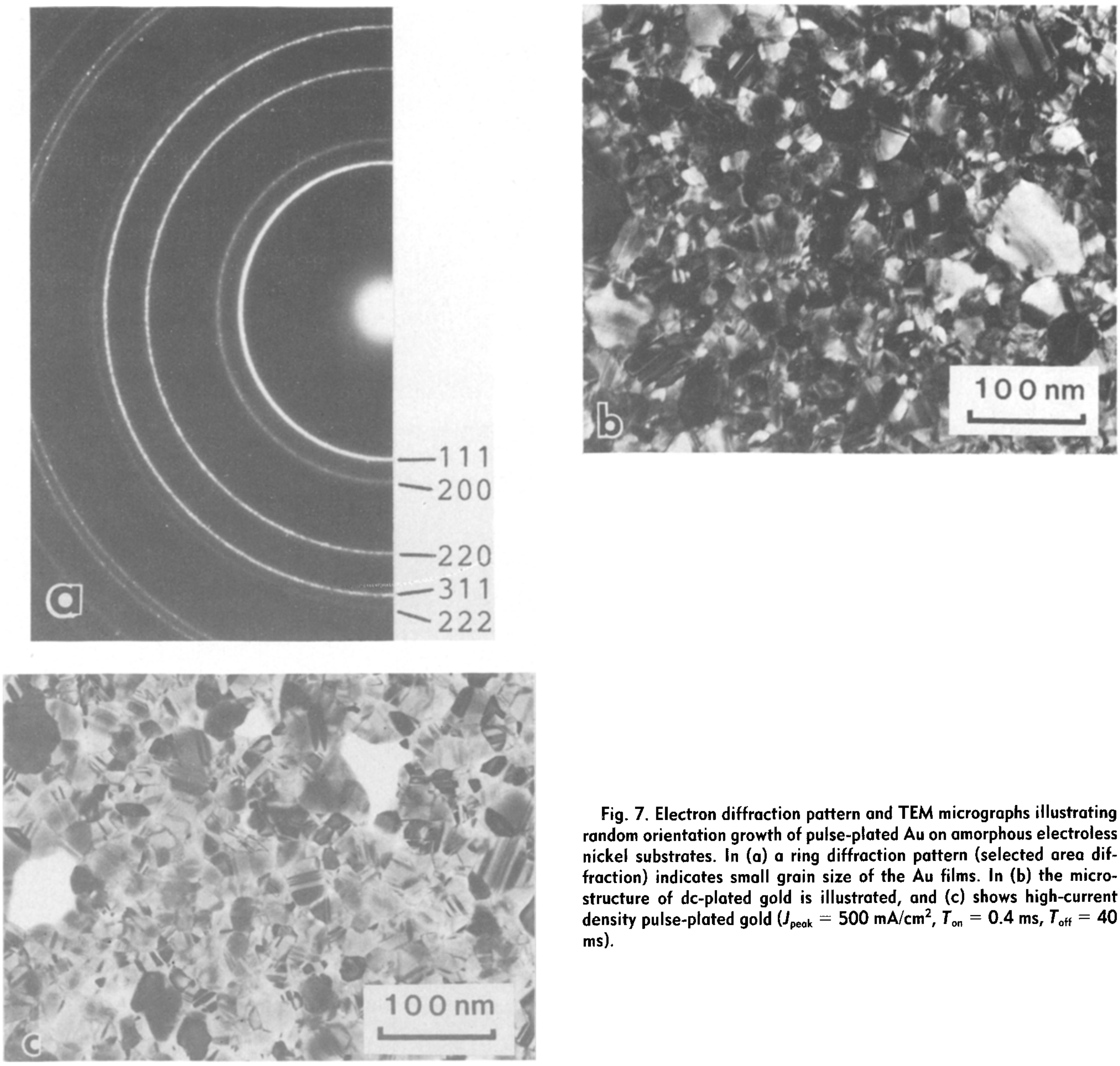

Fig. 7. Electron diffraction pattern and TEM micrographs illustrating random orientation growth of pulse-plated Au on amorphous electroless nickel substrates. In (a) a ring diffraction pattern (selected area diffraction) indicates small grain size of the Au films. In (b) the microstructure of dc-plated gold is illustrated, and (c) shows high-current density pulse-plated gold (J_{peak} = 500 mA/cm^2, T_{on} = 0.4 ms, T_{off} = 40 ms).

tected. The large grains are of the order of 25-50 nm for high-current density deposits and 50-70 nm for low-current density deposits, which is of the same order as the film thickness.

Discussion

Bockris and Damjanovic (15) have shown that the rate of homogeneous nucleation can be expressed by the following equation

$$R = 2\pi\, r_c n^2 \sqrt{kT/2\pi m}\, \exp\,[-(\Delta F_c + E)/kT] \qquad [1]$$

where r_c is the critical radius of the nucleus, n the number of arriving adions, ΔF_c the free energy for formation of the nucleus, and E the activation energy for surface diffusion. In Eq. [1], r_c, n, and ΔF_c are all overpotential-dependent properties. Consequently, one would expect that by pulse plating, where both the overpotential and adion concentration are high compared to that of dc plating, the nucleation rate would be high and the deposits would become fine grained. This type of grain refinement of Cd and Au films was reported by Puippe and Ibl (6) and Rehrig (9).

When Au is deposited onto crystalline Cu, the gold nuclei growing on the same Cu grain will adopt a common growth direction. There is a strong interaction between the Au film and the Cu substrate and the question of whether or not the growth is epitaxial is raised. However, without a direct determination of the orientation relationship of the film and the substrate grains, it cannot be determined. When the boundaries between two nuclei are free from contamination, they coalesce, and the overall grain size becomes comparable with that of the substrate. That is why the grain size of pulse-plated gold on copper in the initial stage of growth does not differ from that of dc-plated gold. In spite of this, the final grain size of a 2 μm thick pulse-plated film is smaller than that of dc-plated films (5). Although the nucleation rate of pulse-plated deposits is higher than that of dc deposits, the grain refinement is due to the different surface diffusion conditions rather than to increased nucleation rate. During pulse plating, the diffusion paths are blocked due to a high adion concentration and the resulting structure becomes columnar and cauliflower-like on the surface (5). By dc plating, the adion mobility is high and a crystalline-like structure is developed (the flake-like type in Fig. 2—500 nm).

Amorphous electroless nickel was used as substrate material to avoid the influence from the substrate grain structure. However, the grain refining effect, as expected from Eq. [1], does not occur. This can be explained by the presence of defects in the amorphous substrate. An amorphous substrate is perfectly homogeneous by definition. In reality, however, the electroless nickel is by no means a perfect amorphous material. Crystalline Ni-phase particles are observed, and there are probably phosphide particles dispersed in the amorphous matrix as well. These types of defects could act as sites for preferential nucleation. At those sites, the nucleation is described in terms of heterogeneous nucleation having a lower activation energy than homogeneous nucleation. The difference is larger at low-current densities. This is illustrated in Fig. 7(b) where a heterogeneous structure is shown. Grains as large as 70 nm are present which were heterogeneously nucleated. As the growth rate was slow, they had time to grow undisturbed. The result is an inhomogeneous structure with abnormally large grains mixed with small homogeneously nucleated grains.

In Fig. 7(c), a high current density deposit is shown. The homogeneous nucleation has caused a deposit within the larger type of grains of only 40 nm diam. The nucleation rate was high due to a high overpotential and the growth during one pulse so rapid that the abnormal grain growth never took place. The resulting grain structure of the deposit is therefore homogeneous.

Summary

The fine grain size of gold prepared by pulse plating onto crystalline copper substrates is due to decreased surface mobility rather than increased nucleation density. The initial growth preserves the grain structure of the substrate. Single-crystalline growth is obtained under pulse plating conditions in [001] Au and [011] Au oriented grains, probably due to desorption of impurities during the off time facilitating the coalescence of adjacent nuclei.

The fine grain size of gold prepared by pulse plating onto amorphous electroless nickel substrates is probably due to the suppression of heterogeneous nucleation. The initial growth exhibits a randomly oriented bimodal grain structure. There are large grains present in the dc and low-current density deposits originating from grains nucleated heterogeneously at defects on the substrate surface. The influence of heterogeneous nucleation is reduced when the pulse current amplitude is increased, resulting in homogeneous and fine-grained deposits.

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The Effect of Anionic Additives on the Volume of Activation for the Electrodeposition of Nickel

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ABSTRACT

Volumes of activation as determined from the effect of pressure on the exchange current were measured for nickel electrodeposition in the presence of several anionic additives. From the results it was concluded that in reaching the activated complex, two water molecules were lost in dilute chloride solutions, one was lost in boric acid and more concentrated chloride solutions, and none were lost in thiocyanate solutions. The results were interpreted in terms of an outer-sphere electron-transfer bridge in the case of the thiocyanate, and inner-sphere bridges in the case of the chloride and the boric acid.

A number of studies have been made on the effect of pressure on equilibrium and rate constants of homogeneous reactions (1-6) with the results being interpreted in terms of changes in overall volume and volumes of activation of the reactions. In the '60s and '70s these studies were extended to electrochemical reactions (7-11).

For electrode processes, the volume of activation for the electron-transfer step can be obtained from the pressure coefficient of ln i_0 (where i_0 is the exchange current density) (9).

$$\Delta V^*_{\text{ideal}} = -RT\,(\partial \ln i_0/\partial P)_{T,\mu,\Phi} \qquad [1]$$

The volume of activation is the sum of an intrinsic part, ΔV^*_{int}, related to bond-making and bond-breaking, and a

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