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Inclusions in Electroplated Additive-Free Hard Gold

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ABSTRACT

Hard gold deposits plated from an additive-free phosphate bath have been analyzed for codeposited inclusions using transmission electron microscopy. Electron diffraction analyses of residues obtained from aqua regia dissolution of the gold deposits and those collected from the surface of thermally aged deposits showed that these residues consist of aurous cyanide (AuCN). These results and other electrochemical evidences suggest that AuCN is codeposited in additive-free hard gold, bringing about a grain refining effect and the resulting increase in hardness.

Hard gold deposits for electronics applications are generally electroplated from baths containing KAu(CN)₂, a citrate or phosphate buffer, and a hardening agent such as a cobalt salt. Recently, it was found that the inclusion of cobalt in the gold at concentrations above a certain limit may cause the formation of a highly resistive, cobalt-containing surface film (CoO) when the gold is aged at moderately high temperatures ($\sim 150^{\circ}$ C) (1). As a practical solution to this

[•] Electrochemical Society Active Member. Key words: electrodeposition, transmission electron microscopy, electron diffraction.

problem it has been suggested to replace the cobalthardened gold (CoHG) with an additive-free hard gold (AFHG) for certain applications (2).

The plating of AFHG was first described by Reinheimer (3), who obtained hard gold deposits by operating at low temperatures (~25°C) the conventional citrate or phosphate bath which normally yields soft gold at elevated temperatures (~70°C). He also observed that the increase in hardness with decreasing plating temperature is accompanied by a corresponding increase in carbon content of the deposit. Subsequently, we carried out a transmission electron microscope (TEM) study of various hard gold deposits (4), and found that AFHG contains a high density of small nonmetallic objects. The present study was undertaken to identify these inclusions and to obtain an understanding of the mechanism of codeposition and the role that the codeposited material might play in determining the structure and properties of AFHG. It is shown that AFHG contains aurous cyanide (AuCN), which is known to form a polymeric structure with infinite linear chains (5, 6). This finding is consistent with the recently proposed mechanism of cathodic gold deposition from $Au(CN)_2^-$, which involves the formation of AuCN as an adsorbed intermediate (7-11).

Experimental

Plating procedure.—The AFHG deposits examined in this work were plated from a phosphate bath with the following composition: $KAu(CN)_2$ 44 g/liter, KH_2PO_4 100 g/liter, KOH 28 g/liter, pH 7.0. The plating was carried out at 40°C using the previously described experimental setup (12) involving a stainless steel rotating cylinder cathode and a concentric anode. The cathode, 2 cm in diameter and 2.1 cm in height, was tightly wrapped with a substrate, which was a sheet of copper, 2.1 imes 6.5 imes 0.005 cm, coated with a thin flash of gold strike. The anode was made of titanium, and it was coated with an active layer consisting of RuO_2 and TiO_2 (12). The inner diameter of the anode measured 2.9 cm. The cathode was rotated at 3600 rpm to obtain a turbulent flow condition which allowed high speed plating at a current density of 250 mA/cm² (12).

Specimen preparation.—The copper substrate was first dissolved off the gold deposit ($\sim 25 \ \mu m$) in 1:1 HNO₃. TEM specimens for direct observation of inclusions were prepared by electropolishing the gold in a mixture of 25 ml ethyl alcohol, 25 ml glycerin, and 50 ml concentrated HCl (4).

The residue obtained upon dissolution of the AFHG deposit in aqua regia was collected on a TEM specimen grid after thorough washing in distilled water. In this procedure the aqua regia had to be replaced by distilled water immediately after complete dissolution of the gold because the residue dissolved rather rapidly in aqua regia. It was noted that the amount of this residue was considerably less than that obtained from a CoHG deposit. The latter was first discovered by Munier (13) and called "polymer," which more recently was identified as cobaltous cyanocobaltate, $Co_3[Co(CN)_6]_2 \cdot xH_2O$ (14). This "polymer" is stable in aqua regia unlike the residue from the AFHG.

The surface residue formed on a thermally aged (150°C, 1 week) AFHG deposit was collected on a small piece of knife edge using the scraping technique described previously (15). The knife edge was directly mounted on a specimen holder for TEM observation.

Transmission electron microscopy.—TEM micrographs were taken with a JEM-200 electron microscope operated at 200 kV. The defocus imaging technique (16) was used for direct observation of nonmetallic inclusions in gold deposits.

Experimental Results

Direct observation.—A TEM micrograph of an AFHG film taken in the under-focused condition [Δf (defocus distance) = $-3.9 \ \mu m$] is shown in Fig. 1. Nonmetallic



Fig. 1. TEM micrograph of electropolished AFHG, showing nonmetallic objects (black and white arrows), voids (denoted by a symbol V), and holes (marked by H). White arrows indicate inclusions inside the deposit, whereas black arrows show objects lying on the surface. The micrograph was taken in slightly underfocused condition in order to reveal the images of inclusions.

objects are seen in this micrograph mostly as small white circles surrounded by black rings (marked by white arrows), while some are seen with an opposite contrast as black circles surrounded by white rings (marked by black arrows). These small image features result from phase contrast, and therefore these objects are sometimes called "phase objects" (17). It can be easily shown from the previously described image analysis based upon geometric optics (18) that the black circles in Fig. 1 are due to objects situated on the specimen surfaces, whereas the white circles are images resulting from objects located inside the specimen. As shown previously (19), the image size measured from under-focused micrographs closely corresponds to the true size of phase objects in the range of about 20-50Å. The micrograph of Fig. 1 shows that approximately 80% of the phase objects measure 20-55Å in diameter, the remainder measuring up to 200Å. The population density was $\sim 1 \times 10^{17}$ /cm³, and the volume ratio was estimated to be 1.3 to 1.9%, assuming the phase objects to be spherical and taking measurements in the regions of thicknesses ranging from 500 to 750Å. A close examination of the micrograph shows that the phase objects are located both within the grains and at grain boundaries. In spite of the presence of these phase objects, the electron diffraction pattern obtained with the gold film did not show any detectable diffraction lines other than those due to gold metal.

It is also seen from Fig. 1 that the size of gold grains ranges from ~250 to 750Å, which is somewhat larger than that of a typical CoHG (225-275Å) (4) but considerably smaller than the grain size of soft gold deposits [typically 1-2 μ m (20)]. Generally, when TEM specimens are prepared by electrothinning, holes surrounded by thin tapered edges are produced. The large holes denoted by H in Fig. 1 are seen to have this feature. On the other hand, the small faceted holes denoted by V are not surrounded by such tapered edges, and their size and shape resemble those of individual grains. Based on these observations, it may be assumed that these small holes are voids produced during film growth. The significance of this assumption will be discussed in a later section.

Residue from aqua regia dissolution.—A TEM micrograph obtained with the residue from aqua regia dissolution is shown in Fig. 2a, and the corresponding electron diffraction pattern in Fig. 2b. It is seen that the residue consists of extremely small crystals (25-

30Å) with poor crystallinity. The analysis of the diffraction pattern shows that the material is AuCN (Table I). It was noted that this material is stable to electron beam irradiation as opposed to the similar aqua regia residue obtained from a cobalt-hardened gold, which was observed to decompose in a few seconds in the electron microscope.

Surface residue.—Figures 3a and 3b show a TEM micrograph obtained with the residue collected from the surface of a thermally aged (150°C, 1 week) deposit and the corresponding electron diffraction pattern. The residue is seen as well-developed needleshaped crystals 100-300Å thick. No such residue was obtained from the surface of as-deposited gold. The analysis of the diffraction pattern also showed that the crystals are AuCN (Table I). The relatively large discrepancy for the largest d-spacing is attributed to an experimental error.

Discussion

Existence of AuCN in deposits.—Reinheimer (3) studied the carbon inclusion in gold deposits plated from additive-free baths as a function of various plating parameters. He unequivocally showed that the carbon results from the inclusion of a cathodically formed product, and considered these compounds as the most likely source of carbon: KCN, AuCN, KAu(CN)₂, and HCN. For cobalt-hardened gold deposits, Raub, Knödler, and Lendvay (21) also considered the possibility of the inclusion of AuCN among other compounds as a source of carbon. Subsequently, Cohen, West, and Antler (22) made a Mössbauer spectroscopic study of cobalt-hardened gold, and reported that the deposit contained no detectable AuCN, $KAu(CN)_2$, or $KAu(CN)_4$. The detection limit for AuCN by this technique was ~ 2 mole percent (m/o) of the total Au. The analysis of AFHG plated under the conditions of the present experiment showed the presence of 0.055 weight percent (w/o) of carbon (2), which corresponds to 0.90 m/o as AuCN if all of the carbon is assumed to be present in this form. Thus, Mössbauer spectroscopy would not detect the AuCN in AFHG. Based on these considerations in conjunction with the results of analysis of aqua regia residue and surface residue, it is postulated that AuCN is codeposited in AFHG.

Mechanism of AuCN codeposition.—The mechanism of gold deposition from $Au(CN)_2^-$ has been studied by many investigators in recent years. All agree that a chemical step precedes the charge transfer step but disagree in detailed description of the chemical step. Harrison and Thompson (8), using a potentiostatic linear sweep technique, found that the reduction of $Au(CN)_2^-$ to be first order in cyanide, and proposed that AuCN is the reducible species

> $Au(CN)_2^- \rightleftharpoons AuCN + CN^-$ [1]

$$AuCN + e^- \rightarrow Au + CN^- (slow)$$
 [2]

Beltowska-Brzezinska and Dutkiewicz (9) determined the dependence of exchange current on con-

Table I. Electron diffraction analysis of agua regia and surface residues in AFHG

Aqua regia residue		Surface residue			
dobs (Å)	Inten- sity	d _{obs} (Å)	Inten- sity	AuCN*	
				d(A) (hkl)	I/Imax
5.06	s	4.90	s	5.08 (001)	100
2.95	S	2.90	s	2.941(100)	100
2.30	S	2,58	5	2.342 (101,002)	25
1.71	M	1.71	м	1.693 (003, 110)	25
1.46	М	1.47	M	1.470 (200)	10

S = strong; M = medium.* Joint committee powder diffraction standard, formerly ASTM diffraction file 11-307.





Fig. 2. Structure of aqua regia residue from AFHG. The image of the residue (a) and its electron diffraction pattern (b). Note details around edges in (a).

centrations and arrived at the same conclusion as above. MacArthur (7) carried out a cyclic voltammetric study and found evidence for the adsorption of AuCN intermediate at low overpotentials. Eisenmann (10) concluded from his kinetic studies of the deposition systems of soft as well as hard gold that the reaction proceeds via a common mechanism involving adsorption equilibria preceding and following the electron transfer step

$$Au(CN)_2 \rightleftharpoons AuCN_{ad} + CN^-$$
 [3]

$$AuCN_{ad} + e^{-} \rightleftharpoons (Au^{\circ}CN)_{ad}^{-}$$
 [4]

$$(Au^{\circ}CN)_{ad} \rightarrow Au \ (lattice) + CN^{-}$$
 [5]

McIntyre and Peck (11) observed a distinct cathodic prewave in their potential scan experiment, which they consider may be attributed to the reduction of an insoluble film of AuCN. These mechanistic evidences are consistent with our experimental results indicating that AuCN is incorporated in the gold deposit.

It was found by Reinheimer (3) that the carbon content of AFHG is strongly temperature dependent, and soft gold plated at 70°C contains only ${\sim}0.001$ w/o C as compared to ~ 0.055 w/o for AFHG. From this result it is clear that soft gold contains essentially no AuCN. A TEM observation of soft gold also did not show any evidence of nonmetallic inclusions (19). This result can be understood if the adsorption of AuCN is involved because the coverage by an adsorbed species decreases exponentially as temperature is increased through an adsorption isotherm (23).

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Fig. 3. Structure of surface residue obtained from thermally aged AFHG. The image of the surface residue (a) and its electron diffraction pattern (b).

AuCN as phase object.—As stated in the preceding section, the volume occupied by the phase object in the specimen amounts to 1.3-1.9%. If it is assumed that these objects are AuCN with a bulk density of 7.12 g/cm³, the carbon content of the specimen corresponding to the AuCN can be calculated to be 0.032 ± 0.006 w/o. Thus, under these assumptions the phase object accounts for approximately 50-70% of total carbon content (0.055 w/o). It appears that two or more sources of carbon exist in AFHG; a similar conclusion has been reached recently for CoHG (14).

The structure of AuCN is known to be polymeric with infinite linear chains arranged in parallel (5, 6)



As noted previously, the size of AuCN crystallites in the aqua regia residue was 25-30Å while the majority of phase objects measured 25-50Å. This similarity in size suggests that the phase objects are, in fact, AuCN crystallites, and they coagulate to form the residue upon dissolution of gold in aqua regia. From the known lattice constants (hexagonal, a = 3.40Å, c = 5.09Å) (6) it can be estimated that each crystallite consists of 5-10 unit cells. The observation of the needleshaped crystals on the surface of thermally aged deposit shows that the small crystallites segregate on the surface to grow in the direction of c-axis upon heating.

It has been found that the density of AFHG determined by the gravimetric method using a specific gravity bottle is equal to 17.40 ± 0.10 g/cm³, as compared to 19.3 g/cm³ for pure bulk gold (2). A simple calculation using the volume percent of the phase object and the density of AuCN shows that the incorporation of AuCN as the phase object accounts for a decrease in density from 19.3 g/cm³ only to 19.1 g/cm³. It appears that the considerably lower density observed is due to the presence of voids. This interpretation is based on the following measurements and calculations. A TEM micrograph taken at a low magnification $(20,000\times)$ yielded $\sim 1 \times 10^{15}$ /cm³ for the population density of voids and 300-650Å for the range of void diameter. Using these values and estimated film thicknesses (750-1000Å), the ratio of the volume occupied by the voids to the film volume can be calculated as 8-14%. These values yield film densities ranging from 16.3 to 17.4 g/cm³ in good agreement with the observed density.1

Role of AuCN.—Hard gold electrodeposits are generally obtained by the addition of small amounts of metal ions such as Co^{2+} or Ni^{2+} . These ions are known to codeposit with gold in at least two different forms, cyano-complex and substitutional alloy (14, 25, 26). The increased hardness is primarily due to the grain refining effect (27) which is brought about by the codeposited cyano-complex (4, 14). Similarly, the codeposited AuCN appears to play the role of a grain refining agent for AFHG either by promoting the nucleation of gold or by inhibiting the growth of gold grains or both.

As was described in a previous communication, the contact resistance stability on thermal aging of AFHG is superior to that of CoHG (2). However, a small increase in contact resistance was found to occur upon heating AFHG at >100°C. The results described indicate that this increase is due to the surface segregation of AuCN at elevated temperatures.

Summary and Conclusion

A transmission electron microscope study of electroplated additive-free hard gold indicated that AuCN is codeposited as an impurity. Electrochemical evidences found in the literature suggest that this compound, which is formed as an adsorbed intermediate during the reduction of $Au(CN)_2^-$, is incorporated in the gold deposit. The amount of AuCN estimated from the volume density of phase objects observed by TEM shows that about 50-70% of the total carbon found by chemical analysis of AFHG can be accounted for by AuCN. The AuCN appears to be present in AFHG as crystallites, each consisting of 5-10 unit cells, within gold grains as well as at grain boundaries. The incorporation of AuCN can explain the decreased grain size, increased hardness, and small contact resistance instability of additive-free hard gold.

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¹ The density of CoHG is also known to be low (17.3-17.8 g/cm³) (24). A TEM examination of this type of gold showed that voids similar to individual grains in size and shape (\sim 250A) are distributed randomly. As in the case of AFHG, the volume of these voids appears to account for the decreased density of CoHG.

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Cyanoaurate(III) Formation and Its Effect on Current Efficiency in Gold Plating

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ABSTRACT

The cyanoaurate (III) ion has been found to form and accumulate in acidic or neutral gold plating baths containing cyanoaurate(I) as the source of gold. This trivalent gold species brings about a decrease in plating current efficiency because its reduction to gold metal requires three faradays per mole, whereas only one faraday is consumed to reduce one mole of Au(I). The accumulation of Au(III) should therefore be minimized to produce gold deposits with a thickness unaffected by bath age. This paper describes various methods for achieving this objective, which include the use of the so-called "dimensionally stable anode" and a techniqe of chemically reducing Au(III) to Au(I).

Thickness control in gold plating has become increasingly important in recent years because of the necessity for saving gold by plating only a minimal thickness required for specific applications. Since deposit thickness is directly proportional to plating current efficiency, it is important to have knowledge of factors affecting the latter. It is recognized that the current efficiency of both soft and hard gold plating from acidic or neutral cyanoaurate(I) baths tends to decrease with increasing extent of bath use, and generally extrinsic contaminants are believed to be responsible for the efficiency deterioration.

During the course of our recent work to develop a polarographic method for analyzing gold plating solutions (1), significant amounts of cyanoaurate(III) ions, $Au(CN)_4^-$, were found in extensively used production baths. It has been established that this species is produced as a result of a reaction at the anode, generally platinum or platinized titanium, and that it is, at least partly, responsible for the decrease in plating current efficiency because of the greater quantity of electricity required to reduce Au(III) than Au(I).

In the present work, the relationship between current efficiency, Au(III) content, and bath age has been

* Electrochemical Society Active Member. Key words: cyanoaurate(III), gold plating, current efficiency, dimensionally stable anode, hydrazine.

studied, and methods for minimizing the formation and accumulation of Au(III) have been investigated.

Experimental

Plating Solutions

Results obtained with two different types of plating solutions are described in this paper: a conventional cobalt-containing hard gold bath (denoted as CoHG) and a high speed, additive-free hard gold bath (AFHG) (2). Make-up compositions and optimum operating conditions of these baths are listed in Table I. During the bath aging experiments, the plating solutions were analyzed for total gold and Au(III) and for Co²⁺ using, respectively, the polarographic and colorimetric methods described previously (1), and the total gold and cobalt concentrations were maintained within approximately $\pm 10\%$ by periodic addition of appropriate salts. The pH was kept constant within ± 0.1 unit by adding citric phosphoric acids for CoHG and AFHG baths, respectively.

Apparatus

CoHG .- A jacketed glass plating cell containing 300 ml of the CoHG plating solution was used. A rigid flat anode (platinum unless noted otherwise) measuring 3.8 imes 3.8 cm was placed vertically at the center of the cell, and two copper sheets with the same dimensions plated

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