Incorporation of Gold Cyanide in Electrodeposited Gold

G. Holmbom and B. E. Jacobson

Department of Physics and Measurement Technology, Linköping Institute of Technology, S-581 83 Linköping, Sweden

Introduction: Gold is still one of the most important contact materials in electronic industry, although efforts have been made to find substitutes like palladium and some of its alloys. Of special interest are the so called hard gold films containing small amounts of cobalt or nickel to provide wear resistance. In addition to these alloying elements, carbonaceous inclusions are found in both pure gold and hard gold films. The effect of their presence have been studied for some decades (1-10). Also, impurities containing nitrogen, oxygen, hydrogen, and potassium frequently exist. It has been stated that large amounts of the carbon and nitrogen form cyanide complexes with the metals in the film.

The temperature dependence of the carbon incorporation was studied by Reinheimer (1). He concluded that an of increase the bath temperature results in a lower carbon content. The reaction kinetics of the gold film formation as a reduction from the dicyanoaurate ion was studied by Eisenmann (2). He found that gold cyanide is adsorbed as an intermediate step on the surface of the growing film. The dominating cyanide complex in pure gold films is gold cyanide according to Nakahara and Okinaka (3) and in hard gold films KCo[(AuCN)2]3 according to Eisenmann (4), while it is AuCN according to Cohen et al. (5). in hard gold films (as Inclusions revealed by TEM) are homogenously distributed in the film (6). They act as preferential sites for nucleation which causes a fine grain size and thus high hardness.

So far, no one has been able to fully verify the presence and location of gold cyanide in pure gold films. With this letter we hope to bring some light on that matter.

Experimental: Pure gold was deposited onto four different types of substrate: coarse grained Oxygen Free High Conductivity (OFHC) copper with grain between 50 sizes and 200 μm, electroformed pure PC-board copper exhibiting a columnar structure with an average grain size \mathbf{of} 3 μm ; electrodeposited nickel; and amorphous electroless nickel with a phosphorous content of approximately 12 wt%. The gold was deposited at 40°C from a citrate buffered gold bath at pH 4.7 with 10 g/l gold added as KAu(CN) and 115 g/l citric acid. The gold was deposited to a thickness of 50 nm at 5 mA/cm^2 current density. The experimental setup was described in detail in a previous paper (7).

The following analytical tools were employed to confirm the presence and location of AuCN in the gold films; transmission electron microscopy (TEM) with selected area diffraction (SAD); Auger electron spectroscopy (AES) including depth profiling with the nitrogen signal used as AuCN indicator; and coulometric detection to measure the carbon content.

Results: Small amounts of crystalline AuCN was found in all gold films deposited onto all types of substrate fine studied. and coarse grained copper. electroplated nickel. and amorphous electroless nickel. The carbon content in deposits grown on copper substrates was 350 ppm.

The grain sizes of both the AuCN crystallites and the gold matrix were small as indicated by the continuous rings in the SAD pattern in Fig. 1. All rings in the SAD pattern are present except the (102) which is probably hidden in the stronger (200) Au ring of pure gold (Table I). The AuCN is present in pockets of sizes up to 15 nm located along grain boundaries of the gold film (Fig. 2). No enrichment of nitrogen was detected in the films, neither at the surface nor at the film/surface interface. The conclusion is that the AuCN is continously distributed throughout the film.

The mechanism for the electrochemical reduction of the dicyanoaurate ion proposed by Eisenmann (2) is described as follows:

Adsorption:

 $Au(CN)_2 = (AuCN)_{ad} + CN$ [1]

Electron transfer:

$$(AuCN)_{ad} + e^{-} \neq (Au^{\circ}CN)_{ad}$$
 [2]

Crystallization:

 $(Au^{\circ}CN)^{-}_{ad} = Au_{lattice} + CN^{-}$ [3]

The rate limiting step under activation controlled conditions is the electron transfer [2]. According to this reaction path it is likely that the adsorbed (AuCN) has time to agglomerate and crystallize as a simultaneous reaction (also suggested in Ref (3)). When the gold film grows,



Figure 1. Selected area diffraction pattern exhibiting a dual phase structure of Au (fcc) and AuCN (hexagonal). The interplanar distances agrees with Powder Diffraction File within 1.7%.

Linköping Institute of Technology assisted in meeting the publication costs of this article. the AuCN agglomerates in the growth fronts and, eventually, concentrates to the gold film grain boundaries.

Summary: Crystalline AuCN is incorporated in the grain boundaries of electrodeposited pure gold. It is produced as an intermediate product in the reduction of the dicyanoaurate ion, agglomerates on the surface during film growth, and eventually concentrates to the grain boundaries of the gold film. Manuscript submitted Oct. 28, 1987. References:

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Figure 2. Bright field (a) and dark field (b) TEM images (g = 001) showing the location of AuCN grains within the Au film. The arrow in a) shows the location of the large AuCN grain in the centre of b).