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Review

Development of new electrolytic and electroless gold plating processes for electronics applications

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Abstract

This article reviews results of our investigations, performed over the period of a decade, on gold plating for electronics applications. Three different topics are covered: (1) development of a new, non-cyanide, soft-gold electroplating bath containing both thiosulfate and sulfite as ligands; (2) evaluation of a known cyanide-based, substrate-catalyzed electroless bath for depositing pure soft gold, and subsequent development of an alternative, non-cyanide, substrate-catalyzed bath; and (3) development of a new process to electroplate amorphous hard-gold alloys for probable future applications as a contact material on nano-scale electronic devices.

Keywords: Gold; Electroplating; Electroless plating; Substrate-catalyzed plating; Amorphous gold alloys

Contents

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1. Introduction

Both electrolytic and electroless gold plating processes are indispensable for the fabrication of electrical contacts in the electronics industry. The materials of plated gold in use for this purpose can be classified into two categories: soft gold and hard gold. Soft gold is used for metallizing bonding pads and fabricating microbumps on silicon IC chips and ceramic packaging boards, while hard gold is used as a contact material on electrical connectors, printed circuit boards, and mechanical relays. Electrolytic methods are available for plating both soft gold and hard gold, whereas electroless methods can produce only soft gold at present. In this article, our past contributions to the development of processes for electro- and electroless-plating of soft gold and electroplating of amorphous hard-gold alloys are reviewed in three sections (Sections 2, 3, and 4).

Section 2 summarizes results of our investigation carried out to formulate a new non-cyanide, soft-gold electroplating bath containing both thiosulfate and sulfite as ligands for Au(I) [1,2]. This bath is highly stable, and unlike the conventional sulfite bath, it does not require the addition of a stabilizing agent.

Section 3, which consists of Sections 3.1 and 3.2, describes our investigation of substrate-catalyzed electroless (hereafter abbreviated as SCEL) processes for depositing pure, soft gold, as distinguished from the conventional galvanic displacement and autocatalytic processes. The SCEL process is of interest because of its two distinct advantages over the other conventional electroless processes: (1) the gold film obtained is much less porous than that deposited in the galvanic displacement bath, and (2) the SCEL bath is much more stable than the autocatalytic bath. The original SCEL bath was developed by Iacovangelo and Zarnoch [3] in 1991. We evaluated this bath in great detail to understand its general characteristics and properties of the gold deposit obtained [4], and the results are summarized in Section 3.1. Subsequently, we extended this work to develop a non-cyanide SCEL bath containing thiosulfate and sulfite as ligands [5,6]. The work on the non-cyanide SCEL bath is reviewed in Section 3.2. Non-cyanide baths are always preferred because they are non-toxic and more likely to be compatible with conventional positive photoresists employed to delineate electronic circuit patterns.

Section 4 of this article reviews results of our more recent attempt to develop a process for electroplating amorphous gold alloys. This work was initiated with the aim of creating an electroplated hard-gold film suitable as an electrical contact material on submicro- and nano-scale electronic devices. Critical mechanical properties, such as hardness and wear resistance, of the conventional crystalline hard-gold films result from their small grain size, of the order of 20–30 nm. Therefore, when the size or the physical dimensions of the contact surface becomes comparable to next generation, the properties of hard-gold films of such small dimensions are expected to deviate significantly from those of bulk hard gold. On the other hand, mechanical properties of amorphous metals and alloys in general are known to be independent of their size because of the absence of crystal grains in such materials. Thus, to be prepared for the future need of an amorphous electrical contact material, we made a preliminary investigation on the possibility of electroplating amorphous Au–Ni alloy from a bath prepared by adding a gold salt into a bath that is already known to deposit an amorphous alloy such as Ni–W [7]. This approach was successful in developing a process to electroplate amorphous Au–Ni alloy with a hardness value greater than twice that of the conventional hard gold without adversely affecting the electrical contact resistance [8,9]. Using a similar approach, we also developed a process for electroplating amorphous Au–Co alloy films [9].

Our contributions to the development of these new plating processes are reviewed below.

2. Non-cyanide thiosulfate–sulfite bath for electroplating soft gold

Electroplating of soft gold is generally carried out with a bath containing $KAu(CN)_2$ in a phosphate buffer of pH 7 at a mildly elevated temperature. It does not contain free cyanide ions initially, but they are generated at the cathode surface as a result of the gold deposition reaction. The cyanide ions are partly converted into HCN, which escape into the atmosphere, and partly remain in the bath. The presence of free cyanide is undesirable not only for its toxicity but also for its incompatibility with photoresists used to delineate circuit patterns through which the gold is to be plated. Cyanide attacks the interface between the substrate and the photoresist, lifting the latter and depositing extraneous gold under the photoresist. To avoid these problems, an Au(I) sulfite bath is used instead. However, the sulfite bath easily undergoes a disproportionation reaction to form Au(III) and metallic Au because of the relatively low stability of the Au(I) sulfite complex, causing the bath to decompose spontaneously on standing, unless a suitable stabilizer is added to the bath. All commercially available Au(I) sulfite baths contain proprietary stabilizing additives.

In contrast, the Au(I) thiosulfate–sulfite mixed ligand bath we developed is highly stable and requires no stabilizing additive [1,2]. We selected this system in view of the fact that it is used successfully for formulating non-cyanide, autocatalytic electroless gold plating baths yielding good bath stability and deposit properties [10–12].

The composition and operating conditions of the bath optimized for obtaining gold deposits with the lowest possible hardness are shown in Table 1. Because the aim of developing this bath was to apply it to the fabrication of gold microbumps to be used for attaching IC chips to

Table 1
Compositions and operating conditions of thiosulfate–sulfite electroplating baths and Vickers hardness values of gold deposits obtained [1]

Reagent	Without Tl^+		With Tl^+
	Bath A	Bath B	Bath C
$NaAuCl_4 \cdot 2H_2O$	0.06 M	0.06 M	0.06 M
Na_2SO_3	0.42 M	1.1–1.4 M	0.42 M
$Na_2S_2O_3$	0.42 M	1.1–1.4 M	0.42 M
Na_2HPO_4	0.30 M	0.30 M	0.30 M
Tl^+ (added as Tl_2SO_4)	0	0	5 ppm
pH	6.0	6.0	6.0
Temperature	60 °C	60 °C	60 °C
Current density	5 mA cm^{-2}	5 mA cm^{-2}	5 mA cm^{-2}
Rotation speed (Disk electrode)	500 rpm	500 rpm	500 rpm
Hardness (kg mm^{-2})			
As deposited	112	87–88	88
After annealing at 350 °C for 30 min	100	45–60	52

(Bath A, low ligand concentration; Bath B, high ligand concentration; Bath C, low ligand concentration with Tl^+ addition).

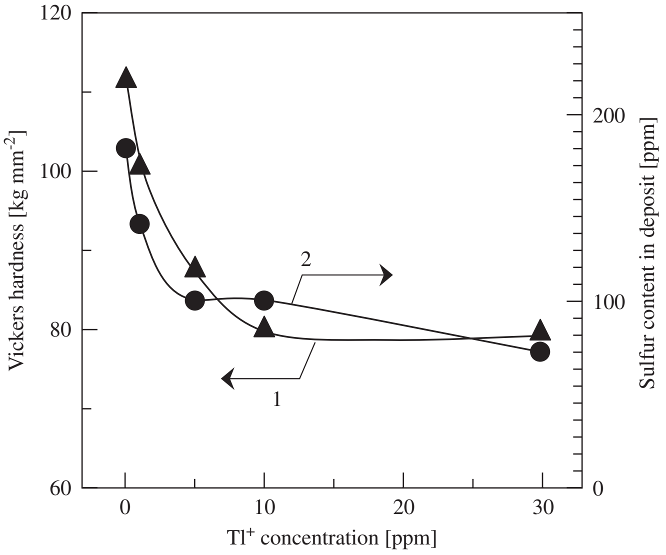

Fig. 1. Effects of thallium ion concentration on hardness (curve 1) and sulfur content (curve 2) of gold deposits obtained in thiosulfate–sulfite electroplating bath [1]. (For concentrations of other bath constituents and operating conditions, see Table 1.)

as low as possible. Our investigation revealed that two approaches, besides annealing, are effective for achieving this purpose. The first approach is to add Tl^+ ions at a concentration as small as 5 ppm to the bath. This method was found to decrease the deposit hardness from 112 to 88 kg mm^{-2} in Vickers hardness (compare Bath A and Bath C in Table 1). For the conventional cyanide bath, Tl^+ is known as a grain refiner. Fig. 1 demonstrates the effect of thallium concentration on the hardness of the gold deposit formed in the thiosulfate–sulfite bath [1]. The second approach we found effective for decreasing the hardness is to increase the thiosulfate concentration. The result shown in Fig. 2 was obtained by varying the total concentration of thiosulfate and sulfite, while the concentration ratio of the two ions was kept equal to unity. Hence, the thiosulfate concentrations were equal to one half of the values of total ligand concentration shown on the horizontal axis. In a separate experiment in which the thiosulfate concentration was varied independently from the sulfite concentration, the observed decrease in hardness was shown to be due to the increase in thiosulfate concentration [2].

We carried out a detailed study for understanding the reason why the deposit hardness is affected by the two variables of bath composition described above. It was found that the observed decrease in hardness closely parallels the decrease in sulfur content of the deposit. The sulfur content is also plotted in Figs. 1 and 2. Our study also showed that the origin of the included sulfur is primarily the adsorbed Au(I) thiosulfate species in the form of $(AuS_2O_3)_{ads}$ formed as an intermediate in the gold deposition reaction from $[Au(S_2O_3)_2]^{3-}$ present in the bath [2].

To demonstrate the practical usefulness of the thiosulfate-sulfite bath, approximately 30-μm-thick bumps mea-

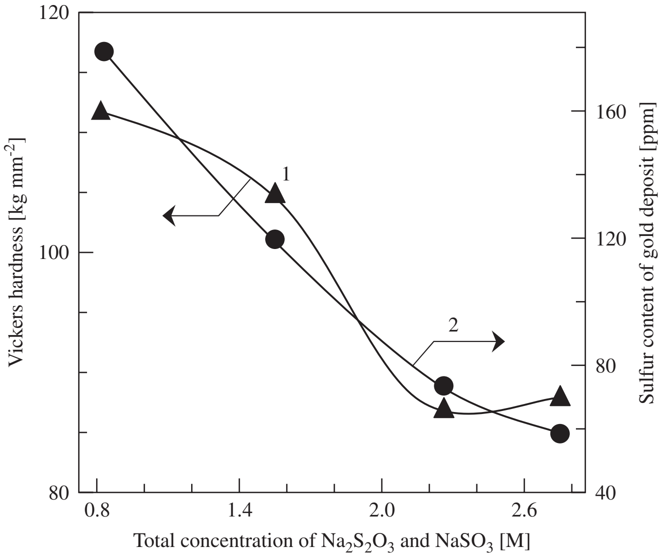

Fig. 2. Effect of total ligand concentration on hardness (curve 1) and sulfur content (curve 2) of gold deposits obtained in thiosulfate–sulfite electroplating bath [1]. ($[Na_2S_2O_3]$:$[Na_2SO_3] = 1{:}1$). (For concentrations of other bath constituents and operating conditions, see Table 1.)

metallized with evaporated thin layers of Al/Ti/W/Au. The bump patterning was carried out using a conventional photoresist. A scanning electron microscopy (SEM) examination of the bumps after removal of the photoresist proved that there was no extraneous gold deposition and that sidewalls of the bumps were straight, indicating that the photoresist withstood without degradation during the

3. Substrate-catalyzed electroless (SCEL) plating of soft gold

Three fundamentally different electroless gold plating processes are known: (1) galvanic displacement process, (2) autocatalytic process, and (3) substrate-catalyzed (SCEL) process. We found that the SCEL process is advantageous over the galvanic displacement process in that the deposit obtained by the former method is significantly less porous than that produced by the latter. [3,4] Compared to the autocatalytic bath, the SCEL bath is more stable and less susceptible to spontaneous decomposition, although the maximum gold thickness obtainable with the latter bath is limited. In spite of these advantages, the SCEL process had been studied to a much lesser extent than the other two types of electroless methods. Our investigation of the SCEL processes described below was initiated under these circumstances.

3.1. *Cyanide bath*

The original SCEL bath described by Iacovangelo and Zarnoch [3] contained $KAu(CN)_2$, KCN, KOH, and K_2CO_3 with hydrazine as the reducing agent (Table 2). Using this original bath, we investigated effects of the composition and the pretreatment procedure of various electroless nickel substrates on the uniformity and adherence of the gold deposits produced. The reason why electroless nickel substrates were chosen for this study was that they are most commonly used as the barrier material to prevent diffusion of copper atoms from the underlying copper substrate through the gold film.

3.1.1. *Ni–B vs. Ni–P as substrate*

The SCEL gold deposited on electroless Ni–B (5.4 wt% B) substrate was found to be invariably adherent and uniform in appearance, whereas the same deposit formed on electroless Ni–P (various P contents) was non-adherent and non-uniform regardless of the P content. The only exception was the low P-content substrate pretreated with a specific solution described in the subsequent section. Fig. 3 compares SEM photographs of SCEL gold plated for various lengths of time on electroless Ni–B (5.4 wt% B) and Ni–P (15.4 wt% P) substrates, both pretreated with 10 vol% HCl. On the Ni–B substrate, numerous crystals of uniform sizes were observed after the initial plating period of only 5 s (Fig. 3–a-1), and after 30 s the substrate was covered uniformly and completely with fine gold crystals (Fig. 3-a-2 and a-3). On the other hand, only a small number of gold crystals were observed on the Ni–P substrate even after 30 s (Fig. 3-b-1). The photograph of Fig. 3-b-2 was taken after 3 min of deposition time, which shows that the crystals observed at 30 s grew in size, while the number density of crystals remained essentially unchanged between 30 s and 3 min, indicating that no further nucleation took place during that period. Fig. 3-b-3, taken after 5 min, shows that the crystals grew further in size and coalesced to form agglomerates. These results indicate that the uniformity and adherence of the gold deposits are related to the density of gold nuclei produced at the initial stages of gold deposition.

Table 2
Composition and operating conditions of cyanide-based substrate-catalyzed electroless gold plating bath [3]

Reagent	Concentration ($mol\,dm^{-3}$)
K_2CO_3	0.75
KOH	0.87
KCN	0.01
$Kau(CN)_2$	0.017
$N_2H_4 \cdot H_2O$	0.50
Agitation	Magnetic stirrer

3.1.2. *Improving the uniformity and adherence of gold deposit on Ni–P*

Because of the significantly better uniformity and adherence of the gold deposited on Ni–B, this material would be preferred to Ni–P as the substrate for gold deposition from the SCEL bath. However, electroless Ni–P is considered more desirable than Ni–B for practical reasons such as the better bath stability, the greater ease of process control, and the lower cost. Therefore, a series of investigations were carried out to find out whether the uniformity and adherence of gold deposits formed on electroless Ni–P can be improved.

To investigate the effect of phosphorus content, Ni–P deposits with high, medium, and low P contents were prepared by varying bath pH [13]. These substrates were subjected to pretreatment with either one of the two solutions: (a) 10 vol% HCl or (b) a mixture of 0.1 M NH_4F and 0.1 M sodium sulfamate (designated as FS mixture) [4]. The FS treatment was performed by immersion in the above mixture for 15 s at 70 °C. Non-adherent, non-uniform deposits were obtained on both high (15.4 wt%) and medium (10.5 wt%) phosphorus content substrates regardless of which solution was used for pretreatment, whereas an adherent and uniform gold deposit was obtained successfully on the low phosphorus content Ni–P (4.7 wt% P) provided that it was pretreated by the FS mixture. Fig. 4 illustrates the effect of P content of electroless Ni–P substrates pretreated with the FS mixture on the morphology of gold deposits produced after various deposition times. It is seen that the nucleation density is much greater on the low P (4.7 wt% P) substrate (Fig. 4-a-1 to a-3) than on the high P (15.4 wt% P) substrate (Fig. 4-b-1 to b-3). On the latter substrate, the nuclei scattered on the surface grew in size with time, but even after 5 min, the coverage was incomplete.

Both HCl and FS pretreatment methods are considered to remove passive oxide films on the surface of Ni–P. It was surprising that the substrate-catalyzed method did not

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