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.

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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 electropating 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 submicron- 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 or even smaller than the grain size in nano-devices of the 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 escapes 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 circuit packages, the hardness of the gold was desired to be...
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 B 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 (AuS₂O₃)₅ads formed as an intermediate in the gold deposition reaction from [Au(S₂O₃)₂]³⁻ present in the bath [2].

To demonstrate the practical usefulness of the thiosulfate–sulfite bath, approximately 30-μm-thick bumps measuring 50 × 50 μm were formed on a silicon wafer 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 gold deposition process [2].

![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.)](image1)

![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]. (For concentrations of other bath constituents and operating conditions, see Table 1.)](image2)

### Table 1

| Reagent                  | Without Tl⁺ | With Tl⁺ |
|-------------------------|-------------|----------|
| NaAuCl₂·2H₂O            | 0.06 M      | 0.06 M   |
| Na₂SO₃                  | 0.42 M      | 1.1–1.4 M|
| Na₂S₂O₃                 | 0.42 M      | 1.1–1.4 M|
| Na₂HPO₄                 | 0.30 M      | 0.30 M   |
| Tl⁺ (added as Tl₂SO₄)   | 0           | 0        |
| pH                      | 6.0         | 6.0      |
| Temperature             | 60 °C       | 60 °C    |
| Current density         | 5 mA cm⁻²   | 5 mA cm⁻²|
| Rotation speed (Disk electrode) | 500 rpm  | 500 rpm  |

| Hardness (kg mm⁻²)      | As deposited | After annealing at 350 °C for 30 min 100 | 45–60 | 52 |
|-------------------------|--------------|----------------------------------------|-------|----|
| Vickers hardness         | 112          | 87–88                                  | 88    |
| Sulfur content in deposit | 160          | 120                                    | 80    |

(Bath A, low ligand concentration; Bath B, high ligand concentration; Bath C, low ligand concentration with Tl⁺ addition).
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$_2$CO$_3$ 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.

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$_4$F 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%) 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%) substrate (Fig. 4-a-1 to a-3) than on the high P (15.4 wt%) 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 yield acceptable gold deposits on the Ni–P substrates with
high and medium P contents even after these pretreatment processes. Apparently, the passive oxide film naturally formed on the high and medium P-content Ni–P substrates was so highly inert that even the FS treatment was ineffective for its removal, whereas the pretreatment easily attacked the passive film on the low-P-content substrate. It was thus concluded that if electroless Ni–P is to be used instead of Ni–B as the substrate to plate gold using the cyanide-based SCEL bath, a low-P-content substrate must be chosen and its surface treated with a suitable activator such as the FS mixture.

3.2. Non-cyanide bath

In spite of the advantages described above, the presence of a high concentration of free cyanide and the high alkalinity of the cyanide SCEL bath are undesirable for the reasons mentioned already. Thus, we attempted to formulate a non-cyanide [5,6] SCEL bath containing thiosulfate and sulfite as ligands for Au(I).

The composition and operating conditions of the non-cyanide SCEL bath are listed in Table 3, which are similar to those of the autocatalytic bath containing the same ligands [10] except that the reducing agent (ascorbic acid) was excluded. For bath makeup, the commonly available trivalent gold salt, NaAuCl₄, is used, but the Au(III) in this salt is reduced immediately to Au(I) upon addition of Na₂SO₃, forming Au(I) sulfite complex. This complex is converted to Au(I) thiosulfate complex and/or Au(I) thiosulfate–sulfite mixed ligand complex ([Au(S₂O₃)(SO₃)]₃⁻) upon addition of Na₂S₂O₃ because of the greater stability of those complexes than the sulfite complex.[11,12] We have shown by electrochemical polarization measurements [6] that in this SCEL system, sulfite ions serve as the reducing agent. The composition of the galvanic displacement bath used for comparison is shown in Table 4.

3.2.1. Identification of the mechanism of gold deposition

Fig. 5 compares the two substrates, electroless Ni–B film and pure gold sheet, for the variation of gold deposit thickness with plating time in the non-cyanide SCEL bath. Gold deposition took place only on Ni–B and not on the gold sheet. This result clearly shows that the gold deposition reaction is not autocatalytic. To find out whether galvanic displacement is involved in the gold deposition on Ni–B, the concentration of dissolved nickel ions was determined after immersion of the substrate in 100 mL of the bath for 60 min. It was found to be 0.99 ppm, which is equivalent to 0.04 μm in gold thickness, whereas
the actual gold thickness measured was as large as 0.21 μm. Thus, the galvanic displacement reaction accounted for approximately 19% of the total deposit thickness, and there was another mechanism by which the remaining 81% of the gold was deposited. This mechanism is accounted for by the substrate-catalyzed reaction. Fig. 6 compares the calculated and actual gold thicknesses of the deposit formed in the bath of Table 3 and those of the deposit produced in the galvanic displacement bath of Table 4. It is seen that for the latter bath, the gold thickness calculated from the amount of dissolved nickel agrees well with the actually determined thickness as expected.

For practical applications, it is important to ascertain that the process produces gold deposits with acceptable appearance, uniformity, adherence, and low or preferably no porosity. Also from the practical standpoint, it is desirable to understand effects of various variables such as bath composition and substrates on the above attributes.

We conducted a systematic study of those effects with substrates of not only electroless Ni–B film but also electroless Ni–P films with high and low P contents.

### 3.2.2. Gold deposits formed on Ni–B

As mentioned in Section 3.1, the cyanide-based SCEL bath always yielded adherent and uniform gold deposits on the Ni–B substrate pretreated by simple immersion in 10 vol% HCl. In contrast, the non-cyanide, thiosulfate–sulfite bath with the standard composition shown in

![Fig. 4. SEM images of gold deposits formed in cyanide-based substrate-catalyzed bath on low- and high-P-content Ni–P substrates: (a) Ni–P (4.7 wt% P) and (b) Ni–P (15.4 wt% P) pretreated with FS mixture. Plating time: (a-1) 5 s, (a-2) 30 s, and (a-3) 3 min; (b-1) 30 s, (b-2) 3 min, and (b-3) 5 min [4].](image-url)
Table 3 yielded gold deposits with non-uniform appearance on Ni–B. For the cyanide-based system, the substrate pretreatment in the FS mixture at 70 °C was highly effective for producing gold deposits with uniform and bright appearance, as described in the preceding section. For the non-cyanide SCEL system, this pretreatment procedure was found to be only slightly more effective than the HCl treatment for improving the deposit uniformity. Unlike the case of the low P content Ni–P substrate described in the subsequent section, the pretreatment with 0.1 M Na₂SO₃ did not improve the uniformity of the deposit produced on the Ni–B substrate. To learn whether the deposit uniformity can be improved by manipulating the bath composition, effects of thiosulfate and sulfite concentrations were investigated. The results are illustrated in Fig. 7. In this series of experiments, the Ni–B substrates were pretreated only by room-temperature immersion in 10 vol% HCl. The deposit uniformity clearly improved as the thiosulfate concentration was decreased from 0.08 to 0.01 M at all three sulfite concentrations of 0.08, 0.16, and 0.32 M. This observation points to the speculation that thiosulfate is responsible for the deposit non-uniformity observed more prominently at the higher thiosulfate concentrations. In an attempt to clarify the cause of the observed non-uniformity, Auger electron spectroscopy (AES) was performed on a specimen with a non-uniform gold film deposited on Ni–B [4]. The AES analysis of the Ni–B surface exposed after peeling off the gold film from a blistered area showed the presence of S in addition to O and C, whereas the AES depth profile of an adherent portion of the gold film did not reveal the presence of S. These AES results appear to indicate that the localized presence of an S-containing species is responsible for the loss of adherence of the gold film to the Ni–B substrate.

3.2.3. Gold deposits formed on Ni–P

As was the case with the cyanide-based system [4], it was not possible to produce an adherent and uniform gold deposit on the high P content (15.4 wt% P) Ni–P substrate. The introduction of a pretreatment procedure using either 10 vol% HCl, the FS mixture, or 0.1 M Na₂SO₃, did not help improve the deposit characteristics. Modification of the bath composition did not result in any improvement. The reason for this behavior of the high P content Ni–P is believed to be the presence of a highly stable, tenacious passive oxide film and the inability of the simple pretreatment procedures to remove such a film.

In contrast to the high P content Ni–P, the low P content (4.7 wt% P) Ni–P substrate pretreated with 0.1 M Na₂SO₃ yielded a very uniform, adherent gold film at the thiosulfate concentration of 0.01 M. Even when the thiosulfate concentration was increased to the level of the basic bath (0.08 M), the deposit uniformity was good. Fig. 8 shows the variation of gold thickness with deposition time at three different thiosulfate concentrations. Concentrations of other bath constituents and bath operating conditions were the same as those for the basic bath (Table 3). It is seen that the gold thickness reaches a maximum constant value after approximately 60 min of plating at all thiosulfate concentrations used, and that the maximum thickness value increases with increasing thiosulfate concentration. A similar dependence of the maximum gold thickness on ligand concentration is known for the cyanide-based system [3,4]. The photographs pasted in the large squares on both sides of the graph in Fig. 8 show the appearance of the specimens tested for porosity. The dark spots and areas in each specimen show the presence of colored Ni-dimethylglyoxime complex formed in the test from exposed Ni metal through the pores in the gold film. The actual color of these spots and areas was pink. The three
photographs on the right side of the figure represent specimens obtained after 60 min of deposition time at the three different thiosulfate concentrations. Remarkably, an essentially pore-free gold film was obtained at the thickness measuring only 0.05 μm when the thiosulfate concentration was 0.01 M. As the thiosulfate concentration was increased, the maximum gold thickness increased to 0.28 μm at 0.24 M; nevertheless, the porosity also increased dramatically. The three specimens shown on the left side of Fig. 8 were obtained at the deposition time of 30 min. At 0.24 M thiosulfate, the specimen obtained at 30 min was more porous than that obtained after 60 min. Comparison of the 30 min specimen prepared at 0.24 M thiosulfate with the ones made after 30 or 60 min at 0.08 M thiosulfate (specimens in the middle of both the right and the left rows) clearly shows that, despite the identical gold thickness of all three specimens, the film produced at the higher thiosulfate concentration was significantly more porous.

To understand the mechanism determining the dependence of the maximum gold thickness and porosity on thiosulfate concentration, surface morphology was examined using SEM for gold deposits produced at different deposition times in baths containing various thiosulfate concentrations. The SEM images obtained are shown in Fig. 9. Comparison of the three images obtained at 5 s shows clearly that the initial deposit formed in the 0.01 M thiosulfate bath consisted of more densely packed, smaller crystals than did the deposits formed in the 0.08 and 0.24 M baths. This effect of thiosulfate concentration became more evident as the gold deposition progressed with time. In 30 s, the size of individual gold crystals increased, but it is seen that at higher thiosulfate concentrations, the larger areas of the substrate still remained uncovered by gold crystals. The images taken at 3 min reveal that the size of individual gold crystals was largest for the deposit produced at the highest thiosulfate concentration. It is apparent that the observed effects of thiosulfate concentration on both the maximum thickness obtainable and the porosity are closely related to its effect on deposit morphology. The maximum thickness of the gold film deposited in a bath containing a high concentration of thiosulfate is large, but the film consists of large...
crystals or agglomerates of crystals which are loosely packed with a large total area of substrate still exposed. On the other hand, the thin gold film produced at a low thiosulfate concentration consisted of closely packed fine crystals covering the substrate surface effectively.

The results described above indicate that, to produce a gold film with low or no porosity, the thiosulfate concentration should be made as low as practical to meet the thickness requirement for the specific application, and a sufficient time should be allowed for the film to grow to the desired thickness.
4. Electroplating of amorphous gold alloys

Electroplated hard gold is the most commonly used contact material for high reliability electrical connectors, electromechanical relays, and printed circuit boards [14]. It is polycrystalline in microstructure with its grain size in the range of 20–30 nm, and its hardness is as high as 170–200 kg mm⁻² in Knoop hardness compared to 50–80 kg mm⁻² for pure, soft gold [15]. The detailed study of the hardening mechanism of the hard gold performed by Lo et al. [16] shows that the major factor determining the hardness is the grain size. These authors found that the well-known Hall–Petch equation, relating hardness linearly with \( d^{-1/2} \) (where \( d \) is the grain diameter), holds for the electroplated hard gold containing Co as the hardening agent (hereafter called cobalt-hardened gold, CoHG). Holmbom et al. [17] reported that the Hall–Petch relation holds also for nickel-hardened gold (NiHG). However, for both CoHG and NiHG, the published data indicate that the hardness tends to decrease as the grain diameter is made smaller than about 15–20 nm. A similar deviation from the Hall–Petch relation in the range of very small grain diameters was investigated in great detail for the case of electroplated Ni–P deposit by Rofagha and Erb [18]. With the recent advances in the fabrication technology of submicro- and nano-scale electronic devices, dimensions of electrical contact areas in such devices will soon approach the grain size of the hard gold. In the dimensional range of nanometers, the hardness of the hard gold is expected to decrease with decreasing size of the contact area. This dependence of the hardness of contact material on the size of contact area, which is unique to nano-scale devices, is undesirable because of the adverse effect of decreased hardness on wear resistance of the contact material. One approach to avoiding this problem would be to use an amorphous gold or gold alloy in place of the microcrystalline hard gold, because the hardness of amorphous materials with no crystal grains is, in general, known to be independent of the size, or physical dimensions, of the materials. Thus, an amorphous gold or gold alloy should be of interest for possible applications as a contact material on submicro- and nano-scale devices.

We have successfully developed a new process for electroplating amorphous gold–nickel alloy by using a bath prepared by adding a gold salt into a known plating bath that produces amorphous nickel–tungsten alloy [7]. The bath composition and plating conditions are listed in Table 5. To this bath, KAu(CN)₂ was added as the source of gold. Results of characterization of the amorphous gold alloy obtained are summarized below.

### Table 5

| Reagent                      | Concentration (mol dm⁻³) |
|------------------------------|--------------------------|
| NiSO₄·6H₂O                   | 0.076                    |
| Na₂WO₄·2H₂O                 | 0.182                    |
| Citric acid                 | 0.258                    |
| pH (adjusted with NH₄OH)    | 6.0                      |
| Agitation                   | None                     |
| Temperature                 | 70 °C                    |
| Current density             | 150 mA cm⁻²              |

Fig. 10. Effect of KAu(CN)₂ concentration on the composition of Au–Ni–W film [8].

4.1. Effect of the addition of KAu(CN)₂ in the Ni–W bath

Various amounts of KAu(CN)₂ were added into the amorphous Ni–W bath (Table 5), and an approximately 5 μm thick film deposited from each bath was analyzed for Ni, W, and Au. The analytical results obtained are plotted in Fig. 10. It is seen that the gold content of the deposit increased with increasing concentration of gold in the bath, and the gold content reached 50.5 at% at the KAu(CN)₂ concentration of 10 g L⁻¹. In contrast, the tungsten content decreased with increasing concentration of the gold salt, and essentially no tungsten was found in the deposit at KAu(CN)₂ concentrations higher than 5 g L⁻¹.

Fig. 11 shows XRD patterns of the films obtained from the baths containing various amounts of KAu(CN)₂. The concentration of the gold salt was varied from 0.1 to 15 g L⁻¹. The solutions became unstable when the concentration of the gold salt exceeded the latter value. This figure shows evidence for the formation of a metastable phase when 1.0 g L⁻¹ of KAu(CN)₂ was added. The peak location of this metastable phase is 41.5°. It is also seen that the position of diffraction peak shifted toward lower 2θ values with increasing KAu(CN)₂ concentration beyond 1.0 g L⁻¹. Here, it is important to note that the shape of the
diffraction pattern was broad when the concentration of the gold salt was 5.0 and 10 g L$^{-1}$. These results suggest that the gold alloy films obtained at these two concentrations are amorphous at least to the XRD analysis. To obtain a proof for the amorphous nature at a higher resolution, TEM analysis was performed on the film obtained from the bath containing 10 g L$^{-1}$ of KAu(CN)$_2$. Fig. 12 shows TEM images and the corresponding transmission high-energy electron diffraction (THEED) patterns of the gold–nickel alloy film (a) and a hard-gold film containing cobalt as the hardening agent (b). The conventional hard gold is known to consist of fine crystals, which has been confirmed by the TEM image and THEED pattern shown in Fig. 12b. In contrast, the TEM image and the THEED pattern in Fig. 12a show conclusively that the gold–nickel alloy film examined here was amorphous.

4.2. Physical properties of amorphous gold–nickel alloy film

Properties of the amorphous Au–Ni alloy film were evaluated from the standpoint of its application as an electrical contact material. Fig. 13 summarizes the results of Knoop hardness measurements performed on the amorphous Au–Ni alloy film, three different kinds of conventional hard gold (additive-free hard gold (AFHG), NiHG, and CoHG), and pure soft gold. The gold contents of the various gold deposits are included in the figure for comparison. Each sample was subjected to hardness measurements at five different locations, and the average value of the five measurements is shown for each sample. The average Knoop hardness of the amorphous Au–Ni alloy film was 464 kg mm$^{-2}$, which is more than twice as high as that of the hard-gold deposits ranging from 160 to

Fig. 11. XRD patterns of plated films obtained from the baths prepared by adding various amounts of KAu(CN)$_2$ in amorphous Ni–W bath [8].

Fig. 12. TEM images and THEED patterns of (a) gold alloy film obtained from the Ni–W bath containing 10 g L$^{-1}$ KAu(CN)$_2$, and (b) conventional cobalt-hardened gold [8].
184 kg mm\(^{-2}\). Although it is known that hardness is not the only factor controlling wear resistance of a material, high hardness is believed to be one factor contributing to achieving good wear resistance. Table 6 compares the amorphous Au–Ni alloy with the conventional CoHG for resistivity and contact resistance. The resistivity measurement was carried out with gold films plated on silicon substrates sputter-coated with a 20-nm-thick layer of Ta and a 150-nm-thick Cu layer. The thickness of the films was 5 μm. The resistivity of the amorphous Au–Ni alloy film was found to be significantly higher than that of CoHG. It is known that quite generally, the resistivity of amorphous materials is higher than that of crystalline materials with identical compositions, because the lack of long-range periodicity in atomic arrangement in amorphous materials causes the scattering of conducting electrons. Amorphous alloys in general are known to possess the following characteristics of resistivity [19,20]: (i) the resistivity value is generally in the range of 50–350 μΩ cm at 300 K; (ii) the resistivity is 10–100 times as high as that of crystalline materials. Thus, the measured resistivity value of the amorphous Au–Ni alloy film is considered reasonable. However, the high resistivity may present a problem in certain applications, and this aspect requires a further study. The contact resistance was measured on films with a thickness of 0.2 μm. The contact resistance found on the amorphous Au–Ni alloy film was as low as that on CoHG. Apparently, the surface oxidation of Ni in the amorphous Au–Ni alloy does not present a problem as far as contact resistance is concerned.

### 4.3. Amorphous Au–Co alloy film

Based on the same principle as was used for the amorphous Au–Ni alloy, we formulated a bath to electroplate Au–Co alloy film. The composition of the amorphous Co–W bath used as the starting solution was identical to that of the amorphous Ni–W alloy bath (Table 5), except that NiSO\(_4\)·6H\(_2\)O was replaced by CoSO\(_4\)·7H\(_2\)O. As in the case of the Au–Ni–W system, the gold content of the Au–Co deposit obtained increased with increasing gold concentration in the bath, and it reached 38.0 at% at the KAu(CN)\(_2\) concentration of 10 g L\(^{-1}\). All XRD peaks for the films plated in the Au–Co–W bath containing KAu(CN)\(_2\) at concentrations ranging from 1 to 10 g L\(^{-1}\) were broad, indicating the amorphous nature of the films. The deposits obtained at a current density greater than 5 mA cm\(^{-2}\) were all amorphous to XRD, and they contained essentially no W, as in the case of the Au–Ni–W system.

Further details of the electroplating of amorphous Au–Co alloy will appear in the paper to be published shortly from this laboratory [9].

### 5. Summary

A review was presented of our contributions to the development of new processes to electroplate and electroless plate pure soft gold and amorphous hard-gold alloys. Three different topics were covered. The first topic was concerned with a new non-cyanide, electrolytic soft-gold plating bath containing both thiosulfate and sulfite as
ligands for Au(I). This bath is recommended in place of the commonly available sulfite bath because of the advantage of the greater stability without the necessity of adding a stabilizer. The second topic discussed was the SCEL plating of soft gold, as distinguished from the more common, galvanic displacement and autocatalytic processes. The bath we developed also contained thiosulfate and sulfite as ligands, but no conventional reducing agent. It was shown that in this system, sulfite serves also as the reducing agent. This new bath is recommended because of two significant advantages: (1) the gold deposit obtained can be much less porous than that produced by galvanic displacement, and (2) the substrate-catalyzed bath is much more stable than autocatalytic baths. With a proper choice of bath composition, plating conditions, and substrate pretreatment procedure, the new bath can produce pore-free gold films at a thickness as small as 0.05 μm. The third topic covered was the development of electroplating baths producing amorphous hard-gold alloys. The approach taken to achieve the successful development of these baths is based on the addition of a gold salt to baths that are known to produce amorphous alloys such as Ni–W and Co–W. Using this approach, we obtained amorphous Au–Ni and Au–Co alloys containing up to 50–60 at% of Au and no W. These amorphous gold alloys had a hardness value greater than twice that of the conventional hard-gold deposits, while the electrical contact resistance of the amorphous materials was identical to that of the hard gold. The amorphous gold alloys may find useful applications in the future when the area or size of electrical contacts in electronic devices becomes comparable to that of the grain size of the hard gold, 20–30 nm. The amorphous gold alloys may also find applications in areas other than contacts in electronic devices where a high hardness and high wear resistance is required. It should be noted, however, that bulk resistivity of amorphous materials is generally higher than that of crystalline materials with comparable compositions. This aspect may require a further investigation for improvement.

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