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Electrochimica Acta 51 (2005) 882–887

ELECTROCHIMICA Acta

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Preparation and characterization of electroplated amorphous gold–nickel alloy film for electrical contact applications

Norihiro Togasaki[a], Yutaka Okinaka[b], Takayuki Homma[a,b,1], Tetsuya Osaka[a,b,*,1]

[a] *Department of Applied Chemistry, Waseda University, Okubo, Shinjuku, Tokyo 169-8555, Japan*
[b] *Advanced Research Institute for Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo 169-8555, Japan*

Received 22 October 2004; received in revised form 21 February 2005; accepted 15 April 2005

Abstract

A process for electroplating amorphous gold–nickel alloy with the atomic ratio of unity was developed. The plating bath was prepared by adding potassium cyanoaurate(I) into a known plating bath which produces amorphous nickel-tungsten alloy. At a sufficiently high gold concentration, the alloy deposit did not contain any tungsten. The amorphous nature of the Au–Ni alloy produced in the new bath was confirmed by using TEM and THEED. Hardness, resistivity, and contact resistance of this new alloy were determined, and the results are discussed for applications as an electrical contact material.

Keywords: Amorphous gold–nickel alloy; Nickel–tungsten alloy; Hardness; Resistivity; Contact resistance

1. Introduction

Electroplated hard gold is the most commonly used contact material for high reliability electrical connectors, miniature electromechanical relays, and printed circuit boards. 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 [1]. The detailed study of the hardening mechanism of the hard gold performed by Lo et al. [2] 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. [3] 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 [4].

With the recent advances in the fabrication technology of micro- and nano-scale electronic devices, it is expected that dimensions of electrical contact areas in such devices will soon approach, and may even become smaller than, 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 unique dependence of the hardness of contact material on the size of contact area is, of course, undesirable because of the adverse effect of decreased hardness on wear resistance of the contact material. One approach to avoid 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 micro- and nano-scale devices, provided that its physical properties meet the require-

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[*] Corresponding author. Tel.: +81 3 5286 3202; fax: +81 3 3205 2074.
E-mail address: osakatet@waseda.jp (T. Osaka).
[1] ISE member.

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doi:10.1016/j.electacta.2005.04.057

ment for electrical contact applications. However, as far as we are aware, there is no electroplating process available at the present time to produce amorphous gold or gold alloys.

In the present study, we 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. With the addition of a sufficient amount of the gold salt, it was possible to plate gold–nickel amorphous alloy without the incorporation of tungsten. This paper describes details of the plating process and properties of the deposit obtained.

2. Experimental

The amorphous Ni–W alloy plating bath used in this study as the starting bath was that described by Omi et al. [5]. The bath composition and plating conditions are listed in Table 1. To this bath was added either $KAu(CN)_2$ or $Na_3Au(SO_3)_2$. All chemicals used were of reagent grade.

Three different kinds of substrate were used: a copper plate (10 mm × 30 mm × 0.1 mm, purity: 99.96%), a 2.5 inch hard disc (NiP/Al), and a silicon wafer sputter-coated with a 20 nm thick layer of Ta and a 150 nm thick Cu layer. The copper plate was used as the cathode in the electrochemical polarization experiment. The hard disc substrate was used for resistivity measurements, while the sputtered copper substrate was used to measure contact resistance. An insulating tape was used to expose the active area of copper measuring 10 mm × 10 mm. All substrates were pretreated by successive immersion in a degreasing solution (10% PAC-200, Murata Co.), an etching solution (0.5 M sodium persulphate + 1 mL L^{-1} H_2SO_4), and an activator (10% sulfuric acid).

Electrodeposition and polarization measurements were performed using a computer controlled potentio-galvanostat (Model HZ3000, Hokuto Denko Co.). Polarization measurements were conducted by scanning the potential at the rate of 5 mV s^{-1} using an Ag/AgCl reference electrode. The test solution was deaerated by bubbling pure nitrogen gas for 30 min.

The composition of electroplated films was determined by energy-dispersive spectroscopy (Model JAX-8600, JEOL). Surface morphology of deposits produced was examined by scannig electron microscopy (Model S-3000M, HITACHI). The microstructure of the deposits was investigated by means of both X-ray diffraction (RINT-TTR, RIGAKU) and transmission electron microscopy (H8100A, HITACHI). TEM samples were prepared by the microtome method (EM-SUPER NOVA). The hardness was measured by using a Knoop hardness tester (Model HMV2000, SHIMADZU). Resistivity was measured by the four point-probe technique (Model K502RE150, KYOWA RIKEN). Contact resistance was measured by the four-terminal method (Model CRS-113-AU, YAMAZAKI SEIKI Co.) against a gold wire with 0.5 mm in diameter.

Table 1
Bath composition and plating conditions

Reagents	mol dm^{-3}
$NiSO_4{\cdot}6H_2O$	0.076
$Na_2WO_4{\cdot}2H_2O$	0.182
Citric acid	0.258
pH	6.0 (adjusted with NH_4OH)
Temperature	70 °C
Current density	150 mA cm^{-2}
Agitation	None

3. Results and discussion

3.1. Evaluation of Ni–W alloys

First, we performed XRD measurements to confirm the structure of a Ni–W alloy film electroplated by using the procedure described by Omi et al. [5]. This film was composed of approximately 70 at.% of Ni and 30 at.% of W as determined by EDX. Fig. 1 shows the XRD pattern of the Ni–W alloy film. The XRD pattern of electroplated Ni–P (P: 14.9 wt.%) alloy film is also shown in this figure for comparison. The thickness of both films was 5 μm. The structure of Ni–P film with the above composition was reported to be amorphous [6]. The diffraction pattern obtained with the Ni–W alloy film shows a single broad peak at $2\theta = 44°$, and it is similar in shape to the XRD of the Ni–P alloy. Thus, it appeared that the Ni–W alloy we prepared also had an amorphous structure to the XRD analysis. Fig. 2 shows an SEM image of the Ni–W alloy film. Elemental mapping across the deposit surface as well as in the cross-sectional direction confirmed that both Ni and W were distributed uniformly on the surface as well as within the film.

3.2. Selection of a gold salt

In selecting a suitable gold salt to be added in the amorphous Ni–W bath, cathodic polarization measurements were

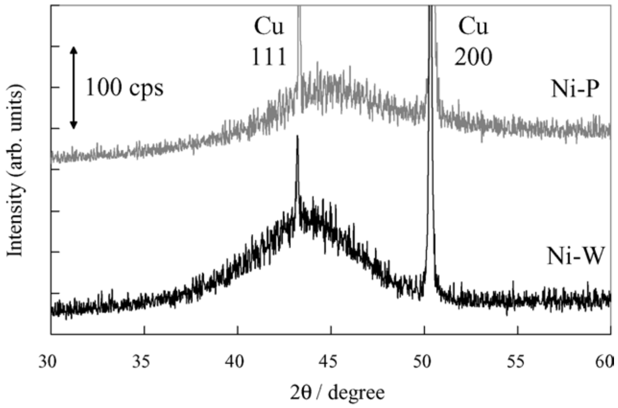

Fig. 1. XRD patterns of Ni–W and Ni–P alloy films (Cu peaks are from the substrate.).