ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 4. 2004

The Electrodeposition Conditions of Functional Gold Films for Microelectronics

Oksana BERSIROVA[*], **Valery KUBLANOVSKY**

Vernadskii Institute of General and Inorganic Chemistry, 32-34 Palladin prosp., 03680 Kyiv 142, Ukraine

Received 31 August 2004; accepted 08 October 2004

The morphology and physico-mechanical properties of electrodeposited gold films have been studied. The electrodeposition was performed in the phosphoric bath. The formulation and deposition condition were following: 0.05M $KAu(CN)_2$ + 0.25M $(NH_4)H_2HPO_4$ + 0.40M $(NH_4)_2HHPO_4$ without and with additives of surfactants, namely 10 mg l^{-1} oxyethylendiphosphoric acid (H_4OEtDP) + 0.75 mg l^{-1} cyanethilendiamine (CyEn), at pH 5.6, 60 – 70 °C and current density 0.2 – 0.6 A dm^{-2}. The morphology of obtained films was studied by means of SEM, and texture of obtained films on a brass substrate was studied by means of X-ray diffractometry. The gold films consist of crystallites which size varies 0.8 to 1.6 µm. Correlation between texture and mechanical stresses in the deposits is discussed.

The physico-mechanical properties (internal stress, porosity, microhardness) of gold coatings electrodeposited from the phosphoric acid bath on the brass substrate depend on current densities and strongly correlate with their morphology.

The adding of H_4OEtDP and CyEn into phosphoric gilding bath enables to obtain the gold films possessing reasonable properties for the microelectronics application in wider range of current densities (up to 0.6 A dm^{-2}).

Keywords: gold films, electrodeposition, morphology, texture, additives, microhardness, porosity.

INTRODUCTION

In modern technologies the electroplating processes are still used widely for the interconnectors fabrication. The gilding being used in the electronic industry can be broadly classified into soft gold and hard gold [1]. Soft gold is used as a surface finishing for bonding gold or aluminum wires in the conventional method of mounting semiconductor devices on a circuit board. In more recent years, with the advent of the so-called surface mount technology; the wire bonding has been replaced by the direct bonding of microbumps fabricated on the silicon wafers by the electroplating of soft gold. Since the bonding of a large number of bumps is involved for each chip, the uniformity of the bumps geometry is importance. Obtained gold must be sufficiently soft so that the bumps are easily deformable to accommodate small variation in thickness. Photolithography is employed to delineate patterns for the formation of bumps. However, cyanide-ions presenting in conventional conventional soft gold plating baths are able to rip up photo resists. Therefore, baths not containing at least free cyanide-ions must be used for this purpose.

The conventional cyanide bath for electroplating soft gold has been extensively studied in the past, and a considerable volume of information about occurring processes, properties of electroplated films, and their microstructure is published, e.g. [1 – 6]. The acquired knowledge about the cyanide systems has been applied to a great extent to the recent development of non-cyanide systems [7 – 13]. The various types of gold electroplating baths were developed: sulfite [14 – 17], tiosulfate [18], tiosulfate-sulfite [19].

Also, the gilding baths where $KAu(CN)_2$ is a source of Au, but not-containing "free cyanides" have advantages over cyanide baths and are perspective from the practical point of view [20]. Since the phosphoric buffer is used to maintain a required pH value, such type of baths often is called as "phosphoric bath". More theoretical and practical aspects related with this type of gold electroplating baths were studied recently such as: the conditions for gold coatings deposition on different substrates, which are utilized in the manufacture of integrated-circuit packages [21 – 26]; the ionic composition of a phosphoric acid gilding electrolyte in the bulk of solutions as well as in the pre-cathode layer has been numerically calculated in terms of the Nernst diffusion model [23]. Also, the kinetics and mechanism of the cathodic reduction of gold has been studied by different stationary and nonstationary methods, and transfer coefficients, exchange currents and diffusion coefficients at different temperatures and activation energy on different substrates have been determined [24 – 26].

In general, the physico-mechanical properties of electroplated metals are determined by their microstructure (forms, sizes and orientation crystallites on a substrate) which in one's turn is dependent on physical and chemical conditions of a process (bath composition, electrolysis regime) [7, 10, 27 – 28].

As a continuation of the previous investigations, the aim of the present work is the study of morphology and physico-mechanical properties of gold films electroplated from the phosphoric gilding baths on the brass substrate with and without additive of surfactants at various current densities.

EXPERIMENTAL

The electroplated Au films were obtained from the bath consisting of a mixture: 0.05M $KAu(CN)_2$ + 0.25M $(NH_4)H_2HPO_4$ + 0.40M $(NH_4)_2HHPO_4$ without and with additives of surfactants, namely 10 mg l^{-1} oxyethylendiphosphoric acid (H_4OEtDP) + 0.75 mg l^{-1} cyanethilendiamine (CyEn) at 60 – 70 °C and pH 5.6. The deposition was performed at the cathodic current densities 0.2 to 0.7 A dm^{-2} on the brass substrate using Pt anode. The thickness of deposited gold films was 5 µm. After

---

[*] Corresponding author. Tel.: +380-44-4243311; fax: +380-44-4243070
E-mail address: *bol@ionc.kar.net* (O. Bersirova)

deposition the specimens were degreased with ethanol, washed with distilled water and dried with filter paper.

The morphology of obtained Au films was examined visually as well as by scanning electron microscope (SEM) LEO-435VP.

X-ray diffractometer DRON-3M equipped with a graphite monochromator on reflective beam and CuK_{α} – radiation (λ = 1.54 Å) was employed for structural analysis and internal stress of electroplated gold films. The texture of Au films on the brass substrate was studied using thin X-ray beam sliding at low grazing angles to sample technique [29]. This technique enables to perform structural study in dependence on beam penetration depth and film thickness by changing incidence angle α. The changes of Au films structure were evaluated based upon intensities as a function of beam incidence angle for the most intensive lines corresponding to <111> and <200> orientations:

$$N = \frac{\left(I_{111}/I_{200}\right)_{\exp} - \left(I_{111}/I_{200}\right)_{metallur}}{\left(I_{111}/I_{200}\right)_{metallur}} \qquad (1)$$

where I_{111} and I_{200} are the intensities of lines corresponding to <111> and <200> textures, respectively; index "exp" corresponds to the examined sample, and "metallur" corresponds to the metallurgically prepared sample.

Internal stresses (P) were calculated according to equation [29]:

$$P = \frac{E \cdot \Delta\theta}{\mu \tan\theta_{metallur}} \qquad (2)$$

where $\theta_{metallur}$, $\Delta\theta$ are the Bragg's angle for metallurgical material and shift of angle for examined material, respectively; μ is the Poisson's ratio; E is the modulus of elasticity.

The porosity of the deposited Au films was estimated using the standard procedure which comprise an applying filter paper damped in the solution (g/l): $K_3[Fe(CN)_6]$ – 3; NaCl – 10.

Microhardness was measured using PMT device by the indentation of a square-base diamond pyramid with an apex angle of 136° between the opposite faces under load of p = 50 g.

RESULTS AND DISCUSSIONS

SEM images of Au films deposited at various current densities are shown in Fig. 1. As it is seen, the surface of films obtained at low current densities is inhomogeneous and exhibit coarse-crystalline structure, and proportions of single coarse grains are various (Fig. 1, a). Evidently, this current density is too low to form enough number of nucleation centers and their growing.

The gold coatings obtained at higher current densities are extremely irregular. The crystal size decreases distinctly (Fig. 1, b). In this case, the number of crystallizing nucleus is increasing with the current density increase. The crystals are grown both in normal and tangential direction. However, the growing in direction perpendicular to surface is determined by nearness of neighboring crystals. Therefore, the crystals are grown obliquely to surface and comparatively fine-crystalline structure is obtained.

The intensive hydrogen evolution on the cathode is observed at the current density 0.35 A dm^{-2} or higher. That process leads to peeling off, gold films become porous and poorly adhered to substrate, and film consists on separate spheroids (see Fig. 1, c). The color of coatings is changed. In this case, the size of crystallites of the gold deposits was of 0.8 – 1.6 μm.

Well known, good adhesion between deposited film and substrate is observed if film continues the orientation of substrate or crystallographic regular adaptation takes place. The substrate structure influences a film growing up to of 1 – 3 μm: at first, the growing film reiterates substrate, and then becomes form an own structure defined by the deposition conditions. The transition stripe is placed between these zones.

The textures of electrodeposited gold films are shown in Fig. 2. Orientation of the electroplated at 0.2 A dm^{-2} film layer are similar to the substrate and continues its structure. Therefore, the adhesion between film and substrate increases at lower current densities (0.2 A dm^{-2}). The gold films deposited at higher current densities are easily pilling off from the substrate because the structures of substrate and film are different.

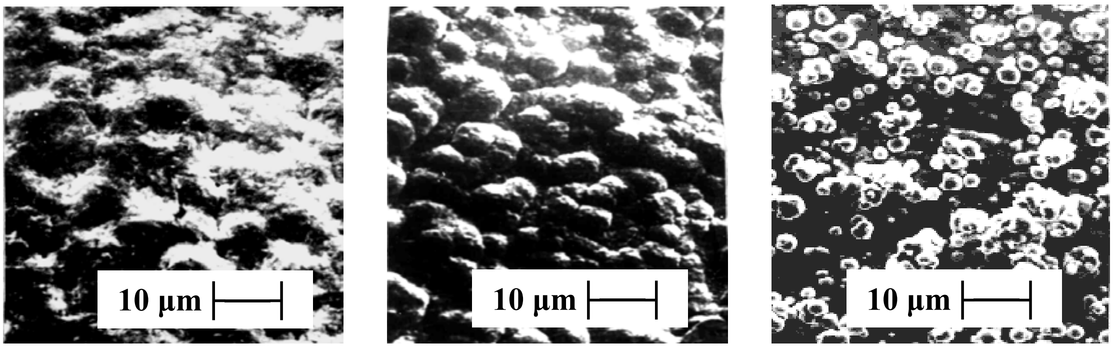
Also, a correlation between the texture and mechanical stresses in films exists. Deformation processes being important for texture of deposited golden film are defined by internal stress emerging during electrolysis process (Au <100> – compressive, and Au <111> – tensile).

The internal stress as a function of current density is shown in Fig. 3. This dependence has a maximal numerical value at current density 0.25 A dm^{-2}. When the current density is low, the element of crystals is arisen. They grow in direction tangential to the surface of substrate, and the structure becomes incomplete. The dislocation irregularities of lattice arise that results the increase in value of internal stress.

The increasing of current density leading a rise in quantity of the simultaneously inceptive crystals, and coating structure becomes triturated. In addition, the hydrogen evolution occurring at higher current densities loosens a coating and probably yields to decrease of internal stress of depositing gold films.

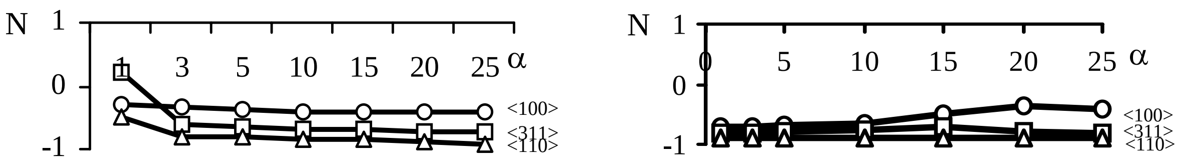
The microhardness of electroplated Au films might be coherent with both internal stresses appearing in the deposit and perfection of depositing layers structure. The obtained effects of current density on the microhardenss of obtained Au films are shown in Fig. 4. The marked range of microhardness reveals with the minimal reasonable values of microhardness of gold films suitable for microelectronic applications. The microhardness of Au films electroplated from the bath do not contained surfactants is up to 87 MN m^{-2}.

Based on the internal stress and microhardness data, the range of current densities 0.25 – 0.4 A dm^{-2} might be defined as optimal to obtain functional gold films for microelectronics applications. However, the obtained films under mentioned conditions are porous (see data presented in Table 1).



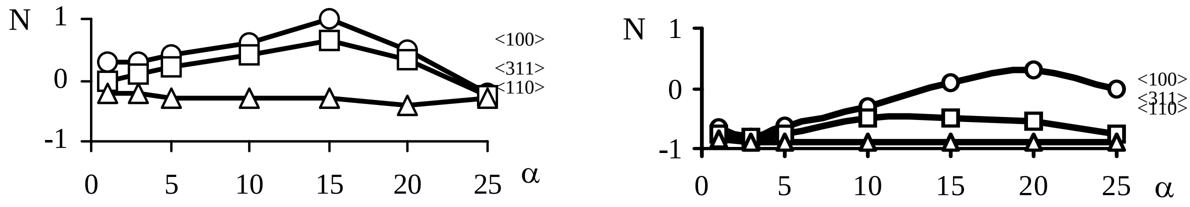
a b c

Fig. 1. Morphology of the gold coatings that were electroplated at different current densities, A dm^{-2}: 0.2 (a), 0.25 (b) and 0.3 (c)



substrate

0.2 A dm^{-2}



0.25 A dm^{-2}

0.35 A dm^{-2}

Fig. 2. The fractions of textures of electroplated films obtained at various current densities

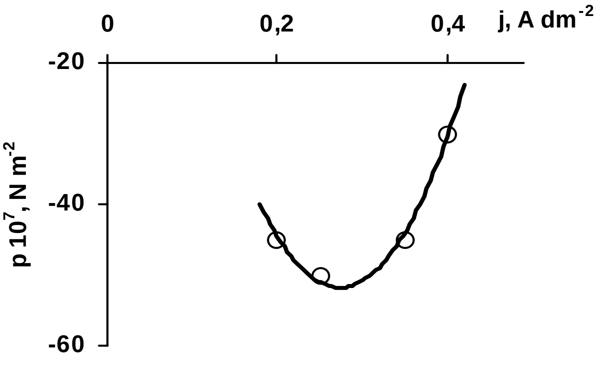


Fig. 3. The internal stresses in gold coating deposited on brass substrate as a function of current density

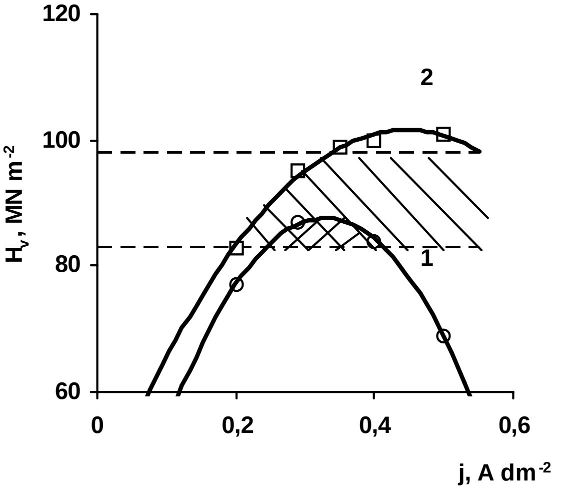


Fig. 4. The microhardness of gold coatings obtained from the phosphoric acid electrolytes without surfactants (1) and with surfactants (2)

Table 1. Comparative properties of the gold coatings produced at different condition of electrolysis

Properties	Samples, deposited from phosphate baths at current densities, A dm^{-2}					
	without additives			with additives of H_4OEtDP and CyEn		
	0.2	0.3	0.5	0.2	0.3	0.5
Rate of deposition, μm hour^{-1}	13	13	12	13	16	15
Porosity, number porous per cm^2	2	5	7	–	–	1

In order to reduce the porosity of film the effect of some surfactants was studied. The positive effect of composition additives (H_4OEtDP and CyEn) is revealed. The optimal composition of surfactants is: 10 mg l^{-1} H_4OEtDP and 0.75 mg l^{-1} CyEn. The gold films obtained from phosphoric acid bath with additives are light, fine-crystalline, well-adherent to the brass substrate. Adding of these specific surfactants almost excludes the pores in electroplated film. Simultaneously the gold electrodeposition rate increases at higher current densities 0.3 – 0.5 A dm^{-2} due to reducing the hydrogen evolution rate (see Table 1). Moreover, the adding of these surfactants enable to obtain Au films (at 0.5 A dm^{-2}) that possess the excellent microhardness. In our opinion, the increase of microhardness is resulted by the grain size decrease with increasing cathodic current density.

So, the adding of H_4OEtDP and CyEn to the phosphoric gilding bath expands the range of current densities up to 0.6 A dm^{-2}. Properties of the obtained films are reasonable for microelectronics application (see Fig. 3). Meantime, this type of bath is under industrial tests.

CONCLUSIONS

1. Electroplated gold films obtained at low current densities have coarse-crystalline structure with irregular grain size. The relatively fine-crystalline structure but with extremely irregularly developed morphology appears when current density increases. In this case the isolated spheroids are formed. The coatings peel off due to intensive hydrogen evolution on the cathode.
2. The different textures of brass substrate and gold film, namely the rise fraction of texture <111> in coating which determines the compressive internal stresses yields to low adhesion and peeling off the Au films at current densities higher than 0.25 A dm^{-2}.
3. Au films obtained at low current density (0.2 A dm^{-2}) have the same texture as a brass substrate (<100>), that results the improvement of adhesion.
4. Adding of surfactants H_4OEtDP and CyEn to phosphoric gilding solution yields to form nonporous, fine-crystalline Au films with high values of microhardness in more wide range of current densities: 0.2 – 0.6 A dm^{-2}. Obtained functional gold films posses properties enabling them to use in microelectronic industry.

Acknowledgments

Authors are grateful to Ukrainian State Foundation for Fundamental Research under Ministry of Education and Science (grant No. 03.07.117). Moreover, this study performed in frame of grant C 03047 supported by Lithuanian Science and Study Foundation.

REFERENCES

1. **Okinaka, Y., Hoshino, M.** Some Recent Topics in Gold Plating for Electronics Applications *Gold Bulletin* 31(1) 3 1998.
2. **Lochet, J.** Electrolyte Solution and Process for High Speed Gold Plating. Pat.US N 04670107, 1987.
3. **Lochet, J.** Electrolyte Solution and Process for Gold Electroplating. Pat.US N 04795534, 1989.
4. **Survila, A., Mockiavichus, V., Vishomirskis, R.** Chronopotentiometric Investigation of Gold Electrodeposition from Cyanide Solutions *Electrochemistry* 6 1986: pp. 816 – 821.
5. **Baltrunas, G., Mockiavichus, V., Jankauskas, T.** Passivation Surfaces of Silver, Gold and Platinum by Cyanide Ions *Electrochemistry* 6 1998: pp. 645 – 648.
6. **Bek, R., Kosolapov, G.** Electrochemical Behavior of Gold in Alkaline Cyanide Solutions *Proceedings of the Academy of Sciences USSR* 5 1988: pp. 7 – 18.
7. **Gruev, I., Matveev, N., Sergeeva, N.** Electrodeposited Coatings for Electronic Devices. Radio i Sviaz, Moscow, 1988 (in Russian).
8. Bath for Gold Electrodeposition. Metalor technologies International S.A. Pat.WO No. 2004005589, 2004.
9. **Virbilis, S.** Galvanotechnic for Masters. Metallurgy, Moscow, 1990.
10. **Gruev, I., Matveev, N., Sergeeva, N.** Gold, Silver and Palladium Galvanic Plating in Radioelectronic Devices Industries. Radio i Sviaz, Moscow, 1981 (in Russian).
11. **Dini, J. W.** Electrodeposition: the Materials Science of Coatings and Substrates, William Andrew Publishing, New York, 1993. Gold and Gold Alloys, and Uses Thereof. Pat.US N 20040065225, 2004.
12. Electrical Contact Surface Coating. Pat.WO N 1987005057, 1987.
13. **Vishomirskis, R.** Kinetics of Metals Electrodeposition from Complexes Electrolytes. Nauka, Moscow, 1969.
14. Gold Plating Technology, Ed. F.H.Reid and W.Goldie. Electrochemical Publications, Ltd., Ayr, Scotland, 1974.
15. **Baltrunas, G.** Electrochemical Impedance Study of the Gold Electrode Surface State in Gold (I)-sulfite Electrolyte *Chemija* 2 1999: pp. 112 – 116.
16. **Baltrunas, G., Valiuniene, A., Valiunas, R.** The analysis of Electrochemical Impedance Spectra Obtained for Electroreduction of Gold (I)-sulfite Complexes. *Environmental and Chemical Physics* 25 2003: pp. 51 – 57.
17. **Baltrunas, G., Valiuniene, A., Valiunas, R.** Influence of Chemisorption of Sulfite Ions on Electroreduction of Gold (I)-sulfite Complexes. *Polish J.Chem.* 77 2003: pp. 1819 – 1831.

18. **Rapson, W. S., Groenewald, T.** Gold Usage. Academic Press, Inc, New York, 1978.

19. **Okinaka, Y.** In EAST Report 1991: Precious Metals in Modern Technologies and Applications, Schwäbish Gmünd, Germany, 1992: pp. 8 – 18.

20. **Miroshnichenko, V., Litovchenko, K., Kublanovsky, V., Emelianov, V., L.Anufriev.** Gilding Electrolyte. Pat.USSR N1667416, 1989.

21. **Kublanovsky, V., Bersirova, O., Emelyanov, V., Anufriev, L., Rubtsevich, I.** Electrodeposition and Corrosion Properties of Gold Coatings *Physico-chemical Mechanics of Materials* 2 (4) 2004: pp. 373 – 377 (in Russian).

22. **Kublanovsky, V., Bersirova, O., Anufriev, L., Rubtsevich, I.** The Structure and Physical-mechanical Properties of Galvanic Gold Coatings for Electronics. *International Conference "Egycorr",* Cairo, Egypt, 2003.

23. **Kublanovsky, V., Miroshnichenko, V., Litovchenko, K., Emelianov, V.** Concentration Changing in Solution Bulk and Precathode Layer at Gold Electrodeposition From Phosphoric acid Electrolytes *Ukrainskij Khimicheskij Zhurnal* 6 1993: p. 595.

24. **Litovchenko, K., Kublanovsky, V., Emelianov, V., Anufriev, L.** Kinetics and mechanism of Gold (I) Cathode Reduction from Phosphoric Acid Electrolytes *Ukrainskij Khimicheskij Zhurnal* 5 1997: p. 43.

25. **Miroshnichenko, V., Litovchenko, K., Kublanovsky, V.** Potential of Gold Electrode in Phosphoric Acid Gilding Electrolytes *Proceeding of AC USSR* 5 1991: pp. 130 – 133.

26. **Kublanovsky, V., Litovchenko, K., Emelianov, V.** Influence of Electrolysis Regime on the Structure and Physical-chemical Properties of Gold Coatings *Galvanotechnic and Surface Finishing* 3 1993: pp. 33 – 36.

27. **Cesiulis, H., Bersirova, O., Valiuniene, A., Prosycevas, I., Baltrunas,G.** Structure and Morphology of Silver Electrodeposits *Materials Science* (*Medžiagotyra*) 10 (2) 2004: pp. 142 – 146.

28. **Bersirova, O., Cesiulis, H., Donten, M., Krolikowski, A., Stojek, Z., Baltrunas, G.** Corrosion and Anodic Behavior of Electrodeposited Ni-Mo Alloys *J. Physicochemical Mechanics of Materials (ISSN 0430-6252)* 4 2004: pp. 620 – 625.

29. **Baturinskaya, N. Ya., Kalchuk, N. A., Chyornyj, V. G.** The Determination of Fine Crystallic Structure in the Surface Layers by Means of X-ray Diffractometer *Zavodsk. Lab* 48 (7) 1982: pp. 38 – 40.