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THE INFLUENCE OF NOVEL ORGANIC GOLD COMPLEX ON PHOTORESIST LAYERS OF PRINTED CIRCUIT BOARDS

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Abstract

The goal of this paper was to study the influence of organic gold complex based on mercaptotriazole on photoresist layers used in manufacturing of printed circuit boards (PCBs). Investigations were performed by immersion the previously prepared boards in electrolytes with different pH values (pH=2, 4, 7, 9 and 12) at gold concentration of 2.5 g/dm^3 and in gold complexes with different gold concentrations (1.5; 2.0; 2.5; 3.0 and 3.5 g/dm^3) at pH value of pH=9. Investigations showed that photoresist layers on boards are the most resistant at optimal operating conditions, pH=9 and concentration of gold of 2.5 g/dm^3.

Key words: organic gold complex, mercaptotriazole, photoresist effect, printed circuit boards.

Introduction

Electrodeposition of gold is not a new process, but its application is increasingly important in the areas such as automotive industry, biomedicine and electronics industry (computers, telecommunications, etc). Combination of excellent electrical conductivity and high corrosion resistance led to the adoption of gold as the standard material for interconnectors. Gold coatings are used in electronics industry due to their exceptional characteristics in terms of electrical, chemical and optical properties, such as high purity combined with resistance to abrasion of deposits [1].

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Gold is deposited on metal from solution by the electrolysis process such as:

a) Decorative gold plating: a very thin gold layer (thickness of 0.05÷0.1 μm, rarely up to 0.2 μm) with a very shiny and smooth surface.
b) Hard gold plating: thicker layers of gold in relation to the decorative gold plating. These are layers with thickness of 0.5 μm and higher [2-3].

Electrochemical coatings of gold can be classified as soft gold and hard gold [1].

Hard gold is used as a contact material for electrical connectors and printed circuit boards (PCBs), relays and switches in which contacts must be resistant to wear with simultaneous low electrical resistance [4-6].

Hard gold is obtained by co-deposition with metals such as nickel, cobalt and iron, which are utilized as additives for increasing of hardness [5, 7]. The inclusion of these metals significantly changes the properties of deposit, such as an increase in hardness and wear resistance [8].

On the other hand, soft gold is used to establish connections within the electronic components such as the case with making interconnections of integrated circuits (ICs), or forming connections with external devices (TAB) or chip-on-glass (aquavaristique) and chip on a flexible base (chip-on-flex (COF) technique) [9,10].

Due to high price of gold, it is important to accurately identify the types of baths for obtaining the best gold deposits. Therefore, the industry of microelectronics, optoelectronics and microsystems are still engaged in the research of electrolytes, which should be economically viable to use and at the same time to fulfil all desirable characteristics of micro-devices [1].

Baths for gold plating can be classified into different categories depending on which gold salts are used, the reaction mechanism, pH value of baths, as well as the properties of the obtained deposits [11]. However, the basic division of gold plating baths is reduced to cyanide and non-cyanide ones.

The acidic, neutral and alkaline electrolytic cyanide baths are in use for depositing the hard and soft gold. Electrolytic cyanide baths are used as acidic (pH = 3 to 6), neutral (pH = 6 to 8.5) or alkaline (pH = 8.5 to 13) wherein the gold may be a monovalent or trivalent [2, 11]. On the other hand, non-cyanide baths can be used only as a neutral or alkaline with only limited application in the coatings of soft gold. Hard gold plating can be only obtained from cyanide baths [2].

The non-cyanide baths in use are: sulphite and amino sulphite baths, Au (I) thiosulfate baths, thiosulphate-sulphite baths, baths on the basis of thiourea, baths with ascorbic acid, baths without reducing agent, Au (III) halogenido baths and Au (I) thiomalate baths [1].

Traditionally, the gold coatings are obtained from cyanide electrolytes, where gold (Au^+) is in a complex with cyanide (CN^-) as ligand. Cyanide electrolytes are extremely stable (constant stability of AuCN is around 10^{38}). However, in regard to safety and disposal of waste water, a growing concern is present [12].

Considering the application of printed circuit board in the industry and in the field of microelectronics and optoelectronics in general, the important fact is that cyanide ions attack the surface between the protective film and substrate lifting the film, which is manifested by gold deposition under the protective layer. These unwelcome processes result in changing the form of micro-devices causing the loss of performances called "under plating" [12, 13].

Due to this reason, especially in recent times, there are trends in formulation and application of electrolytes without cyanide. Composition of these electrolytes is mainly based on gold complexes with different organic compounds. Their use, however, has not yet found a satisfactory industrial application due to the low stability constant, which is manifested by decomposition of the complex and disjointing of elemental gold from electrolyte.

Non-cyanide baths containing only sulphites or thiosulphates as complexing agents have limited use due to low stability of the system.

It was found that a mixed bath containing sulphite and thiosulphate ligands is very stable even without the presence of stabilizer. This bath was originally developed for chemical deposition [17] and later version was developed for electrochemical deposition [18]. In essence, this bath can be used in the neutral or slightly acidic conditions, what makes it incompatible with photoresist materials. The improved stability of the mixed bath is attributed to the formation of gold thiosulfate or mixed sulphite-tiosulphate complex with high stability constant.

In comparison with previous complex, organic complex of gold based on mercaptotriazole, formulated and synthesized in the Institute for Mining and Metallurgy in Bor showed to be more stable over a longer period of time. Additionally, the coatings obtained from this complex fully meet the requirements of decorative coatings [21-23]. Since detailed testing of this complex was done in the previous research, both in liquid and solid state, the aim of this study was to investigate the effect of complex on the photoresist layers used in making the printed circuit boards.

Experimental Work

Study of the effects of organic gold complex, based on mercaptotriazole on photoresist layers that are used in making the printed circuit boards, was done on previously prepared printed circuit boards. Printed circuit boards with a developed net of 1.3×1.3 mm (with edges - lines of 0.7×0.7 mm on which the lacquer was applied) are cut to the dimensions of 15×15 mm.

In the experimental work, the following effects on photoresist layers were tested:

a) pH value of electrolyte in the range of its stability (2-12) at optimal concentration of gold (in terms of the coating quality) in electrolyte of C_{Au}=2.5 g/dm^3 [15];
b) concentration of gold (1.5, 2.0, 2.5, 3.0 and 3.5 g/dm^3) at optimum pH value of electrolyte of pH = 9 [15].

Freshly prepared electrolytes were used for tests [21, 22].

Coatings of thickness of 0.1 μm are used for electronics industry the most frequently. Considering the fact that the required time for applying the coatings of this thickness from organic gold complex with mercaptotriazole is 105 s, the tests up to 180 s were performed [22, 23].

Tests were carried out by simple immersion of plates into working electrolyte for 30, 60, 90, 120, 150 and 180 s.

The results of these tests are shown in of macro and micro look of plate surfaces as well as micro look of their cross section.

Macro and micro look were recorded with digital photo camera SAMSUNG ES15. The optical microscope EPY TIP 2 was used for recording the micro look.

Fig. 1a shows the macro and Fig. 1b micro look of plate surface before treating with electrolytes. Fig. 1c shows the micro look of plate edge before being immersed in electrolyte.

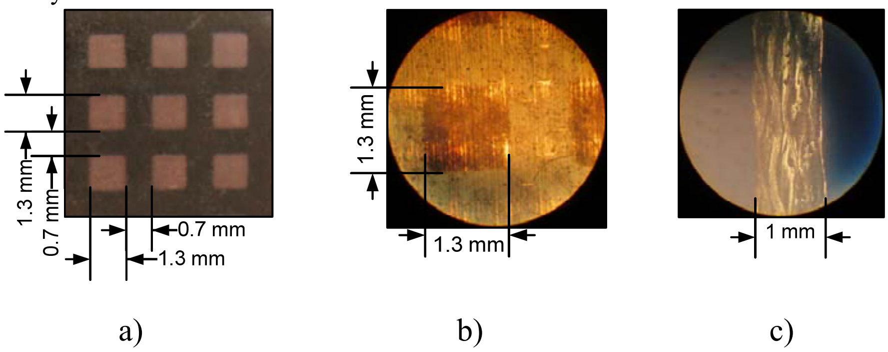

Fig. 1. Photo of circuit board before treating with electrolytes: a) surface macro look, b) surface micro look and c) edge micro look

Results and discussion

The effect of electrolytes of different pH values on photoresist layers was tested in the first series of experiment.

It can be seen from Fig.2 showing the macro look of circuit boards and Fig. 3 (micro look of circuit board), treated with electrolyte for 30, 60, 90, 120, 150 and 180 s at different pH values (pH=2, 4, 7, 9 and 12) that the photoresist layers on boards are resistant to the negative effect of electrolyte at pH values of 2, 7 and 9. At pH 4, the first visual changes can be observed after 150 s whereas at pH = 12, the first changes occur after 30 s. It can be seen from macro and micro looks that the circuit boards are the most resistant to the effects of electrolyte having pH value of 9, which is of great importance due to the fact that previous studies have shown that the best coatings are obtained with this particular electrolyte (at pH = 9) [15].

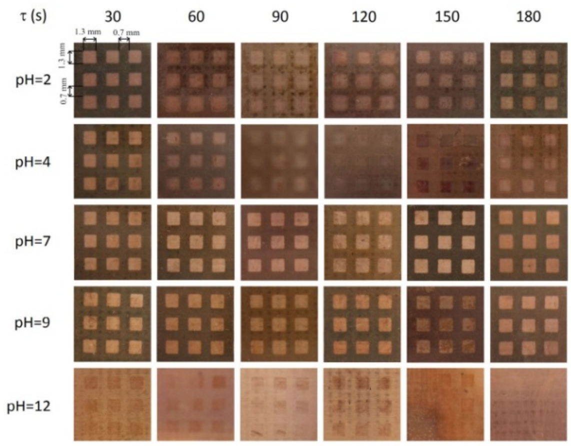

Fig. 2. Macro look of circuit boards recorded after 30, 60, 90, 120, 150 and 180 s of immersion at pH=2, 4, 7 ,9 and 12

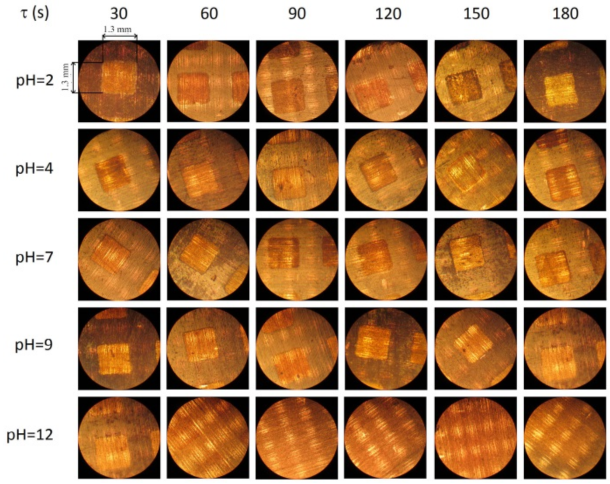

Fig. 3. Micro look of circuit boards recorded after 30, 60, 90, 120, 150 and 180 s of immersion at pH=2, 4, 7 ,9 and 12

The effect of gold concentration in electrolyte on photoresist layers was tested in the second series of experiment.

It can be seen from Fig.4, showing the macro look, and Fig.5, showing the micro look of circuit boards treated for 30, 60, 90, 120, 150 and 180 s with electrolytes (at pH=9) having different gold concentrations (C_{Au}=1,5; 2,0; 2,5; 3,0 and 3,5 g/dm^3), that the photoresist layers on boards are resistant in all cases.

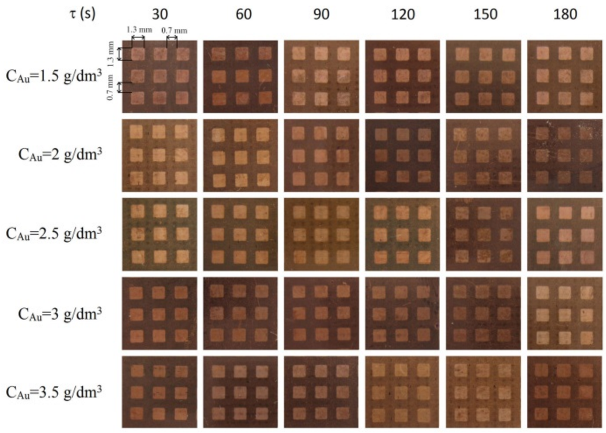

Fig. 4. Macro look of circuit boards recorded after 30, 60, 90, 120, 150 and 180 s of immersion at pH=9 and gold concentrations in electrolyte of 1.5; 2.0; 2.5; 3.0 and 3.5 g/dm^3

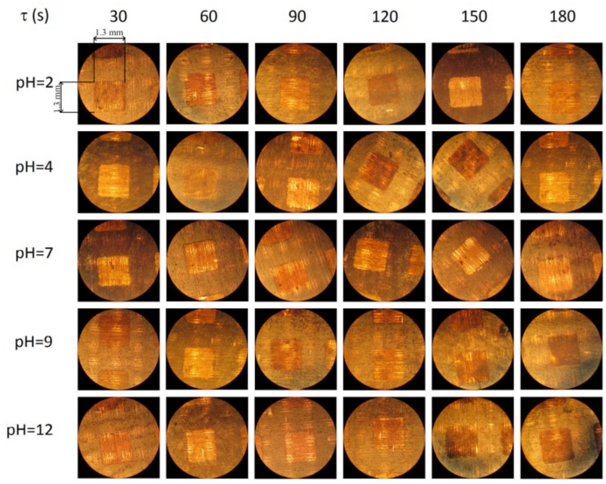

Fig. 5. Micro look of circuit boards recorded after 30, 60, 90, 120, 150 and 180 s of immersion at pH=9 and gold concentrations in electrolyte of 1.5; 2.0; 2.5; 3.0 and 3.5 g/dm^3

Figure 6, showing the micro look of edges of circuit boards recorded after 180s of treating the plates with electrolyte at different pH values, clearly illustrate that the plates are the most resistant to the effect of electrolyte at pH = 9 and that the largest etching of edges is at pH = 12.

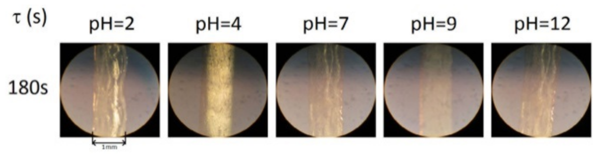

Fig. 6. Micro look of edges of circuit boards recorded after 180 s of immersion at pH=9 and gold concentrations of 1.5; 2.0; 2.5; 3.0 and 3.5 g/dm^3

Conclusions

Study of the effect of pH value of electrolyte, in the range of its stability (2-12), at optimal gold concentration in electrolyte of C_{Au}=2.5 g/dm^3 on photoresist layers, has found that they are resistant to the effect of electrolytes that were obtained at pH values of 2, 7 and 9. At pH=4, the first visual changes can be observed after 150 s, whereas at pH = 12, the first changes occur after 30 s. It can be also seen from micro look of surfaces of circuit boards that the photoresist layers of boards are the most resistant to the effect of electrolyte at pH = 2 and pH = 9. Additionally, at pH = 9, the photoresist layers on circuit boards are resistant to the effects of electrolytes at all tested concentrations of gold.

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