Abstract
The history of gold deposition began in the early nineteenth century when many art objects were electroplated with gold. It has been traced to the early work of Brugnatelli in 1805. Gold electroplating formulations based on the double salt gold potassium cyanide was patented in 1840. Since then, gold has been plated from cyanide electrolytes, where (Au⁺) is ligated with cyanide (CN⁻). With regard to the two main disadvantages of cyanide electrolytes, toxicity and risky for technical personnel, there is trend for using non-cyanide electrolytes. This article is an overview of the history of gold coatings and investigations of gold complex based on mercaptotriazole.

Key words: history; gold coatings; electroplating; cyanide electrolyte; mercaptotriazole
Introduction

The gold coatings are mentioned as the first galvanic coatings. The first gilding report is from 1800, and the first patent about gold deposition was published in 1840. The subject of this patent was deposition of gold layer on metals from the alkaline cyanoaurate solution by electric current. This year is considered the beginning of gilding [1-2].

The beginning of electrodepositon is related Volt's invention of the source of direct current, the Volta piler (cell). The first reference related to gold plating and the deposition of a uniform metal film, was a letter sent by Luigi Brugnatelli to his friend Professor Jean Baptiste Van Noss in 1803, in which he describes the gold plating of two large silver medals from a gold solution, a mixture of ammonia and oxide gold (so-called " ammoniuret ").

Michael Faraday performed his first experiments on the deposition of copper on zinc and vice versa with the electroplating in 1812, but he did not publish them. Faraday thought about this phenomenon for years, but he could not dedicate himself to it until 1832, when he began a well-known series of electrochemical decomposition which he published in December 1833. Many of the terms, found by Faraday are used today. He proposed the terms: anode and cathode instead of Voltod and Galvanod. Later, on this basis, the terms anion and cation were formed. Also, he proposed the terms of electrolysis and electrolyte [3].
Elkingtons and John Wrights were first patented the procedure for gold plating from cyanide solution. Elkington's first patent from 1836 did not include electrodeposition, only chemical gilding by immersion in solution. Patent recognition was exactly 6 months after the application (September 25, 1840). Next years, Elington and its associates employed a dozen workers in the department for silver plating and gilding, and in 1851, they had more than 500 employees. They also earned from the sale of patent rights (patent from 1840) and regularly purchased patent rights from this area, (Henry Beaumont's from 1842 (No. 9374) and Pat. 9431 submitted by John Stephen Woolrich in August 1842 were the most significant patent was (using sulphite of silver and gold). The first successful gilding with a coherent and well-fitting gold deposit carried out by Dr. Joan Wright in his home in Bordeaux in the Birmingham area is shown in Figure 1.

Figure 1. First successful gilding Joan Wright – 1845 [3]
Two gold-plated vases, gilded by Alexander Parkes in 1845, today are presented in the Science Museum in London. In the middle of the 19th century, electrodeposition, except in England and France, was developed in Germany (then still confederations) and Russia.

Werner Siemens, who later founded Siemens, made the first invention in the field of electrodeposition. He used French, "lion's" gold coins. The process (patent) was sold to the jeweler from Maddenburg.

However, the most significant development of the gilding was in Russia. Under the patronage of Emperor Nicholas I, Jakobi supported the development of electrodeposition in any form. He repeated the methods of de la Rive, Rulce and Elkington and submitted a report to the Academy of Sciences in Petersburg. The industrial development of gilding begins in 1844 by the opening of a large electrodeposition plant in St. Petersburg.

The greatest and astounding achievement of this plant at that time was the gilding bronze dome of the Church of the Savior of Christ, built in Moscow. Until then, the gilding of dome was done using golden foil or by immersion in molten gold, but the electrochemical gilding, at that time, was not enough progress for using in such a large project. The method of gold plating included the following stages: bringing dome in to the gilding plant, marking of parts, disassembling, gilding and installation on the church itself. Three large wooden tubs were used for gold plating, of 5000 dm³ of cyanide solution, and sheets (foils) were made manually. The largest dome was 30 m in diameter. The specification required one ounce (28.44 g) of gold per square meter, with a tolerance of 20%, and if the procedures were not followed, the entire batch would be rejected. The total mass of gold deposits on the church was slightly less than 500 kilograms. Unfortunately, the church was destroyed during the Revolution, but later it was renovated. Figure 2 shows the church images before and after renovation [1-3].
Figure 2 Church of the Savior of Christ in Moscow before and after renovation [3.4]
However, the application of gold coatings in most countries in the world for a long time was prevented with the laws relating to the trade of precious metals, so that they did not find wide application until the Second World War. During the Second World War there was a great need for badges for marking of genera and ranks in the United States, which led to the intensive use of gold coatings, and after the war to the massive use of gold coatings in the production of jewelry [1].

Intensive use of gold coatings has started during the Second World War, and continued in the post-war period, especially in the jewelry industry and electrical engineering. [1-2]. Since then, until now, cyanide and ferrocyanide gold solutions are commonly used in practice. These compounds are very toxic, and the formation and maintenance of cyanide baths is expensive and risky for technical staff. The costs of waste water treatment reach 30% of the total investment, and the technology is high risk technology. For this reason, especially in recent times, use an electrolyte that does not contain cyanides is increasing. The composition of these electrolytes is mainly based on a complex of gold with an organic compound. However, their use has not yet found satisfactory industrial application due to a small stability constant, which is manifested by the decomposition of the complex and the precipitation of elemental gold from electrolytes [2, 5]
2. Classification of gold plating baths

Gold plating baths can be classified into various categories depending on the gold salt used, the reaction mechanism, bath pH, and properties of the deposit obtained. The diagram shown in Figure 3 illustrates this classification [5].

Figure 3. Classification of gold plating [6]
The electrolytic cyanide-type baths include those operated at acidic, neutral, or alkaline pH’s, and they can deposit either hard gold or soft gold. Non-cyanide type baths can be operated only at neutral or alkaline pH’s by either an electrolytic or electroless mechanism, but the baths presently available can deposit soft gold only. Hard gold can be deposited only from a cyanide-type electroplating bath at present, neither a cyanide-type electroless hard gold plating bath nor a non-cyanide type electrolytic nor electroless hard gold plating bath has not yet been developed to the authors’ knowledge [6].

This paper reviews currently available non-cyanide electrolytes for gold plating: sulfite bath, thiosulfate bath, mixed sulfite-thiosulfate bath, thiourea bath, ascorbic acid bath, baths containing no additional reducing agent, Au(I) thiomalate bath, other baths and bath based on mercaptotriazole.

2.1 Sulfite bath

The use of a gold sulfite complex for gold plating has been known since 1842 [7] and it is still the gold complex most commonly used to prepare non-cyanide baths. From gold sulfite baths it can be produced smooth, bright, and ductile pure gold deposits with good microthrowing power. For microelectronic and optoelectronic applications, sulfite based baths possess a number of important advantages over cyanide processes: better throwing power and this can result in better bump thickness uniformity across the wafer [8].

Most importantly, they are non-toxic. The stability constant of is, however, \(10^{11}\) times lower than for the corresponding cyanide complex but gold sulfite baths still possess relatively high stability, particularly under alkaline conditions [8]. Their compatibility with most photo-resists is also good, and as long as the pH is maintained below 10, dissolution and delamination of the photoresist is not observed [8-11]. In order to satisfy the requirements of resist compatibility and bath stability most commercial gold sulfite processes are operated in the pH range 9 to 10.
2.2 Thiosulfate bath
The electrodeposition of gold from an Au(I)-thiosulfate complex has been known as early as 1913. [12], but it has never been used for making a practical plating bath. The stability constant of the complex is equal to $10^{26}$. In contrast to the sulfite and cyanide baths, there has been little attention paid to the development of gold thiosulfate plating processes [12-15]. This is somewhat surprising given the potentially low toxicity of a thiosulfate bath and the relatively high stability of the complex, but presumably has arisen because the inherent instability of the thiosulfate anion with respect to disproportionation [12-14].

2.3 Mixed sulfite-thiosulfate bath
The non-cyanide baths described above containing either sulfite or thiosulfate as a sole complexing agent appear to be of limited use because of insufficient stability of the systems. In view of the prior successful development of electroless gold plating baths containing both thiosulfate and sulfite, Pauradier and Gadet [12], as well as Alymore and Muir [16], investigated the possibility of electroplating soft gold from a bath containing the two ligands. It was found that the mixed ligand bath is highly stable even without the addition of any stabilizer [16]. Crucially, mixed sulfite-thiosulfate bath could be operated at near neutral or slightly acidic conditions which make it compatible with essentially all photoresistant materials.
Osaka and coworkers [17] investigated the possibility of electroplating soft gold from a thiosulfate-sulfite mixed ligand bath, specifically for application to the formation of microbumps on silicon wafers. Based on the mixed ligand electrolyte of Osaka, a group of authors at Newcastle University has developed an electrolyte for soft gold electrodeposition which has attempted to eliminate Na$_2$HPO$_4$ and Tl$^+$. 

2.4 Thiourea bath

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi, Ltd. [14, 16]. In this system thiourea has been shown to undergo complex chemical reactions through the formation of a radical intermediate, (NH)(NH$_2$)CS, to form final products including urea, a major product, and dicyandiamide.

•2.5 Ascorbic Acid Bath

In the studies [16-17] authors developed a thiosulfate-sulfite mixed ligand bath with ascorbic acid as the reducing agent.

The possibility of developing these baths was initially investigated based on the well-known mixed potential theory combined with partial polarization curves measured at a gold electrode.

2.6 Baths Containing No Additional Reducing Agent

Krulik and Mandich [18] reported that the Au(I) thiosulfate-sulfite mixed ligand system functions as an autocatalytic bath in the absence of any conventional reducing agent. They believed that the thiosulfate-sulfite mixture itself is a reducing agent system, and that sulfite functions as the main reducing agent in this bath. Sato [19] as well as Leblanc [20] and collaborators studied the reaction mechanism of this system in detail.
2.7 Au(I) thiomalate bath
Gold thiomalate complex is used in the plating baths in the form of NaAu(I) thiomalate (C₄H₄AuNaO₄S or C₃H₃AuNa₂O₄S). A basic characteristic of this complex is the high stability of and it has important application in obtaining Au-Sn alloys [12]. Significant use of gold thiomalate is in medicine for the treatment of rheumatoid arthritis [21].

2.8 Other baths
In practice, however, solutions containing halide, ammonia, hydroxide, thiocyanate and hydroxide ligands have all been found to be unsuitable due to a combination of poor deposit properties, instability or toxicity [12, 13]. In the late 1970s an alternative non-cyanide gold bath based on a nitro-sulfito complex was proposed [21]. Gold plating baths based on complexes between Au(I) and mercapto-alkylsulfonic acid ligands such as 2-mercaptopethanoic acid (MES), 3-mercaptopropanoic acids (MPS) and 2,3-dimercaptopropane-1-sulfonic acid (DMPS) have also been developed [13]. More recently, gold plating baths employing hydantoin ligands have been proposed [21].
2.9 Bath based on mercaptotriazole

The organic gold complex based on mercaptotriazole was investigated in Mining and Metallurgy Institute Bor and Technical faculty in Bor, Serbia [22-26]. Electrolyte was stable for one year without visible signs of degradation and precipitation of elementary gold. Detailed investigations were carried out in order to determine the optimum conditions for obtaining quality decorative gold plating from this electrolyte and to compare it with the quality of gold plating obtained from the classic cyanide electrolyte.

In the first stages of experimental investigations, in the aim of detailed comparison of bath composition and operating conditions polarization curves were recorded and determined the limiting current densities for electrolyte based on mercaptotriazole (without and with additives) and classic cyanide electrolyte (AUROCIN DPB-trade mark). Based on recorded polarization curves for gold complex with mercaptotriazole with various gold concentrations without additives, it was concluded that limiting current density increases with an increase of gold ion concentration in electrolyte (0.07 A/dm² for C_Au=3 g/dm³ to 0.01 A/dm² for C_Au=1 g/dm³), as well as in cyanide baths, and that the values of limiting current densities are lower regarding to cyanide of baths. Polarization curves for solution with C_Au= 2.5 g/dm³ without additives and solution of the same concentration with various concentration of TC EHC additive show that the presence of the additive even in the lowest investigate concentration (0.03 g/dm³) significantly decreases limiting current density, while further increase in concentration practically has no effect on value of limit current density [23-26]. Bath composition and operating conditions of electrolyte based on mercaptotriazole are shown in Table 1 [27].
Table 1. Bath composition and operating conditions of electrolyte based on mercaptotriazole [27]

<table>
<thead>
<tr>
<th>Bath constituent</th>
<th>Au-mercaptotriazole</th>
</tr>
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<tbody>
<tr>
<td>Gold concentration (g/dm$^3$)</td>
<td>2.5</td>
</tr>
<tr>
<td>pH</td>
<td>9</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>22</td>
</tr>
<tr>
<td>Time (s)</td>
<td>105</td>
</tr>
<tr>
<td>Cathode current density (A/dm$^2$)</td>
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</tr>
<tr>
<td>Current intensity (A)</td>
<td>0.12</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Table 2. Optimal parameters of the deposition of decorative gold coatings and measured values of coating thickness, surface roughness and microhardness

<table>
<thead>
<tr>
<th>Gold concentration (g/dm³)</th>
<th>Cyanide electrolyte AUROCIN DPB</th>
<th>1.5</th>
<th>Gold complex based on Mercaptotriazole Au-MT</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode current density (A/dm²)</td>
<td>1</td>
<td>1</td>
<td></td>
<td>1</td>
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<tr>
<td>Temperature (°C)</td>
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<td>20</td>
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<tr>
<td>pH</td>
<td>9</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration of additives</td>
<td>AUROCIN DPB additive 1 – (20 g/dm³)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AUROCIN DPB additive 2 – (4 ml/dm³)</td>
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<td></td>
<td></td>
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<tr>
<td>Thickness b (µm)</td>
<td>0.08</td>
<td>0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface roughness Rₐ (µm)</td>
<td>0.052</td>
<td>0.066</td>
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<tr>
<td>Microhardness HK (MPa)</td>
<td>740</td>
<td>660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>Good adhesion</td>
<td></td>
<td>Good adhesion</td>
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</tbody>
</table>
3. CONCLUSION
This article provides an overview of the history of gold coatings and electrolytes used for gold electrodeposition and results of authors own investigations of gold complex based on mercaptotriazole. The traditional gold plating baths containing KAu(CN)$_2$ as the source of gold have served well for many years in the past for various applications in the electronics industry. In recent years, however, disadvantages of the cyanide system have become more apparent not only because of the greater consciousness about the use of toxic materials, but also because of the incompatibility of cyanide with photo resists and other materials used in the packaging of high density circuits. The developed non-cyanide electrolytes have been compared with the traditional ones. Experimental investigations showed that the quality of decorative gold plating, obtained from organic complex of gold based on mercaptotriazole satisfy all the requirements of decorative gold plating; at the same time current density effect on view and thickness of coating is lower than in classic cyanide bath.

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Thank you for the attention!