Electrochemical Deposition of Gold in Citrate Solution Containing Thallium

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In memoriam to professor Nada Ciković (1939–2005)

Abstract

Electrochemical deposition of gold from citrate solution, with and without thallium, has been studied using a rotating disc electrode (RDE) and linear sweep voltammetry. RDE was made from a mono-crystal silicon wafer, coated with a thin film of gold, deposited by a vapor deposition process (VDP), serving as a substrate for the electrochemical deposition of gold.

Limiting current density is achieved neither in citrate nor in thallium free electrolyte. The rotation speed significantly influences the process rate only at lower temperatures. At elevated temperatures gold deposition occurs in a kinetic domain. Tafel slopes confirmed that the electrochemical reaction occurs in two steps, depending on both the electrode potential and the presence of thallium ions in the electrolyte. The reaction kinetics changes in the presence of thallium ions as well. The mechanism of gold deposition is predominantly dependent on the electrolyte composition. In the citrate, thallium free solution, the adsorption of $Au(CN)^-$ and CN^- on the electrode surface is presumed, resulting in the formation of $AuCN_{ad}$ species, which are afterwards being reduced to the metallic gold. Thallium presence in the citrate solution leads to the adsorption of Tl^+ ion on the surface at a potential of -750 $mV/_{SCE}$, including it's catalytic effect as an ad-atom. AES and SEM analyses did not detect thallium presence in the deposited gold layer. It was found that the presence of thallium in the citrate solution shifts the deposition potential towards more positive values.

Keywords: AES and SEM analysis, citrate solution, cyclic voltammetry, electrodeposition of gold, thallium ions

1. Introduction

Gold coatings produced either by VDP (vapor deposition process) or by electrochemical methods are widely used in industry – particularly in electronics industry, due to their good electrical conductivity and high corrosion resistance. In contrast to the gold coatings produced by means of VDP, the electrodeposited gold exhibits, among other things, higher purity, lower porosity and an excellent adhesion to the substrate. Having also good alloying characteristics with some other metals, it is possible to achieve either hard or soft gold coatings, depending on requirements. Such properties of gold make it a perfect material for metal finishing processes, giving top quality products, having also aesthetic features. In addition, gold has the ability to form a very good thermo-compression bond.[1] It is noteworthy to say that empirical studies have at the very beginning resulted in successful device applications, which utilize such properties.

Later, more attention has been paid to the research of electrochemical and mass transport in order to establish relationships between this phenomenon and deposited gold structure. The importance of gold coating characteristics to the electronics industry has resulted in many fundamental studies of gold electroplating[2–6] (and references cited there in). These studies have been reporting about determination of the conditions in production of hard gold deposits, adding small amount of cobalt or nickel ions to the plating bath, as well as of soft gold film, in the presence of lead or thallium ions in the electrolytes. In the first

case small-grain-size coatings have been produced while in the second one coarser-grain-coatings have been deposited. It has also been shown that the presence of these ions or others (e.g. Sb) has changed the deposition potential exhibiting the depolarizing effect of the used ions serving as Pb, Tl, Co i Ni ad-atoms.[5,6] Parallel with the investigation of the ad-atoms contribution to the coating features, great attention has been paid to studies on the kinetics and mechanism of gold electrodeposition from electrolytes containing various ad-atoms. The aim of these studies was to highlight the role of added ions on them.[2,6,8,9,10] Depending on the bath composition and type of metal ions as well as on the applied potential, two reduction pathways have been presented. The first pathway occurs at low potentials involving the formation of an adsorbed intermediate $(AuCN)_{ad}$, while the second one takes place at higher potentials, meaning a direct charge transfer to the ionic state of gold cyanide.[3,7,11]

On the other hand, a considerable attention has been paid to the electroplating of silicon used in semiconductor production either directly or previously pretreated by VDP of gold as it has been done in the industrial semiconductor production.

This study was undertaken to investigate the effect of thallium ions as one of the base metals that influence not only kinetics and mechanism of gold electrodeposition but also the microstructure of such deposits. The aim was to get more evidence about the influence of Tl^+ ions on the deposition process and deposit structure, comparing them with the one carried out in the thallium-free electrolyte. In such way silicon wafers plating process can be improved, leading to a certain reduction of waste products.

2. Experimental

Experiments have been carried out in a conventional, thermostatically controlled three-electrode cell. The cell had two openings. The first one was for a thermometer and the second one was a tube for nitrogen inlet for purging the oxygen out of the electrolyte.

Working electrodes used in these experiments were prepared from a monocrystal silicon wafer having either (111) or (100) orientation. The front side of the silicon wafer was active semiconductive component, while the backside was covered by a thin layer of gold, which has previously been deposited using VDP and then alloyed at 703 K in the nitrogen atmosphere. In such way an eutectic Au – Si alloy has been achieved. The surface area of the working electrode was 0.385 cm². The front side of silicon wafer was protected by Shiply's positive photoresist AZ 1350J. In all experiments the electrolyte was a citrate solution prepared from the p.a. grade chemicals:

Di-basic ammonium citrate – $C_6H_{14}N_2O_7$
Potassium gold (I) cyanide – $KAu(CN)_2$
Thallium (I) nitrate – $TlNO_3$

Table 1. Composition of the electrolytes used in the experiments.

Electrolyte No.	Composition	Concentration (mol dm⁻³)
1	$C_6H_{14}N_2O_7$	0.22
	$KAu(CN)_2$	6.94×10^{-2}
	$C_6H_{14}N2O_7$	0.22
2	$KAu(CN)_2$	6.94×10^{-2}
	$TlNO_3$	3.75×10^{-5}
	$C_6H_{14}N_2O_7$	0.22
3	$KAu(CN)_2$	6.94×10^{-2}
	$TlNO_3$	1.78×10^{-4}
	$C_6H_{14}N_2O_7$	0.22
4	$KAu(CN)_2$	6.94×10^{-2}
	$TlNO_3$	3.75×10^{-4}

All chemicals were supplied by Merck, (Germany), and Kemika (Croatia).

Concentration of thallium ions was the main parameter in these investigations. The composition of the electrolytes, used in these investigations, is given in Table 1.

The electrolytes were prepared using ultra-pure deionized water having the resistivity of 18 M Ω cm⁻¹. The pH value of these baths was kept in the range of 5.8 to 6.2 by adding di-basic ammonium citrate or KOH. The electrolyte volume was 0.250 dm³ in all experiments.

Platinized titanium grid has been used as an anode, while the saturated calomel electrode served as a reference electrode.

Potentiostat/galvanostat Wenking, model VSG 72 was used as a power supplier.

Experiments were performed under nitrogen atmosphere, in the temperature range from 298 to 343 K.

Each silicon wafer piece coated and alloyed with gold, as already described, serving as a working electrode, was mounted on a disc electrode and placed into the cell filled with chosen electrolyte, previously warmed up to a given temperature and purged with nitrogen. Potentiodynamic measurements have been performed with the polarization rate of 20 mVs⁻¹ in the potential range from +95 mV (steady state potential value) up to –1000 mV/$_{SCE}$ and at different rotation speeds in the range from 500 up to 2000 min⁻¹.

Auger electron spectroscopy (AES) analysis of the electrochemically deposited gold was performed with PHI, SAM model 545A. SEM micrographs of the investigated samples were obtained with JEOL JSM T300 scanning electron microscope.[6]

3. Results and Discussion

3. 1. Voltammetric Study

Linear sweep voltammetry measurements of gold deposition from the thallium free electrolyte (electrolyte 1) have been carried out at different rotation speeds and at

two temperatures: at 298 K (Figure 1) and at 343 K (Figure 2). Hysteresis on the polarization curves (Figure 1), recorded at lower potentials (below 750 mV) are attributed rather to a change in the mechanism of gold deposition than to a modification of the surface area, due to the gold deposited on the substrate.
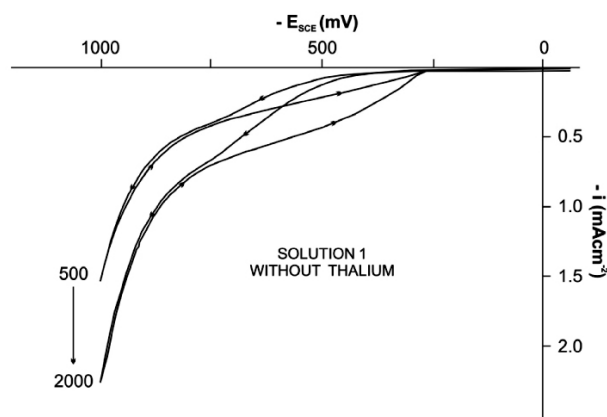

Figure 1. Voltammograms of cathodic polarization without Tl[+]; T = 298 K, polarization rate 20 mVs[−1], rotation speed 500 to 2000 min^{−1}.

The supposition is based on the results published by Bindra et al,[11] that a very thin layer containing only a few monolayers of an insoluble AuCN, is formed in the first reaction step, followed by the reduction of this intermediate salt to the metal gold as the final step. No limiting current has been observed in the investigated potential range. By increasing the electrolyte temperature only the reaction rate increased, while the hysteresis on the obtained voltammograms became smaller (Figure 2). This indicates a lower influence of adsorption and direct reduction of $Au(CN)_2^-$ to the metallic gold. In the second case as well (Figure 2), the influence of rotation speed is less pronounced. As a matter of fact, a change of hydrodynamic conditions does not significantly influence the obtai-
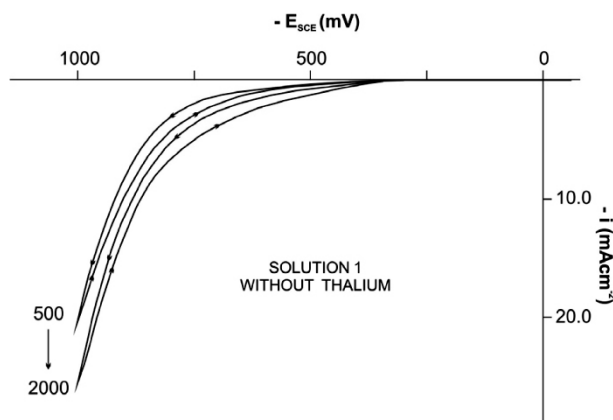
ned current density, meaning that the charge transfer process is the rate-determining step. It is assumed that only cyanide complexes of gold are formed in electrolyte but not citrates. Gold in aqueous solution forms a complex with cyanide $[Au(CN)_2]^-$. This complex is one of the most stable complexes formed by gold (stability constant $B_2^I \sim 10^{40}$).[13]

Adding thallium ions to the electrolyte (solutions 2, 3 and 4) current density considerably increases at lower electrode potentials. The shape of voltammetric curves is changed too. The hysteresis are now shifted towards more negative potentials, which corresponds to a mechanism of gold deposition *via* direct charge transfer of $Au(CN)^{2-}$ – ions from the electrolyte. Also, in the presence of thallium ions, limiting current plateaus are recorded, as presented in Figure 3.
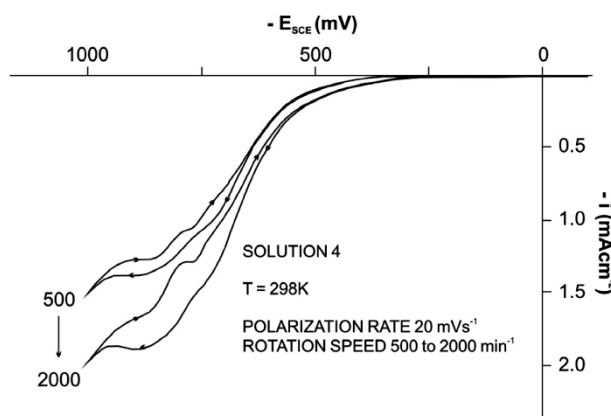

Figure 3. Voltammograms of cathodic polarization with Tl[+]; T = 298 K, polarization rate 20 mVs[−1], rotation speed 500 and 2000 min^{−1}.

At higher temperature, these plateaus were recorded only at lower electrode rotation speeds and disappeared completely at the highest electrode rotation speed. Hysteresis is less pronounced at this temperature, as shown in Figure 4.
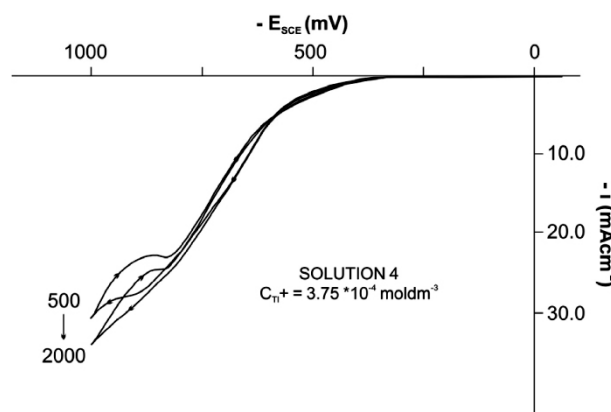

Figure 2. Voltammograms of cathodic polarization without Tl[+]; T = 343 K, polarization rate 20 mVs[−1], rotation speed 500 to 2000 min^{−1}.

Figure 4. Voltammograms of cathodic polarization with Tl[+]; T = 343 K, polarization rate 20 mVs[−1], rotation speed 500 to 2000 min^{−1}.

It should be mentioned that the directions of current branches, both ascending and descending, in the presence of thallium ions are opposite to the current behavior in the thallium-free electrolyte (Figures 1 and 2). The dependence of current density on the rotation speed is also evident at lower temperature, compared to the ones obtained in thallium free solution, for the same polarization potential range. At higher temperature current density increases with increasing electrode rotation speed (Figures 3 and 4). It is also evident that at higher temperature the influence of rotation speed on the current density is less expressed.

At the same time, the addition of thallium ions shifts the deposition potential towards more positive values. In Figure 5 the effect of thallium concentration on the electrode polarization curves is given and compared to the thallium-free electrolyte polarization curve. Only ascending branches are presented here. The contribution of thallium ions on the deposition rate is evident. Current density increases approximately three to four times in the investigated range of the Tl^+ concentration.
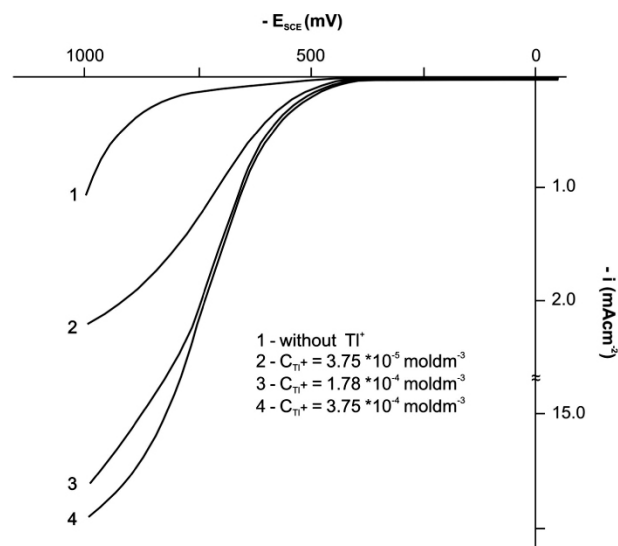
Figure 5. Voltammograms of cathodic polarization – effect of Tl^+ – ion concentration; T = 343 K, polarization rate 20 mVs^{-1}, rotation speed 500 min^{-1}.

Due to the fact that the limiting current values are not well defined or were not even achieved under certain experimental conditions, such as elevated temperatures or higher rotation speeds, they were evaluated by using certain dimensionless equations given in the literature.[3]

Although the concentrations of cyanide and citrate ions in the electrolyte are high, monovalent thallium does not form stable complexes.[14, 15]

3. 2. AES and SEM Analysis

AES analysis of gold deposit has not shown the presence of thallium on the surface. By ionic etching, up to

Au–Si interface, the presence of deposited thallium was not detected (Figure 6). The Nernst equilibrium potential $E_{Tl/Tl(I)}$ calculated from Pourbaix equations is equal –0.63 V in 10^{-5} mol dm^{-3} and –0.57 V in 10^{-4} mol dm^{-3} Tl^+ solutions.[6, 16, 17]

Addition of thallium into the electrolyte causes an increase of current density as well as a change of the gold coating structure as illustrated in Figures 7a and 7b.
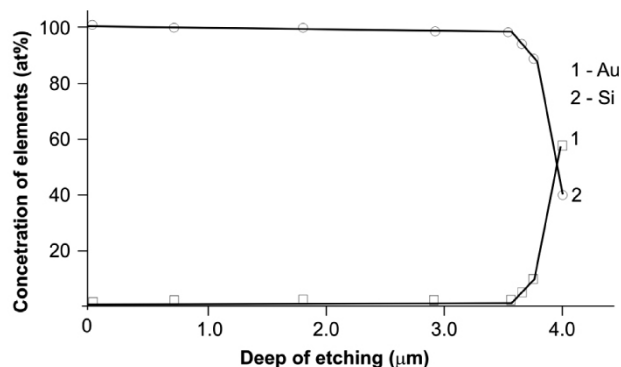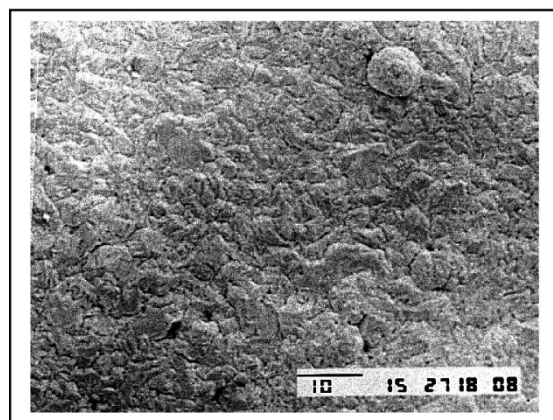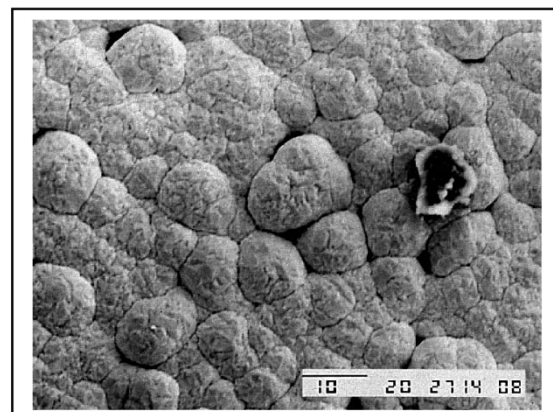
Figure 6. AES profile analysis of deposit; C_{Tl} = 3.75 10^{-4} mol dm^{-3} T = 343 K, i = 9.87 mA cm^{-2}, rotation speed 500 min^{-1}.

a

b

Figure 7. SEM analysis of deposit: (a) without Tl^+: T = 343 K, current density 1.5 mA cm^{-2}, rotation speed 500 min^{-1}, (b) with Tl^+ in electrolyte (C_{Tl+} = 3.75 10^{-4} mol dm^{-3}): T = 343 K, current density 9.87 mA cm^{-2}, rotation speed 500 min^{-1}.

The morphology of the surface has changed depending on the type of grinding, etching, alloying the vaporized gold as well as the electrochemical conditions of the experiment.[4,6] The gold deposit obtained from the electrolyte without thallium (Figure 7a) has a compact and small grained structure with an appropriate adhesion on the electrode surface. The addition of thallium electrolyte ensures the increase of the current density which influences the deposit morphology. Crystal grains are increased but the surface structure of the deposit is compact and nonporous (Figure 7b).

3. 3. Influence of the Rotation Speed

Polarization curves, obtained at different electrode rotation speeds, could be analyzed using the Levich equation.[18] For the first order reaction rate, with respect to the reacting ions ($Au(CN)^-_2$ in this case), current density could be expressed in the linearized form, as:[1,11]

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L} \tag{1}$$

Where: i, i_k and i_L represents total, kinetics and limiting current density, respectively.

Limiting current density is defined by well-known equation:

$$i_L = k_L zFC_o \tag{2}$$

Mass transfer coefficient k_L may be defined for a given geometrical and hydrodynamic conditions used in these experiments by the following equation:

$$Sh = \frac{0.554Pe^{1/2}Sc^{-1/6}}{0.8934 + 0.316Sc^{-1/3}} \tag{3}$$

In equation (3) Sherwood and Peclet numbers are defined based on the diameter of rotating electrode, i.e.:

$$Sh = \frac{k_L d}{D} \text{ and } Pe = \frac{\omega d^2}{D}$$

in which: d is the electrode diameter; D – diffusion coefficient and ω – angular velocity.

Solving the equation (3) explicitly for the mass transfer coefficient, and substituting the obtained term in equation (2), the following relationship is obtained:

$$i_L = \frac{0.554D^{2/3}v^{-1/6}\omega^{1/2}zFC_o}{0.8934 + 0.316Sc^{-1/3}} \tag{4}$$

Where Sc denotes Schmidt number, defined as Sc = ν/D.

Assuming constant physical characteristics of the electrolyte during the experiments (D = const; ν = const),

and keeping the concentration of reacting ions in the bulk at a constant value, the equation (1) may be reduced to the form:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{K}{\omega^{1/2}} \tag{5}$$

Where K represents the following term:

$$K = \frac{0.8934 + 0.316Sc^{-1/3}}{0.554zFC_oD^{2/3}v^{-1/6}} \tag{6}$$

Since the diffusion coefficient of $Au(CN)^{2-}$ solution is: $D = 1.67 \times 10^{-5}$ cm^2 s^{-1} and the corresponding kinematics viscosity[19] $v = 5.18 \times 10^{-3}$ cm^2 s^{-1}, the value of K may be estimated from equation (6) and inserted into the equation (5). According to equation (5), a plot of $1/i$ vs. $\omega^{-1/2}$ is established giving straight lines for three different electrode potentials, as presented in Figure 8, where the intercepts represent $1/i_k$ values and the slopes are values of K.
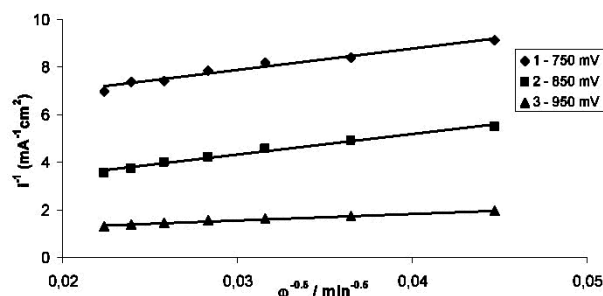

Figure 8. Dependence of i^{-1} on $\omega^{-0.5}$; solution 1, T = 298 K.

Lines 1 and 2 (Figure 8) are almost parallel, which results from the equation (5), while the line 3 has a lower slope value. Since all other variables constituting the term K were constant, it comes out that only the number of transferred charge z is changed. In the case of gold deposition from thallium free-electrolyte, the mechanism of discharging of $Au(CN)^-_2$ ions changes at higher potentials (around –950 mV). Similar effect has also been reported by Bindra et al.,[11] relating to a similar model system.

Undoubtedly, the reaction of gold reduction is the first order reaction with respect to the $Au(CN)^-_2$ ions. Though, with regards to the obtained voltammograms (Figure 1), we could not achieve a potential at which this reaction is entirely mass transfer controlled.

Equation (5) may also be applied for the solution containing thallium ions. This is illustrated in Figure 9.

One may conclude, with regards to the lines 3–5 in Figure 9, that the process occurs under the kinetic control at higher temperatures (> 333K). At lower temperatures a diffusion contribution increases (line 2), achieving a pure diffusion control at temperatures close to ambient temperature, as shown in Figure 9 line 1.
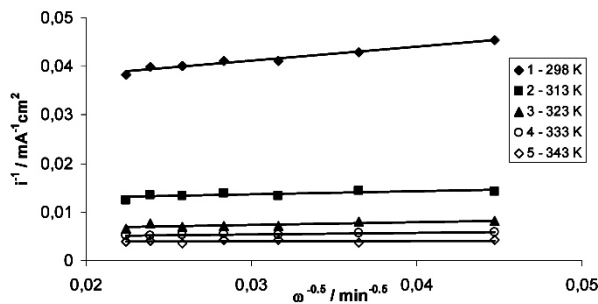
Figure 9. Dependence of i^{-1} on $\omega^{-0.5}$ given for different temperatures $C_{Tl^+} = 3.75 \times 10^{-5}$ mol dm^{-3}, E = 900 mV/$_{SCE}$.

3. 3. 1. Tafel Slopes

If the faradic charge transfer is the rate determining step, far from equilibrium so that the back reaction is assumed to be negligible, and for a mixed kinetics, the kinetic current density i_k is defined by Tafel equation, as:

$$i_k = i_o \exp[-\beta zF \frac{E - E_o}{RT}] \qquad (7)$$

Where: i_o is exchange current density, and
β – Coefficient of symmetry

Eliminating i_k by using equations (1) and (7), the following relationship is obtained:

$$\frac{i_L i}{i_L - i} = i_o \exp\left[-\beta zF \frac{E - E_o}{RT}\right] \qquad (8)$$

giving a connection between i and E, that could be linearized leading to the following expression:

$$\ln \frac{i}{i_L - i} = \ln \frac{i_o}{i_L} - \frac{\beta zF(E - E_o)}{RT} \qquad (9)$$

For a constant temperature the equation (9) gives a straight line in a semi-logarithmic scale, plotting the term $\log \frac{i}{i_L - i}$ against the electrode potential E, as shown in Fi-
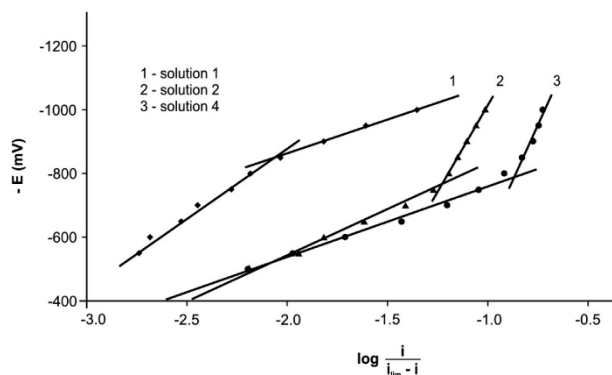

Figure 10. Dependence of E vs. $\log \frac{i}{i_L - i}$ at 298 K; polarization rate 20 mVs^{-1}, rotation speed 500 min^{-1}.

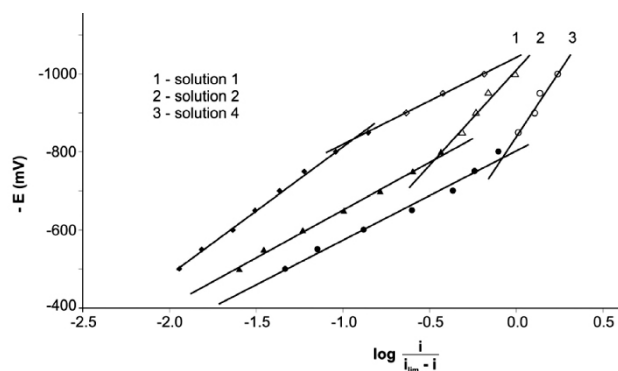gure 10, for the temperature of 298 K, and in Figure 11, for 343 K.

Figure 11. Dependence of E vs. $\log \frac{i}{i_L - i}$ at 343 K; solution 1, 2 and 3; polarization rate 20 mVs^{-1}; rotation speed 500 min^{-1}.

The addition of thallium strongly affects the shape of the curves, giving higher values of the slopes at potentials higher than 800 mV. Also, the potential at which the slope change occurs (curves 2 and 3 in Fig. 11) decreases in the presence of thallium in the electrolyte, indicating a change in reaction mechanism. Obtained Tafel slopes do not depend on the electrode rotation speed, but depend on the temperature as shown in Table 2.

Table 2. The values of the Tafel slopes at 298 and 343 K.

Line	Tafel slopes mV dec^{-1} (298 K)		Tafel slopes mV dec^{-1} (343 K)	
	First	Second	First	Second
1	440	214	326	222
2	290	1089	246	490
3	223	1380	229	680

The first linear part on curves 1, corresponding to the potentials above –800 mV, yields the Tafel slope of 440 mVdec^{-1} at 298 K and 326 mVdec^{-1} at 343 K. Such high Tafel slope values are difficult to interpret in terms of elementary charge transfer, but may be explained assuming a specific adsorption of charged intermediates, as has already been described.[3,11]

Obtained voltammograms, as well as the Tafel slope values, computed for the thallium free electrolyte, could be interpreted in such a way that both AuCN and CN$^-$ ions are adsorbed on the electrode, leading to a presumption that the reaction of gold deposition occurs through the following reaction steps:[7]

$$Au(CN)_2^- \quad \rightarrow \quad |AuCN|_{ad} + |CN|_{ad}^- \qquad (10)$$

Adsorbed AuCN will be reduced to the metallic Au at lower potentials, according to the following stoichiome-

tric equations:[6,9,10,19,20]

$$| AuCN |_{ad} + e^- \rightarrow (AuCN^-)_{ads} \qquad (11)$$

$$(AuCN^-)_{ads} + K^+ \rightarrow Au + KCN \qquad (12)$$

One can suppose that at more negative potentials, an existence of a ligand assisted charge transfer to a metal ion complex as $Au[CN]_2^-$ and the following stoichiometric equation:[3]

$$Au[CN]_2^- + e^- + 2K^+ \rightarrow Au + 2KCN \qquad (13)$$
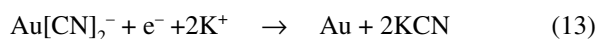
As a matter of fact, the current course in the potential range between –500 and –800 mV indicates an adsorption and discharging of the adsorbed $Au(CN)_2^-$ ions.[9,19,20] Since the value of obtained current density depends on the temperature, this indicates that the electrochemical deposition of gold most likely occurs via some intermediary compound.[5,21] Slope change of logarithm of current density that occurs at a potential close to –750 mV indicates a direct discharging process of the $Au(CN)_2^-$ ions. Accordingly $Au(CN)_2^-$ ions are transported to the electrode by the mass transport mechanism, as described by equation (13).

3. 3. 2. The Effect of Thallium Ions Concentration

The addition of thallium into the electrolyte significantly changes the Tafel slopes as well as the curves shape, affecting the exchange of both reaction mechanism and kinetics.[11] The potential at which this change occurs is shifted towards more positive values (see Table 3), but the slopes are much steeper, as presented in Table 2.

Table 3. Potential of the slope change (evaluated from Figures 10 and 11).

Line	-ESCE/mV at 298 K	-ESCE/mV at 343 K
1	740	837
2	683	786
3	697	784

The reaction kinetics of gold deposition apparently changes. As it has already been mentioned, limiting current density has not been observed using pure citrate electrolytes with no thallium.

The potential value of gold deposition, in thallium free citrate solution, is about –850 mV/$_{SCE}$. With thallium addition the deposition potential is shifted towards more positive values (Figure 5), and the current density increases simultaneously. The current density shows higher values, with increasing the concentration of thallium, approaching to a certain maximum value. It could be assumed that higher concentrations of thallium would not affect an ad-

ditional change neither of current density nor of deposition potential of gold.

At lower temperatures no remarkable effect of thallium on the current density was detected. However, at elevated temperatures a linear relationship (in semi-logarithmic scale), between i and C_{Tl}^+ exists within the potential range from –800 to –850 mV/$_{SCE}$, but at the reverse branch of the polarization curves (Figure 12).
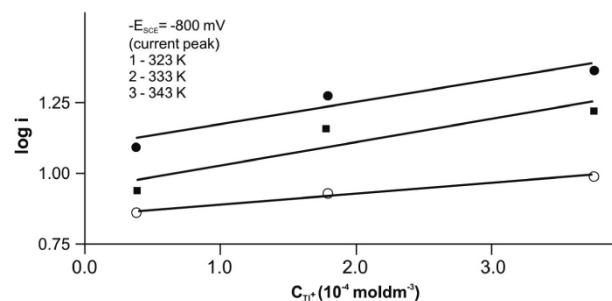

Figure 12. Influence of Tl^+– ions concentration on the current density; polarization rate 20 mVs^{-1}, rotation speed 500 min^{-1}

In fact, Tl^+ – ions exhibit high hydrogen overpotential and therefore inhibit it's evolution during the gold deposition process. It is obvious that the presence of thallium influences the current efficiency. Voltammetric measurements, in the presence of thallium, show that the catalytic effect depends on the temperature at which the deposition occurs (Figure 7). It is clear from the graphs that the catalytic effect of thallium does not occur at 298 K. However, in citrate solution it is present even at lower temperatures (at 313 K or even lower).

The absence of catalytic effect of adatoms at lower temperatures can be explained by the fact that AuCN and $Au(CN)^-$ have a stronger adsorption force than an adatom. This also proves that catalytic effect of adatom is not connected to the increase on the number of places for 2D nucleation in the presence of adatoms. If this causes the catalytic effect, it should occur at lower temperatures.[5]

4. Conclusions

The mechanism of electrochemical deposition of gold from citrate solutions depends on the electrolyte composition and applied potential. During the electrode polarization, in citrate electrolytes, limiting current density is not obtained at the potentials performed.

In the thallium free electrolyte, a mechanism of adsorption of $Au(CN)^-$ and CN^- ions is supposed, as well as the formation of $AuCN_{ad}$ species, followed by their reduction to the metallic Au.

At the same time, the addition of thallium ions to the electrolyte affects higher current density of gold deposi-

tion, changing the deposition mechanism due to their catalytic effect.

It was observed that adsorption/desorption of thallium ions on the electrode, occurs at potential of about –800 to –850 mV_{SCE}. A linear relationship between current density and thallium ion concentration in a semi-logarithmic scale has been observed as well.

5. Acknowledgment

6. List of Symbols

C_o	bulk concentration of $Au(CN)_2^-$ [mol dm^{-3}]
D	diffusion coefficient of $Au(CN)_2^-$ [cm^2 s^{-1}]
E	electrode potential [mV]
F	Faraday's constant [C mol^{-1}]
i	current density [mA cm^{-2}]
i_k	kinetic current density [mA cm^{-2}]
i_L	limiting current density for gold deposition [mA cm^{-2}]
i_o	exchange current density [mA cm^{-2}]
k_s	reaction rate constant [s^{-1}]
R	universal gas constant [JK^{-1} mol^{-1}]
z	charge trasfer number
β	coefficient of symmetry
ν	kinematics viscosity of solution [cm^2 s^{-1}]
ω	rotation speed [min^{-1}]

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Povzetek

Z uporabo rotirajoče disk elektrode (RDE) ter ciklične voltametrije smo proučevali depozicijo zlata iz raztopine amonijevega citrata z in brez prisotnosti talijevega nitrata. RDE smo izdelali iz monokristalnega silikonskega materiala, ki smo ga s pomočjo parnega nanosa prevlekli s tanko plastjo zlatega filma, ki je služil kot substrat pri elektrokemijski depoziciji zlata. Niti v čisti raztopini citratata niti ob prisotnosti talijevih ionov nismo dosegli limitne gostote toka. Izkazalo se je, da hitrost vrtenja RDE bistveno vpliva na proces odlaganja zlata le pri nižjih temperaturah. Naklon Taflovega diagrama kaže, da elektrokemijski proces poteka v dveh stopnjah in je odvisen tako od elektrodnega potenciala kot tudi od prisotnosti talijevih ionov. Mehanizem depozicije zlata je najbolj odvisen od sestave raztopine elektrolita. V raztopini citrata brez prisotnega talijevih ionov predpostavljamo adsorpcijo $AuCN_{ad}$ speciesov na površini elektrode, ki se potem razgradijo do kovinskega zlata. Prisotnost talijevih ionov v raztopini pri potencialu –750 mV/SCE vodi do adsorpcije talijevih ionov na površini elektrode vendar niti AES niti SEM analiza nista pokazali prisotnosti talija v odloženi plasti zlata.