ABSTRACT

A new, simple and cost-effective electrochemical route was demonstrated in this work. CdS and PbS thin films were grown on polycrystalline gold electrode using co-deposition and ECALE techniques based on accumulation layer by layer. The deposition potentials of cadmium, lead and sulfur were determined separately by cyclic voltammetry. Thin films were created from an electrolyte containing 0.01 mol L\(^{-1}\) CdSO\(_4\), 0.01 mol L\(^{-1}\) Na\(_2\)S and 0.01 mol L\(^{-1}\) Pb(CH\(_3\)COO)\(_2\) in 0.01 mol L\(^{-1}\) EDTA (pH = 3.00). The influence of bath temperature at the deposition potential was studied to determine the crystallinity of deposits. From the chronoamperometry results including the transients which were obtained within the under potential region, the overall shape of the experimental depositions was proposed and the growth process was considered.

Key Words
Underpotential deposition, co-deposition, ECALE.

ÖZ

Bu çalışmada yeni, basit ve uygun maliyetli bir elektrokimyasal rutin gösterildi. CdS ve PbS ince filmler polikristalin altın elektrot üzerinde tabaka tabaka birikirme temeliyle ko-depozisyon ve ECALE teknikleri kullanılarak büyütüldü. Kadmiyum, kurşun ve sülfürün birikirme potansiyelleri ayrı ayrı dönüşümlü voltammetri ile belirlendi. Ince filmler 0.01 mol L\(^{-1}\) EDTA'da (pH = 3.00) 0.01 mol L\(^{-1}\) CdSO\(_4\), 0.01 mol L\(^{-1}\) Na\(_2\)S ve 0.01 mol L\(^{-1}\) Pb(CH\(_3\)COO)\(_2\) içeren elektrolitten oluşturuldu. Birikirme potansiyelindeki sıcaklık etkisi birikintilerin kristallikmini belirlenmesi için çalışıldı. Potansiyel altı alanı içerisinde elde edilen geçişleri kapsayan kronoamperometri sonuçlarından, deneySEL birikimlerin genel şekilleri önerildi ve büyüme süreci değerlendirildi.

Anahtar Kelimeler
Potansiyel altı birikirme, ko-depozisyon, ECALE.

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INTRODUCTION

Cadmium (Cd) and lead (Pb) are electroactive heavy metals, so they can be detected electrochemically. The monitoring of Cd and Pb using sensitive, inexpensive and portable electrochemical methods is an attractive way to determine hazardous heavy metals [1]. At the same time, II-VI semiconductors like cadmium sulfide (CdS) have a wide application in the non-linear optical materials, solar cells, light-emitting diodes, electronic and optoelectronic devices [2] and IV-VI semiconductors like lead (II) sulfide (PbS) are also focused on field-effect thin film transistors, single-electron transistors and flat-panel displays [3]. In such an important field, deposition of these materials is coming into prominence and electrochemistry is a good alternative to conventional deposition methods with a number of advantages such as film thickness control, operation at ambient temperature and pressure [4, 5].

Under potential deposition (UPD) is an electrodeposition technique based on the reduction of a metal cation to a solid metal at a more positive potential than the equilibrium (Nernst) potential for the reduction of this metal [6]. UPD is generally occurs as a result of a strong interaction between the electrodepositing metal (M) and the substrate (S) which is used to construct the electrode. The M-S interaction must be energetically active to the M-M interaction in the crystal lattice of the pure M. Such a process is developed by the observation of UPD which can occur up to a monolayer or two monolayers of M. The reference point for the UPD is characterized by the electrodeposition of M on a S of the same M taking place at an equilibrium potential [7].

As one of the UPD method, electrolytic co-deposition is an electroplating method which consists of the mixing of non-metallic particles into metallic coatings obtained from electrolytes containing the particles in a suspended state [8]. The second phase particles like ethylenediaminotetraacetic acid (EDTA) which dispersed within the metal base such as Cd and Pb form a metal matrix composite (CdEDTA2- and PbEDTA2-) and these composites may show different properties from those of the pure metallic deposits (Cd²⁺ and Pb²⁺). This method is widely applied to create CdS [9] and PbS [10] thin films in single-crystalline forms, but a little effort is made to overcome the problem of polycrystalline deposits.

Electrochemical atomic layer epitaxy (ECALE) is an atomic layer deposition technique based on UPD where an atomic layer of the element is deposited on the surface by an electrochemical surface limited reaction using an electrochemical cell, at an electrode potential lower than it is needed to deposit the element on itself [11]. In ECALE of CdS and PbS: an atomic layer of cadmium or lead is deposited, followed by an atomic layer of sulfur deposition on the cadmium or lead, and then one of cadmium or lead is again deposited on the sulfur as proposed by Stickney [12].

In this work, the electrodepositions of cadmium and lead together with sulfur onto polycrystalline gold electrode were compared using various techniques including co-deposition and ECALE for the first time. Bulk electrolysis and cyclic voltammetry techniques were applied to determine key parameters such as the deposition potential, deposition time and the effect of temperature. At the same time, chronoamperometry method was used to define the dimensionality of the resulting deposits. The present work mainly aims using of polycrystalline surfaces instead of single crystal surfaces which possess a time-consuming preparation procedure to detect not only hazardous heavy metals, but also to create binary systems and thin films by proposed practical new approach.

MATERIALS and METHODS

Chemicals

Before starting the analysis, gold electrode was mechanically polished with 0.05 and 1.00 μm superfine alumina (Al₂O₃) powders and then cleaned electrochemically with successive cycling in 1.00 molL⁻¹ sulphuric acid (H₂SO₄) solution from Sigma-Aldrich between -0.20 V and +1.50 V versus Ag/AgCl until a steady state current was obtained. The prepared 0.01 molL⁻¹ EDTA at pH = 3.00 was used as a supporting electrolyte. Cadmium sulfate (CdSO₄), sodium sulfide (Na₂S) and lead (II) acetate (Pb(CH₃COO)₂) solutions from Sigma-Aldrich were prepared in the concentration amount of 0.01 molL⁻¹. All the other reagents were in analytical grade. At the beginning of analysis, pure N₂ gas was passed from all of the prepared solutions for sufficient period of time to extract oxygen.
Instruments

Bulk electrolysis and cyclic voltammetry techniques were performed on CH Instruments CHI660C model potentiostat in the three electrode setup for electrochemical cells comprising platinum (Pt) wire as the counter electrode, silver/silver chloride (Ag/AgCl) as the reference electrode and gold (Au) electrode with 0.03 cm² area as working electrode. Bulk electrolysis was done at -0.35 V versus Ag/AgCl for Cd, -0.52 V versus Ag/AgCl for S and -0.10 V for Pb versus Ag/AgCl for 10 minutes. Cyclic voltammetry was applied between +0.25 V and -1.60 V versus Ag/AgCl for 10 cycles, and the direction of potential scan was from negative to positive. Chronoamperometry technique was performed between +0.10 V and -0.35 V versus Ag/AgCl for Cd, +0.60 V and -0.43 V versus Ag/AgCl for Pb.

Mechanism of co-deposition and ECALE of cadmium sulfide and lead (II) sulfide

In the mechanism of co-deposition, the second phase particles (EDTA) suspended in the electrolyte adsorb the positively charged metal ions (Cd²⁺ and Pb²⁺). The metal ions enclose the EDTA particles and the resulting complexes (CdEDTA²⁻ and PbEDTA²⁻) arrive at the cathode taking action by the electrostatic attraction and the electrolyte convection. The particles stayed at the cathode surface discharge and the three related interfacial energies including particle-electrolyte, particle-cathode and cathode-electrolyte help to retain the particles on the surface by the bonding force. The metal ions are deposited on the cathode surface around the particles mixing into the metallic deposits. In the case of sulfur, anodic deposition is obtained on the anode surface.

RESULTS and DISCUSSION

UPD of cadmium, sulfur and lead

The formation of the first monolayer is inferred from the declared current peaks at the potential $E > E_{\text{rev}}$, while the bulk deposition occurs at $E < E_{\text{rev}}$, where $E_{\text{rev}}$ specifies the Nernstian equilibrium potential [13]. As it is known, $E_{\text{rev}}$ is ~0.46 V versus Ag/AgCl for Cd/Cd²⁺ and ~0.19 V versus Ag/AgCl for Pb/Pb²⁺. In (Figure 1 A), cyclic voltammogram...
of Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ was compared with bare Au electrode behavior in 0.01 molL⁻¹ EDTA, and bulk potential of Cd was obtained at −0.55 V (less than −0.46 V) versus Ag/AgCl, UPD potential at −0.35 V (more than −0.46 V) versus Ag/AgCl [14]. In (Figure 1 C), cyclic voltammogram of Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Pb(CH₃COO)₂ was compared with bare Au electrode behavior in 0.01 molL⁻¹ EDTA. A broad peak was observed between −0.20 V and 0.00 V versus Ag/AgCl, but two side by side peaks were actually gained. Bulk potential of Pb was obtained at −0.23 V (less than −0.19 V) versus Ag/AgCl, UPD potential at −0.10 V (more than −0.19 V) versus Ag/AgCl [15]. In the case of S, cyclic voltammogram of Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Na₂S was compared with bare Au electrode behavior in 0.01 molL⁻¹ EDTA, but anodic potentials were estimated instead of cathodic potentials (Figure 1 B). The bulk potential of S was obtained at −1.00 V versus Ag/AgCl, UPD potential at −0.52 V versus Ag/AgCl and all results were essentially identical to that reported in literature [16].

Co-deposition versus ECALE
Cyclic voltammetric responses of Au electrode using co-deposition method based on deposition from the same solution of the precursors of the target compound at a constant UPD potential, and using ECALE method based on deposition of each element from their separate solutions at the UPD potential of each element were represented in (Figure 3). In co-deposition method (a), S UPD (−0.52 V versus Ag/AgCl) disappeared, but in ECALE behavior of S over Cd modified Au electrode (c), both Cd (−0.35 V versus Ag/AgCl) and S UPD peaks were observed by a sharper result than Cd over S modified Au electrode (b) presenting the layer formation of S over Cd modified Au electrode (Figure 3A). In the mechanism of CdS electrodeposition, Cd reduction (Cd²⁺ + 2e⁻ = Cd(UPD)) and S oxidation (S²⁻ = S(UPD) + 2e⁻) occurred as 1:1. An atomic layer of S was deposited on one of Cd, and one of Cd was deposited on one of S.

In the case of Pb and S co-deposition method (a), both Pb and S UPD peaks were observed at the actual UPD potentials of Pb (−0.10 V versus Ag/AgCl) and S (−0.52 V versus Ag/AgCl) and the methodological difference in the voltammetric behavior of Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S (Figure 2 A) and in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Na₂S and 0.01 molL⁻¹ Pb(CH₃COO)₂ (Figure 2 B) was determined, and the UPD peaks of Cd, S and Pb were lost in the event of bulk electrolysis. Therefore, the layer formation was performed by increasing number of cycle. The phase purities of CdS and PbS deposited on polycrystalline Au electrode were uniform, so flower-like structures were proposed at long-deposition times [17].

Bulk electrolysis versus cyclic voltammetry
After the determination of UPD potentials of Cd, S and Pb, the deposition of species were made using both bulk electrolysis and cyclic voltammetry techniques. Bulk electrolysis was applied at −0.35 V versus Ag/AgCl for Cd, −0.52 V versus Ag/AgCl for S, −0.10 V versus Ag/AgCl for Pb for 10 minutes while cyclic voltammetry was applied between +0.25 and −1.60 V versus Ag/AgCl for 10 cycles. The methodological difference in the voltammetric behavior of Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S (Figure 2 A) and in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Na₂S and 0.01 molL⁻¹ Pb(CH₃COO)₂ (Figure 2 B) was determined, and the UPD peaks of Cd, S and Pb were lost in the event of bulk electrolysis. Therefore, the layer formation was performed by increasing number of cycle. The phase purities of CdS and PbS deposited on polycrystalline Au electrode were uniform, so flower-like structures were proposed at long-deposition times [17].
versus Ag/AgCl), but in ECALE result of Pb over S modified Au electrode (b), UPD potential of Pb shifted more negative potential (−0.20 V versus Ag/AgCl) weakening the interactions of Pb with the substrate [18], and in S over Pb modified Au electrode response by ECALE (c), Pb UPD was lost (Figure 3B). Therefore, PbS layer was created using co-deposition technique from the same solutions of Pb and S. In the mechanism of PbS electrodeposition, Pb reduction (\( \text{Pb}^{2+} + 2e^- = \text{Pb(UPD)} \)) and S oxidation (\( \text{S}^{2-} = \text{S(UPD)} + 2e^- \)) occurred as 1:1. An atomic layer of S was deposited on one of Pb, and one of Pb was deposited on one of S.

The effect of bath temperature on UPD

The influence of bath temperature on UPD was studied and the bath temperature was varied from 25°C to 40°C to examine the change of composition and microstructure of the deposits. In (Figure 4), the current intensitites of bare Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄, S over Cd modified Au electrode B), and Cd and S co-deposited Au electrode C) in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S were compared. When the bath temperature was increased from 25°C to 40°C (d→a), the potentials shifted to more positive direction, the intensity of the peaks increased gradually for both bare Cd A) and S over Cd B) behaviors, particularly at 40°C the current rised from \( 6.6 \times 10^{-5} \) A to \( 7.4 \times 10^{-5} \) A obviously. In the case of Cd and S co-deposition C), the peak current at 30°C reached its maximum value randomly and a general roll-off rate was observed. Therefore, the layer formation of CdS was carried out using ECALE technique as in UPD results of S over Cd modified Au electrode, and the increase of the bath temperature improved the crystallinity of the CdS deposit [19].

![Figure 3. Cyclic voltammograms of coated Au for 10 cycles in A) 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S using (a) Cd and S by co-deposition, (b) Cd over S by ECALE, (c) S over Cd by ECALE techniques, and B) 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Na₂S and 0.01 molL⁻¹ Pb(CH₃COO)₂ using (a) Pb and S by co-deposition, (b) Pb over S by ECALE, (c) S over Pb by ECALE techniques between +0.25 and -1.60 V versus Ag/AgCl at a scan rate of 100 mV s⁻¹.](image)

![Figure 4. Cyclic voltammograms of coated Au for 10 cycles A) in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄, B) using S over Cd by ECALE, C) using Cd and S by co-deposition techniques in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S between +0.25 and -1.60 V versus Ag/AgCl at a scan rate of 100 mV s⁻¹, and at a bath temperature of (a) 4°C, (b) 35°C, (c) 30°C, (d) 25°C.](image)
(Figure 5) demonstrated the current intensity changes of bare Au electrode in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Pb(CH₃COO)₂, A), S over Pb modified Au electrode B), and Pb and S co-deposited Au electrode C) in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ Pb(CH₃COO)₂ and 0.01 molL⁻¹ Na₂S. As the bath temperature increased from 25°C to 40°C (d→a), the intensity of the peaks increased gradually for both bare Pb A) and S over Pb B) behaviors. When Pb UPD peak at −0.10 V versus Ag/AgCl was taken into account, no peak was observed for S over Pb modified Au electrode B). At the lower bath temperatures (c, d), the content of elemental Pb was slightly greater than that of S A) reaching its current maximum (−1.80 × 10⁻⁵ A) and at the higher bath temperatures (a, b) the content of elemental Pb (−2.60 × 10⁻⁵ A) was slightly less than that of S (+3.40 × 10⁻⁵ A) C). Therefore, the layer formation of PbS was carried out using co-deposition technique as in UPD results of Pb and S co-deposited Au electrode, and the bath temperature had an influence on the composition of the deposited films.

Kinetics of the electrodepositions

Electrodeposition takes place by a process of nucleation on which appears at active sites on the substrate due to nucleation rate law, and growth which occurs by growing via the incorporation of further ions from the solution. Nucleation and growth can be divided into sub-categories such as interfacial controlled and diffusion controlled. In the former, the nucleus growth rate is limited by the speediness at which ions can be incorporated into the new phase. In the later, nucleus growth is limited by the rate at which material is transported through the solution to the electrode surface [20]. The number of various models has been proposed to decide the dominance of adsorption-desorption or nucleation and growth on the chronoamperometric response of systems. Among these models, the evaluation of the current density as the sum of two independent terms, a Langmuir type adsorption-desorption term and a nucleation growth term \( j_{\text{total}} = j_{\text{ads}} + j_{\text{nucl/growth}} \) is the simplest one. Such an approach can be applied on the basis where adsorption is typically a rapid process, while nucleation and growth develop more slowly due to kinetic limitations. In the Butler-Volmer model, adsorption-desorption is followed by surface diffusion control of monolayer nucleation and growth [21]. In cases where the two processes are not decoupled, a more complex model such as that of Bosco and Rangarajan is required [22].

In (Figure 6), chronoamperometric results of bare Au A), and coated Au for 10 cycles B) in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄, coated Au for 10 cycles using Cd and S by co-deposition C), and coated Au for 10 cycles using Cd over S by ECALE D) techniques in 0.01 molL⁻¹ EDTA containing 0.01 molL⁻¹ CdSO₄ and 0.01 molL⁻¹ Na₂S were estimated. In all conditions, the current density \( j \) decreased as a function of elapsing time \( t < 0.03 \) s, right from the start of the transient resulted in no nucleation model giving a clear description of the transient shape. For \( t > 0.03 \) s, the shape of transient supported the formation and growth of 2D nuclei, limited by ad-atom incorporation. As it could be seen in (Figure 6) from B) to D), a current enhancement appeared in Cd monolayer formation and it proceeded by a two-step mechanism involving Langmuir-type adsorption accompanied by nucleation and two dimensional growth. Therefore, Cd deposition was described by the
model \( j_{\text{total}} = j_{\text{AD}} + j_{\text{2D}} \) used by Hölzle et al. [23] in which the electrodeposition process \( j_{\text{total}} \) was the linear sum of a Langmuir-type adsorption term \( j_{\text{AD}} \) and a 2D nucleation process \( j_{\text{2D}} \).

In order to analyze the experimental data by usual procedures, the plots of \( i / t^{1/2} \) for bare Au A) and coated Au for 10 cycles B) in 0.01 mol L\(^{-1}\) EDTA containing 0.01 mol L\(^{-1}\) CdSO\(_4\), coated Au for 10 cycles using Cd and S by co-deposition C), and coated Au for 10 cycles using Cd over S by ECALE D) techniques in 0.01 mol L\(^{-1}\) EDTA containing 0.01 mol L\(^{-1}\) CdSO\(_4\) and 0.01 mol L\(^{-1}\) Na\(_2\)S recorded between (a) +0.10 V and −0.35 V versus Ag/AgCl and (b) −0.35 V and +0.10 V versus Ag/AgCl were given in (Figure 7).

The resulting straight line in all curves (Table 1) showed a diffusion-controlled process according to the Cottrell equation [24] and the higher the slope of graph was obtained in (Figure 7 A) because of the metal ion behavior of Au. For the electrodeposition of Cd from B) to D), the slopes namely diffusion coefficients \( D \sim 1/\eta \) reduced normally because of the absolute viscosity \( \eta \) which was greater for thin films in comparison with free metals.

For the higher potentials, nucleation and growth properties come forward in the chronoamperometry; the reduction current increases until it reaches a maximum with a later decline with time and diffusion becomes the rate-limiting process. Different nucleation and
growth mechanisms were considered in the analysis of the potential step data, and the experimental data was found to be best described using the 3D instantaneous, diffusion-controlled nucleation and growth mechanism [25].

(Figure 8) represented chronoamperometric responses of bare Au A) and coated Au for 10 cycles B) in 0.01 molL\(^{-1}\) EDTA containing 0.01 molL\(^{-1}\) Pb(CH\(_3\)COO)\(_2\), coated Au for 10 cycles using Pb and S by co-deposition C), and coated Au for 10 cycles using Pb over S by ECALE D) techniques in 0.01 molL\(^{-1}\) EDTA containing 0.01 molL\(^{-1}\) Pb(CH\(_3\)COO)\(_2\) and 0.01 molL\(^{-1}\) Na\(_2\)S. A current decline from A) to C) was observed by Pb monolayer formation, but when Pb monolayer was formed over S modified Au electrode D), the current increased again. It proceeded by a two-step mechanism involving 3D instantaneous, diffusion-controlled nucleation and growth mechanism.

In (Figure 9), the plots of \(I\) versus \(t^{1/2}\) and \(t^{-1/2}\) for bare Au A) and coated Au for 10 cycles B) in 0.01 molL\(^{-1}\) EDTA containing 0.01 molL\(^{-1}\) Pb(CH\(_3\)COO)\(_2\), coated Au for 10 cycles using Pb and S by co-deposition C), and coated Au for 10 cycles using Pb over S by ECALE D) techniques in 0.01 molL\(^{-1}\) EDTA containing 0.01 molL\(^{-1}\) Pb(CH\(_3\)COO)\(_2\) and 0.01 molL\(^{-1}\) Na\(_2\)S recorded between +0.60 V and (a) −0.43 V versus Ag/AgCl, (b) −0.44 V versus Ag/AgCl, (c) −0.45 V versus Ag/AgCl, (d) −0.46 V versus Ag/AgCl were indicated.

Table 1. Equations and coefficients of determination for the plots of \(I\) versus \(t^{1/2}\)

<table>
<thead>
<tr>
<th>Potential Range (V)</th>
<th>Bare Au</th>
<th>Au in CdSO(_4)</th>
<th>Cd and S co-deposited on Au</th>
<th>Cd over S by ECALE on Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.10 – (-0.35)</td>
<td>(y=0.1228x-0.1396) (R^2=0.9943)</td>
<td>(y=0.3714x+0.2626) (R^2=0.9991)</td>
<td>(y=0.1541x-0.0247) (R^2=0.9928)</td>
<td>(y=0.2121x+0.0888) (R^2=0.9986)</td>
</tr>
<tr>
<td>-0.35 – (+0.10)</td>
<td>(y=-0.0826x+0.1599) (R^2=0.9656)</td>
<td>(y=-0.3408x+0.4747) (R^2=0.9965)</td>
<td>(y=-0.1183x+0.0148) (R^2=0.9963)</td>
<td>(y=-0.1930x+0.2610) (R^2=0.9878)</td>
</tr>
</tbody>
</table>
For only (Figure 9 A), the graph of $I$ versus $t^{1/2}$ was drawn because of the bent curve of $I$ versus $t^{-1/2}$, and the resulting linearity was obtained by the bare Au (Table 2). For the electrodeposition of Pb from B) to D), the diffusion coefficients ($D \sim 1/\eta$) based on the slopes declined normally because of the absolute viscosity ($\eta$) which was greater for deposits in comparison with free metals B).

**Conclusion**

A simple and new route for the electrodeposition of CdS and PbS based on co-deposition and ECALE techniques was improved as a one-step and cost-effective process. Two different methods to produce semiconducting materials were examined in detail onto polycrystalline electrodes for the first time. Various electrochemical deposition processes such as bulk electrolysis and cyclic voltammetry were used to determine the best layer formation. The effect of bath temperature on UPD was studied to estimate the quality and crystallinity of deposits, and the temperature results were in a good correlation with UPD responses of CdS and PbS. To decide the kinetic behaviors of deposits, another electrochemical technique namely which was chronoamperometry was performed, and two-step mechanism involving adsorption accompanied by nucleation and growth was obtained. In summary, UPD was applied on both pure metals and deposits by means of this work,
Figure 9. The plots of I versus $t^{1/2}$ and $t^{-1/2}$ indicating the current transients of bare Au A), coated Au for 10 cycles B), coated Au for 10 cycles using Pb and S by co-deposition C), and coated Au for 10 cycles using Pb over S by ECALE D) recorded between four potential ranges (+0.60 V - (-0.43 V), (-0.44 V), (-0.45 V), (-0.46 V) versus Ag/AgCl), see in (Figure 8). Two lines surrounding markers showed the linearity ($R^2$ in Table 2) and straight line passing through the points.

Table 2. Equations and coefficients of determination for the plots of I versus $t^{1/2}$ and I versus $t^{-1/2}$.

<table>
<thead>
<tr>
<th>Potential Range (V)</th>
<th>Bare Au</th>
<th>Au in Pb(CH₃COO)₂</th>
<th>Pb and S co-deposited on Au</th>
<th>Pb over S by ECALE on Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.60 - (-0.43)</td>
<td>$y=-2.7545x+1.7783$</td>
<td>$y=1.4679x-1.7302$</td>
<td>$y=1.2905x-0.0938$</td>
<td>$y=1.1969x-0.6208$</td>
</tr>
<tr>
<td></td>
<td>$R^2=0.9955$</td>
<td>$R^2=0.9992$</td>
<td>$R^2=0.9989$</td>
<td>$R^2=0.9993$</td>
</tr>
<tr>
<td>+0.60 - (-0.44)</td>
<td>$y=-2.8487x+1.7739$</td>
<td>$y=1.2163x-1.345$</td>
<td>$y=0.9104x+0.0869$</td>
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<td>$R^2=0.9983$</td>
<td>$R^2=0.9997$</td>
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<td>$y=0.7709x+0.3862$</td>
<td>$y=0.8615x-0.1841$</td>
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<tr>
<td></td>
<td>$R^2=0.9959$</td>
<td>$R^2=0.9982$</td>
<td>$R^2=0.9987$</td>
<td>$R^2=0.9998$</td>
</tr>
<tr>
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<td>$y=0.6849x+0.6410$</td>
<td>$y=0.8143x-0.1690$</td>
</tr>
<tr>
<td></td>
<td>$R^2=0.9969$</td>
<td>$R^2=0.9987$</td>
<td>$R^2=0.9973$</td>
<td>$R^2=0.9999$</td>
</tr>
</tbody>
</table>
so the proposed method may serve as a model for semiconducting industry and environmental science.

References