

Electrochemical Studies of Simple Element Films: Cu, Sn, and Zn Prepared by Electrodeposition for Photovoltaic Application

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Abstract— In the perspective to contribute to the study of the development of thin films semiconductors for the photovoltaic, we proposed to study the electrodeposition of simple elements in order to bring more information to understand the mechanisms of the elaboration of ternary and quaternary compounds. The electrodeposition of copper, tin, and zinc as a simple element was studied using the cyclic voltammetry and ICP analyses and confirmed by using the gold electrode as a comparison system. The effect of the complexing agent (sodium citrate) was characterised by cyclic voltammetry. In this work, we report the influence of the deposition potential of the electrodeposition process and the composition films. The experimental results show that the electrochemical behaviour of Cu, Zn and Sn electrodeposits varied with the complexing agent. The ICP measurement showed that the composition of copper, zinc and tin thin films was varied with the applied potential and it confirmed the electrodeposition. This work will be followed by another work devoted to the sulphur electrodeposition. Contrary to the first three elements mentioned above, the sulphur remains an element less, if not studied by the electrochemical deposition.

Keywords— Electrodeposition, Complexing Agent, Thin films, Deposition Potential, ICP, CZT, Photovoltaic.

I. INTRODUCTION

While fossil fuels end up with contaminating the global environment and changing the global climate, photovoltaics remains one of the clean energy options for a pollution-free globe and is going to be the major means of the future energy-harvesting system. Solar cells utilise the mechanism of photovoltaic effect and convert sunlight directly into electricity without any intermediate steps [1]. The solar cells based on single-crystal silicon were known by their high efficiency on electricity production. In order to increase the use of solar power, there is a need for new technologies to both decrease the cost and increase the efficiency of photovoltaics. Thin film solar cells offer the opportunity to lower the price of solar energy by using small amounts of materials and low-cost manufacturing technologies. A lot of studies have focused on semiconductor thin films deposition, some researchers have

adopted non-vacuum approach owing to low cost and simple process which includes spin coating and microwave-assisted solution method [2][3][4], sputtering techniques [5], drop coating [6], spray pyrolysis [7], and electro and photochemical deposition [8]–[11]. Many semiconductors are employed for replacing silicon cells, including binary compounds like ZnO [12], CdS [13] and CdTe [14]..., ternary as CIS [15] and quaternary thus CIGS [8] and CZTS [16].

Copper, zinc, tin, sulphur (CZTS), is a semiconductor with a band gap of about 1.5 eV, which makes it suitable for incorporation in photovoltaic devices, as an absorber in thin films solar cells. Moreover, the abundance of its elements and its non-toxicity makes it an excellent candidate for large scale utilisation [17]. Many physical and chemical techniques have been employed for preparing CZTS thin films as a light absorber. In this field the electrochemical route appears of great interest because it is easy to conduct, it is a non-vacuum and low-cost technology, working at room temperature and using non-toxic solvents and reagents, with high throughput and high materials utilisation. Moreover, the electrodeposition has the advantage of being an industrially established process of a large area semiconductor deposition with superior uniformity in composition. There are two different electrochemical approaches to form CZTS thin films: a single step electrodeposition method that provides all constituents from the same electrolyte and sequential electroplating, where to make the final film, different layers were deposited in sequence. The CZTS thin films have been synthesised by electrodepositing S/Sn/S/Cu/S/Zn/S/Cu-layers [18] or by sequential electrodeposition of the constituent metals followed by annealing in sulphur sources (sulphur vapour and H₂S) [16][17]. The electrodeposition can be made with a pulsed and direct current [21], [22].

This paper reports on the electrodeposition of Copper, Zinc and Tin as a simple element, on ITO, coated glass substrates and on Gold.

The plan is to start with managing the electrodeposition of simple elements thin films on conductive glass by modulating the parameters that influence the electrodeposition, such as supporting electrolyte, pH, annealing time and deposition time for reaching finally, the suitable deposition potential for each element, and thereafter, simplifying the explication of the electrodeposition process of binary and ternary elements. In addition, in the end, achieve our major goal, which is the realisation of thin films quaternary semiconductors. In this article, we were limited to the studies of the elements Cu, Zn, Sn. A next article will be reserved to the electrodeposition of sulphur to complete the study of the four elements compounds CZTS.

Typically, the experimental approaches habitually used to achieve the electrochemical studies of the deposit are surface analyses by SEM, XPS, and EDX.... Our approach based on the utilisation of the electrodeposition on the gold electrode as an electrochemical comparison system and the use of the ICP analysis as an analysis method of the coating composition constitutes an original contribution to the study of the thin films electrodeposition mechanisms. Cyclic Voltammetry proves the electrochemical studies on an ITO coated glass substrate and a gold electrode. In both cases, the confirmation of the materials deposition obtained using the ICP analytical method. The work extension to the ICP analysis was to provide more data and details for explaining the electrodeposition.

II. EXPERIMENTAL DETAILS

Cyclic voltammetry and electrodeposition experiments were performed using a potentiostat/galvanostat AUTOLAB (Metrohm-Autolab, Utrecht Netherlands) PGSTAT302N controlled by GPES and FRA software version 4.9, connected to a three-electrode cell. In all electrochemical experiments, the working electrode was Indium tin oxide (ITO)-coated glass substrate with a deposition area of 1 cm^2 and a Gold electrode 2 mm^2 . Before experiments, the ITO glass working electrodes were cleaned by a pre-treatment consisting in an ultrasonic degreasing in organic solvents (first step: acetone, second step: methanol alcohol, and deionized water 7min each step), and the gold electrode was soaked in concentrated nitric acid for about 5 min. The counter electrode was a platinum foil, and the reference electrode was Ag/AgCl/sat. KCl.

Different electrolytic solutions were made by a combination of the supporting electrolyte and depositing element salts. The Cu, Zn and Sn aqueous solution was prepared from CuSO_4 , ZnSO_4 , SnCl_2 . The cyclic voltammetry (CV) was employed in all the experiments to find an optimum potential for the deposition of Copper, Zinc and Tin thin film with potentiostatic electrodeposition. The compositional properties of the as-deposited thin films were studied using an ICP analysis.

In this job, we opt to couple the electrochemical study with the compositional study by ICP and to compare the electrodeposition on the ITO glass with the electrodeposition on the Gold electrode.

III. RESULTS AND DISCUSSION

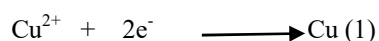
A. Effect of the complexing agent:

Cyclic voltammetry was considered one of the most adaptable electro-analytical techniques currently available. It is generally the first experiment to be run when dealing with any electrochemically active species. The basic theory behind cyclic voltammetry is to measure the current response at the electrode surface to a specific range of potentials in an unstirred solution.

Each element has a unique standard reduction potential and reduction kinetic; it was proven a challenge to deposit a compounds element simultaneously to form a thin film with desired elements composition due to their different redox potential at standard conditions. To resolve the problem of the potential difference, a lot of works have decided to use complexing agents such as tartaric acid [23] and the tri-sodium citrate [18], [24], [25]. In this work, the effect of the complexing agent was distinctive in nature to obtain an optimum electrodeposition potential. The original idea in this work is to make our electrolyte both a complexing agent and a supporting electrolyte. The cyclic voltammetry measurement was performed to investigate the growth parameters and to optimise the electrodeposited potential in the electrolyte with a scan rate of 50 mV s^{-1} . Figure 1 illustrates cyclic voltammetry of simple Cu, Zn, and Sn in an electrolyte solution with pH 4, with and without the presence of the complexing agent, which is the Sodium Citrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$.

We were opted to expose the electrochemical responses of different ions in an electrolytic environment in the whole area of polarisation (anodic and cathodic zone). In the different voltammograms a presence of a cathodic structure characterised by the presence of a cathodic peak (A) and an anodic structure characterised by the presence of an anodic peak. Some start of the duplication peaks can be observed in function of the environment and polarisation used. In our study, we were more interested in the study of the cathodic area where there was a reduction of the metal ion studied (deposition of the corresponding element). It is in this area that we can achieve the desired layers. The study in the anodic area (which corresponds to the oxidation of the elements trained in cathodic and to the evolution of their oxidation) can do another study.

The copper voltammograms (a) with and without the complexing agent have the same appearance. There is a departure in cathodic current from 0.0 V in the case of the absence of the complexing agent and the maximum was manifested by a peak at - 0.6 V. In the presence of the complexing agent, the departure was observed from - 0.25 V and the maximum is at about - 0.85V. The appearance of the cathodic current (in both cases) corresponds to the beginning of the reduction of Cu^{2+} (eq. (1)). In both cases, the voltammogram ends in a more cathodic potential, by a departure more intense in current, which corresponds to the evolution of hydrogen because of the protons reduction.



The Zinc voltammograms (b) present the same appearance. One cathodic peak was observed at about $-0.88\text{V}/\text{Ag}/\text{AgCl}$ in the absence of the complexing agent, and at about $-1.1\text{V}/\text{Ag}/\text{AgCl}$ at the presence of complexing agent, which are responsible for the reduction of Zn^{2+} to Zn according to Eq (2). In both cases, the voltammogram ends in a more cathodic potential, by a departure more intense in current, which corresponds to the evolution of hydrogen because of the protons reduction.



The tin voltammograms (b) present the same appearance, one cathodic peak was observed at $-0.80\text{V}/\text{Ag}/\text{AgCl}$ at the absence of the complexing agent, and at about $-0.88\text{V}/\text{Ag}/\text{AgCl}$ in the presence of complexing agent, which are, responsible for the reduction of Sn^{2+} to Sn according to Eq. (3)

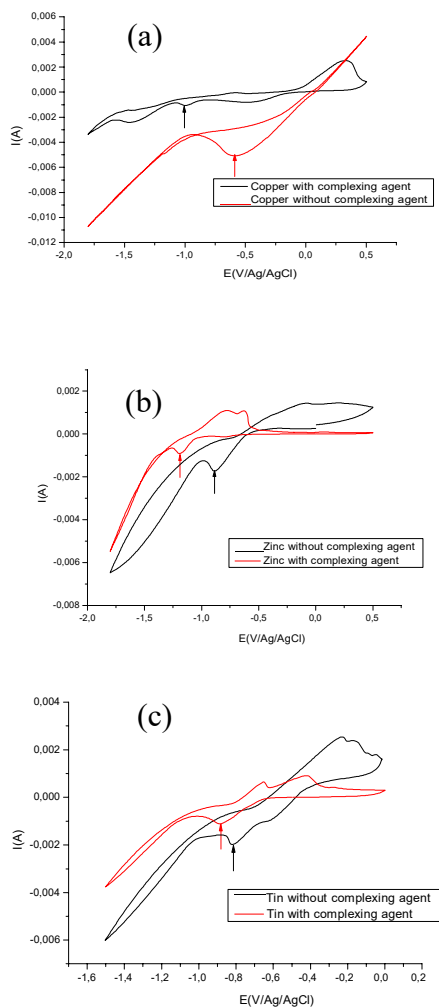


Fig. 1 Cyclic voltammograms on ITO coated glass substrate in (a) Copper concentration with $0.2\text{M Na}_3\text{C}_6\text{H}_5\text{O}_7$ and without complexing agent in Citric Acid; (b) Zinc with $0.2\text{M Na}_3\text{C}_6\text{H}_5\text{O}_7$ and without complexing agent in Citric

acid; (c) Tin concentration with $0.2\text{M Na}_3\text{C}_6\text{H}_5\text{O}_7$ and without complexing agent in Citric Acid

Comparing the cyclic voltammograms, the complexing agent acts on copper, zinc and tin electrodeposition by moving its potential toward the cathodic part. Something that will be useful for determining the potential of the electrodeposition of binary, ternary and quaternary compounds.

B. Electrochemical study

To confirm the potential of elements deposit, an electrochemical and a compositional study of the concentration variation has been made. The use of a comparison system which is the gold to confirm the deposits, especially in the case of tin, which is among the constituents of our working electrode ITO glass. Cyclic voltammetry was performed to understand the electrochemical behaviour of the $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Sn}(\text{II})$ species in different concentration on the ITO glass and on the gold electrode.

Figure 2 shows the cyclic voltammograms of gold and ITO glass electrodes recorded in different concentrations of CuSO_4 dissolved in the supporting electrolyte. In effect, Figure 3 (a) (b) shows a cyclic voltammogram of ITO glass and gold electrode of copper solutions containing different concentration of CuSO_4 (0.05M , 0.01M and 0.005M).

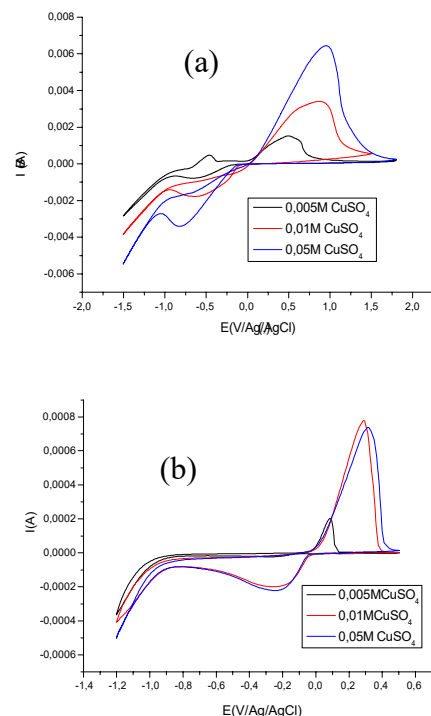


Figure 2: Copper Cyclic voltammograms saved in different concentrations and studied on: (a) ITO coated glass substrate; (b) Gold electrode

By comparing the voltammograms of copper at different concentration for the ITO glass, two sharp peaks were observed at $-0.8\text{V}/\text{Ag}/\text{AgCl}$ and $0.9\text{V}/\text{Ag}/\text{AgCl}$, with different

intensity, which corresponds to a reduction and an oxidation of Cu, respectively. The electrochemical study of Cu on the gold electrode in the same conditions of electrolyte and the same concentration of Cu gives cyclic voltammograms with the same structures that the ones obtained with the ITO glass substrate. This shows that the presence of the anodic and the cathodic structures observed on ITO are due to the electrochemical behaviour of copper.

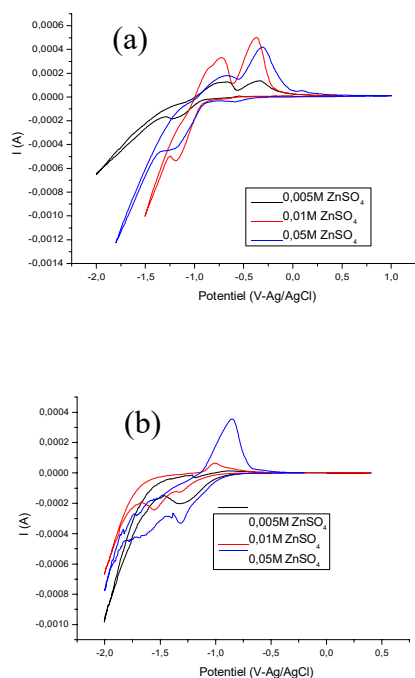


Figure 3: Zinc cyclic voltammograms saved in different concentrations and studied on: a) ITO coated glass substrate; b) Gold electrode

Figure 3 (a) and (b) shows a series of cyclic voltammograms of Zinc for the ITO glass and the gold electrode obtained from a solution of $ZnSO_4$ at different concentrations (0.05M, 0.05M, 0.1M). The CV of Zinc at different temperature shows a similar pace. The zinc ion could be reduced at the ITO glass, only when the potential decreased to -1 V (vs. Ag/AgCl). It has been proved by many works that the zinc component was increasing rapidly when the potential was below -1 V. Two anodic peaks at about -0.8V and 0.3V present the oxidation of Zn. For gold electrode, the cyclic voltammetry response shows one remarkable cathodic peak at about -1.3 V/Ag/AgCl and one anodic peak at -0.8V/Ag/AgCl. These two peaks can be assigned as follow: The anodic peak corresponds to the oxidation of Zn to Zn^{2+} ; and the cathodic peak relates to the reduction of Zn^{2+} to Zn, which coincides with the hydrogen evolution, the reason for which the noises are present on the voltammograms.

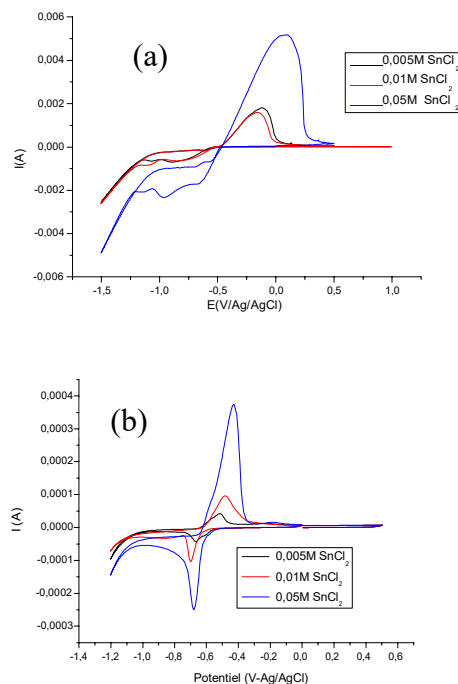


Figure 4: Tin cyclic voltammograms saved in different concentrations and studied on: a) ITO coated glass substrate; b) Gold electrode

For removing the deposit/substrate interaction of the electrodeposition of Sn on ITO glass surfaces, the use of the gold system of comparison has been adopted. Figure 4 (a) and (b) shows cyclic voltammograms obtained in $SnCl_2$ solution at different concentration. The voltammograms obtained shows the presence of cathodic and anodic peaks related to the deposition and oxidation of the Sn metals. In the cathodic scan, it can be observed that the increases in the current were detected at -0.85 V and -0.67V/ Ag/AgCl, being characteristic of the potential deposition processes of Sn into ITO surfaces and the Gold electrode, respectively. After this limit, the hydrogen evolution is predominant. The presence of net peaks on Gold voltammograms shows that it is due to the unique presence of Sn^{2+} coming from the solution. On the other side the peak that risk of splitting in the case of ITO glass substrate shows that the study of Sn is complicated due to the presence of Sn which can also come from the oxide ITO itself which is the working electrode. The Sn can explain the presence of the peaks, not net from ITO, which is in the form Sn (IV).

C. Compositional study

The results of the cyclic voltammetry above show that the suitable potential range for the preparation of the simple element (Cu, Zn, Sn) thin film is between -0.80V and -1.30V. The applied voltage has an important function: a certain voltage was needed before reduction of metal ions at the working electrode can take place. In this work, we will apply for each element its potential of reduction for after choosing a potential that should be suitable to deposit the three elements. The confirmation of the deposit and their composition was studied using the ICP. To elucidate the role of an applied

potential on the composition of simple element, we realise the electrodeposition for each element alone in its optimal deposition potential on two working electrodes: ITO and Gold (Table I);

TABLE I

DEPOSITION POTENTIAL OF THE ELECTRODEPOSITION ON ITO COATED GLASS AND GOLD ELECTRODE

Elements	Applied Voltage for Electrodeposition	
	ITO (V/ Ag/AgCl)	GOLD (V/Ag/AgCl)
Copper	-0.8	-0.25
Zinc	-1.2	-1.3
Tin	-0.8	-0.70

Table II shows the atomic composition of simple element thin film, each one was electrodeposited at its suitable potentials on the ITO glass as a working electrode. From this result, the conclusion made is that the deposition potential plays a role in film composition. Therefore, the electrodeposition process of the compounds elements should be done by choosing a potential, which will allow controlling the quantity of the element.

In the case of the electrodeposition on ITO, the two elements are present in a good quantity (copper 52,65mg/kg, tin 56mg/kg), except the zinc which is present in a composition of 6,38 mg/Kg in a potential deposition of -1,2V/Ag/AgCl. This potential coincides with the hydrogen evolution that can be the cause of its deposition quantity.

TABLE III

ICP COMPOSITIONAL ANALYSIS RESULT OF THE AS-DEPOSITED PRECURSOR FILM ON ITO COATED GLASS

	Zn (mg/kg)	Cu(mg/kg)	Sn(mg/kg)
Blank	2,7	1,09	26
Zn sample	9,08	1,1	30
Deposited Quantity	6,38	0,01	4
Cu Sample	8	53,741	30
Deposited Quantity	5,3	52,651	4
Sn Sample	3	7,12	82
Deposited Quantity	0,3	6,03	56

Table III represents the composition of simple element thin film; each one was electrodeposited at its suitable potentials on the gold as a working electrode. The composition of the films shows that the three elements are present with a major appearance of the zinc (45,11mg/kg) and a poor presence of tin (12,18mg/kg) and Copper (7mg/kg).

TABLE IIIII

ICP COMPOSITIONAL ANALYSIS RESULT OF THE AS-DEPOSITED PRECURSOR FILM ON GOLD ELECTRODE

	Zn (mg/kg)	Cu(mg/kg)	Sn(mg/kg)
Blank	0,01	0,02	0
Zn sample	45,12	0,0018	0

Deposited Quantity	45,11	-0,0182	0
Cu Sample	0,05	7,02	0
Deposited Quantity	0,04	7	0
Sn Sample	0	0,08	12,18
Deposited Quantity	-0,01	0,06	12,18

Table IV shows the Compositional analysis by ICP realized in three different applied potentials (A: -0.8V/Ag/AgCl, B: -1.05V/Ag/AgCl and C: -1.3V/Ag/AgCl). The choice of these values of potential was made by taking in advantage the range of the sustainable potential of each element.

In the case of -0.8V, the composition of the films reveals the presence of the three elements in different proportions. The elements that prevail are copper and tin with an equal ratio (~8mg/kg). Because of its far cathodic potential, the zinc appears with a low quantity (0.38mg/kg).

When we apply -1.05V as a cathodic potential, the composition of the film was changed, the copper is the dominated element in this potential with 7.1 mg/kg, and the tin was decreased but it stills present with a quantity of 2.74mg/kg. The proportion of zinc was grown to 2.9mg/kg.

When the applied voltage is -1.3V/Ag/AgCl which is a value far from the reduction potential of copper and tin and which is near to the reduction potential of zinc, the tin does not appear and the copper presents a non-meaningful value (0.99mg/kg) compared to its proportion in the other samples. However, the zinc is the only element, which extends in this potential (5.15mg/kg) because it is close to its potential reduction.

By comparing the results of the following tables, the conclusion that must be made is that -1.05V/Ag/AgCl is, the sustainable potential, which will lead to the deposition of the three elements, studied (Cu-Zn-Sn). -1.05V is a value that several works have confirmed its optimality as an electrodeposition potential of CZTS compounds [18], [26] but with a step of sulfurization. In the next article, we will make the same study for the sulphur electrodeposition on ITO coated glass to reach the aim of making a deposit of CZTS by electrodeposition without a sulfurization step.

TABLE IVV

ICP COMPOSITIONAL ANALYSIS RESULT OF THE AS-DEPOSITED PRECURSOR FILM ON ITO COATED GLASS AT:
A: -0.8V/AG/AGCL; B: -1.05V/AG/AGCL AND
C: -1.3V/AG/AGCL

	Zn (mg/kg)	Cu(mg/kg)	Sn(mg/kg)	A
Blank	2,7	1,09	26	
Zn sample	3,08	1,1	30	
Deposited Quantity	0,38	0,01	4	
Cu Sample	3	9,35	30	
Deposited Quantity	0,3	8,26	4	
Sn Sample	3	7,12	34	
Deposited Quantity	0,3	6,03	8	

	Zn (mg/kg)	Cu(mg/kg)	Sn(mg/kg)
Blank	2,7	1,09	26
Zn sample	5,6	1,1	30
Deposited Quantity	2,9	0,01	4
Cu Sample	3	8,19	30
Deposited Quantity	0,3	7,1	4
Sn Sample	3	1	28,74
Deposited Quantity	0,3	-0,09	2,74
	Zn (mg/kg)	Cu(mg/kg)	Sn(mg/kg)
Blank	2,7	1,09	26
Zn sample	7,85	1	26
Deposited Quantity	5,15	-0,09	0
Cu Sample	3	2,08	26
Deposited Quantity	0,3	0,99	0
Sn Sample	3	1	26,8
Deposited Quantity	0,3	-0,09	0,8

IV. CONCLUSIONS

The cyclic voltammetry has been used to study the electrochemical behaviour of Cu, Sn, and Zn and to determine their reduction potential to proceed to its electrodeposition from a unitary system. Tri-sodium citrate was used as the complexing agent to reduce the difference in the reduction potentials of each material. After that, it was possible to obtain different simple element deposits, characterised by different chemical compositions and applied in different voltage to find the best experimental conditions leading to understanding the electrodeposition of the simple element films with a suitable composition. We have checked the influence of bath composition on the electrochemical studies of the simple element electrodeposition and the influence of the deposit potential on the quantity of the deposit using ICP analyses.

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