2ème conférence Internationale des énergies renouvelables CIER-2014
Proceedings of Engineering and Technology - PET

Study of mechanisms of electrodeposition of thin films semiconductors, for photovoltaic destination

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Abstract:

In this work, we report some preliminary results concerning the fabrication of quaternary semiconductor Cu_2ZnSnS_4 (CZTS) thin films grown on indium tin oxide (FTO) substrates by electrodeposition, to investigate it as a possible absorber layer in thin film solar cells. The goal is to find out whether electrodeposition is a good method of growing these films, and define the optimal parameters to increase the efficiency of the conversion of the solar cells. The originality of this work is to study the mechanism of the electrodeposition of the simple elements and extend it to reach the quaternary compound (CZTS), on the FTO glass and on a gold electrode as a reference, by a potentiostatic deposition from aqueous baths at room temperature and annealing with a variation of some proprieties. The morphological properties and composition of CZTS thin films were studied using Scanning Microscope Electronics (SEM). These properties are found to be strongly dependent on the concentration of the complexing agent. CZTS thin films having a smooth surface, with a dense and uniform topography were obtained with a complexing agent concentration of 0.2M. The spectrum of the chemical composition of the deposited films showed the presence of all elements constituting the CZTS.

Keywords **–** Electrodepositing, Cu_2ZnSnS_4, CZTS, Thin Films, Solar Cells.

I. Introduction :

The production of renewable energy is based on three conditions: a clean and non-limited energy source [1], high conversion efficiency and a conversion device made of widely abundant components and produced by low energy consumption processes [2]. In this respect, photovoltaic uses the most suitable energy source which is solar light [3-4]. Moreover, conversion efficiencies and costs have reached a level that makes some of these technologies credible of large-scale electricity generations. However, it has been pointed out that solar cell materials are still either highly energy consuming during the fabrication process and/or made of rare components [5-6].

Copper, zinc, tin and sulfur (CZTS), is a semiconductor with a band gap of about 1.5 eV [7], 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 CZTS an excellent candidate for large scale utilization [8-9]. Many physical and chemical techniques have been employed for preparing CZTS thin films as a light absorber such as atom beam sputtering [7], RF magnetron sputtering [10], hybrid sputtering [11], thermal evaporation [12], sulphurisation of electron beam evaporated precursors [13], pulsed laser deposition and spray pyrolysis technique [14], ultrasonic spray pyrolysis, sol–gel spin coating technique[15]. In this field the electrochemical route appears of great interest because easy to conduct, it is a non-vacuum and low-cost technology [7-18], working at room temperature and using non-toxic solvents and reagents, with high throughput and high materials utilization [16]. Moreover, the electrodeposition has the advantage of being an industrially established process of a large area semiconductor deposition with superior uniformity in composition [17].

In the present work, the aim is to optimize the electrochemical deposition process on FTO coated glass,in order to obtain a high quality CZTS thin film. We study in this paper the voltammetric behavior of the CZTS on FTO/glass and gold as a known system to compare it and to decide the effect of the substrate. We proceed by studying the electrodeposition of the simple elements (Zn, Cu, Sn, S) to find suitable electrochemical potential at which the metal cations can be reduced efficiently while unwanted reactions will not occur for reaching at the end the quaternary (CZTS). For the synthesis of CZTS film on the FTO glass, trisodium citrate was used as complexing agent in the solution. The morphological properties and composition of CZTS thin films were studied using Scanning Microscope Electronics (SEM). These properties are found to be strongly dependent on the concentration of the complexing agent.

II. Materials and methods

The goal is to find the right conditions under which a stoichiometric film of CZTS forms on a substrate. The CZTS thin films were prepared from an electrolytic bath consists of 0.5M lactic acid, 0.02M copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), 0.01M zinc sulfate hepthahydrate ($ZnSO_4 \cdot 7H_2O$), 0.01M tin sulfate ($SnSO_4$) and 0.02M sodium thiosulfate ($Na_2S_2O_3$) using a single step electrodeposition method at room temperature for 20min, and the sodium thiosulfate were used as a complexing agent with different concentrations (0,02M, 0,1M and 0, 2M $Na_3C_6H_5O_7$). The initial pH of the electrolyte was 3,5 and then carefully adjusted to 5–5.5 by addition of aqueous NH_3 solution (20%).Three electrode-electrochemical cells were used for deposition. The cell contains silver chloride electrode(Ag/AgCl) as a reference, platinum wire as counter and FTO coated glass substrate or gold as a working electrode, the distance between the working and counter electrodes was kept constant.

Before deposition, a substrate pre-treatment consisting in an ultrasonic degreasing in organic solvents (first step: acetone, second step: methanol alcohol, and deionized water 7min each step) was adopted, in order to obtain uniform deposits. Electrodeposition was performed for 20 min, at a potential of -1.05V vs Ag/AgCl. All electrochemical experiments were performed using Autolab potentiostat. To find out the reduction potential of CZTS, the cyclic voltammetry was performed primarily for the deposition for the simple elements and at the end the quaternary composite. After completing the electrodeposition the samples were rinsed with distilled water and dried in air and then the films have been annealed at 250°C for 30min. Morphological analyses were performed by scanning electrode microscopy (SEM), The general equation for electrodeposition of CZTS can be described as:

$Cu^{2+} + Zn^{2+} + Sn^{4+} + 2S_2O_3^{2-} + 12H^+ + 18e^- \rightarrow Cu_2ZnSnS_4 + 6H_2O$

III. Resultats and discussion :

III.1 Cyclic voltammetry :

a. Working electrode : Gold

We used initially as a working electrode the Gold, gold is a noble element that does not react with the compositions of the electrolyte, which will allow to us the possibility to study the properties of the elements of the electrolyte used.

We studied separately the electrochemical behavior of simple elements, copper, zinc, tin and sulfur in 0.5M of lactic acid (pH = 5 ~ 5.5).

- **Cyclic voltammetry of simple element : Copper, Zinc, Thin and sulfur**

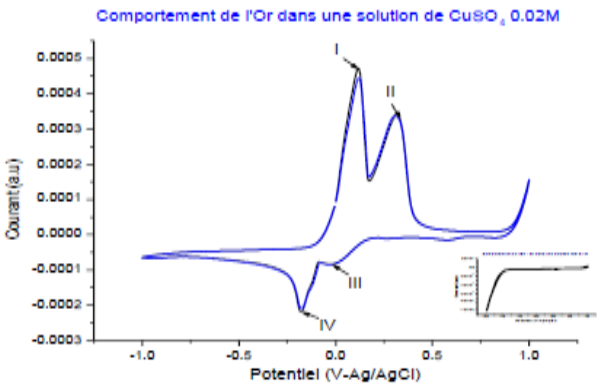


Fig 1 : Gold cyclic voltammetry in 0.5M lactic acid + 0.02M $CuSO_4$

The voltammograme shows two structures, one anodic and one cathodic, each consisting of two peaks. In cathode, the first peak (III) begins to appear from 200 mV and peaked at-7 MV. It corresponds to the reduction of $Cu^{2+}$to Cu^+. The second peak (IV) begins at -80 mV and reaches its up at -200 mV. It corresponds to the reduction of Cu^+ to Cu^0. Anodic peaks I and II correspond respectively to the oxidation of Cu^0 and Cu^+. The electrochemical process in the anodic and cathodic happens in two stages :

Peak III $\quad Cu^{2+} + 1e^- \longleftrightarrow Cu^+$

Peak IV $\quad Cu^+ + 1e^- \longleftrightarrow Cu^0$

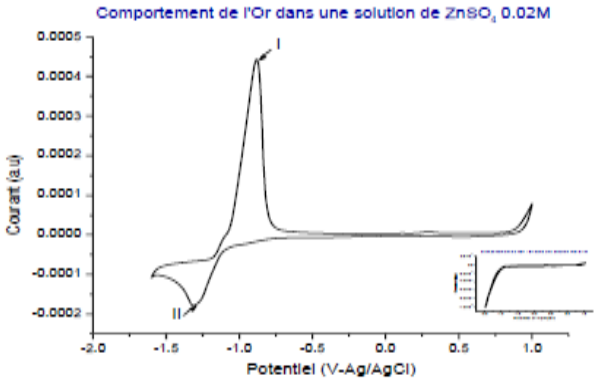


Fig 2 : Gold cyclic voltammetry in 0.5M lactic acid + 0.02M $ZnSO_4$

The voltammograme shows a single peak anodic (I) and one cathodic (II). The reduction peak that starts at -1V and reaches its maximum at a potential of -1,315V corresponds to the reduction of Zn^{2+} to Zn^0.

Peak I which reaches its maximum around -800 mV corresponds to the oxidation of Zn to Zn^{2+}. Therefore reduction of zinc on the gold electrode was carried out in a single Step:

Peak II $\quad Zn^{2+} + 2e^- \longleftrightarrow Zn^0$

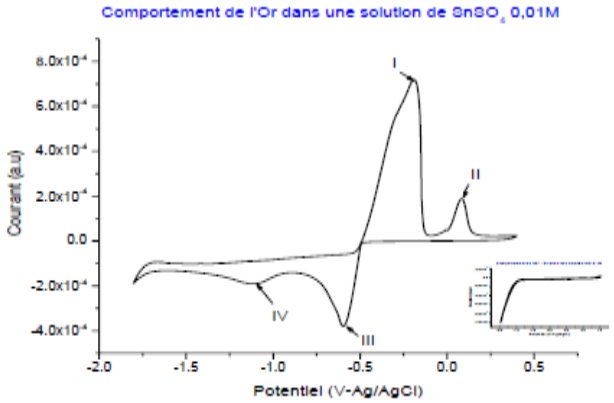


Fig 3 : Gold cyclic voltammetry in 0.5M lactic acid + 0.01M $SnSO_4$

The reduction of tin on gold is done in two steps:

- The first reduction begins at -450 mV; the peak is achieved at -600mV.
- The second reduction begins at -800mV and a peak of reduction is achieved -1.120 mV.

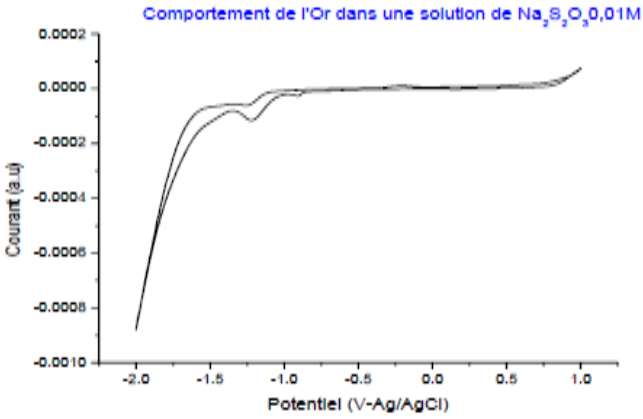


Fig 4 : Gold cyclic voltammetry in 0.5M lactic acid + 0.01M Na2S2O3

The appearance of a cathode peak at -1.25 V which is attributed to the reduction of sulfur.

➢ **Cyclic voltammetry of the binary system: Copper and Zinc**

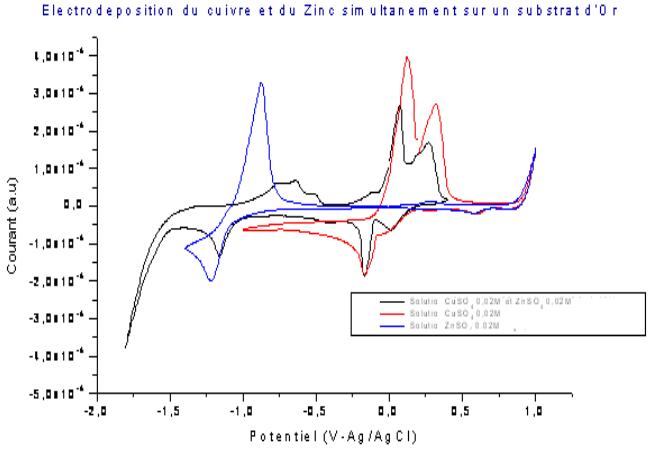


Fig 5 : Electrodeposition of copper and zinc simultaneously from a solution of 0.02M $CuSO_4$ and 0.02M $ZnSO_4$ and 0.5M lactic acid pH = 5 at room temperature; the scan rate was 20 mV / s

We proceeded by deposition of two elements, copper and zinc on a gold electrode by using a mixture containing Cu^{2+} and Zn^{2+} prepared in lactic acid. The Figure.5 shows the obtained voltammograme (black curve). The superposition of the voltammogrames obtained using copper alone (red curve) and zinc alone (blue curve) confirms the simultaneous electrodeposition of Cu and Zn from the mixture.

For copper, the electrochemical response is the same when it is alone in solution or in the mixture. We always have the presence of both anodic and cathodic structures which exhibit oxidation and reduction of copper in two steps. The presence of zinc has hardly changed the behavior of copper.

For zinc, the electrochemical response is substantially the same, on the cathode, when the Zinc is alone or in the presence of copper, a slight positive shift of the peak is seen in the case of binary. But a marked reduction of the intensity is observed of the oxidation peak of zinc with a small positive displacement in the case of binary. This can be explained by the non-dissolution (oxidation) of a large quantity of deposited zinc.

In the binary, the behavior of copper is not affected by the presence of zinc, but the electrochemical behavior anodic of zinc is affected by the presence of copper. The deposition of the binary has the same appearance as electrodeposition of Copper and Zinc separately.

b. Working electrode: glass FTO

Next, we studied separately the electrochemical behavior of simple elements, copper, zinc, tin and sulfur in an environment of 0.5M lactic acid (pH = 5 ~ 5.5). The study was done at different concentrations for each of studied elements.

➢ **Cyclic voltammetry of simple element : Copper, Zinc, Thin and sulfur**

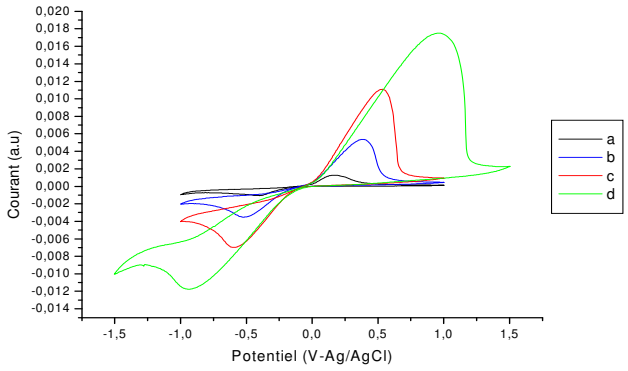


Fig 6: Cyclic voltammetry of the FTO glass: **a)** 0,01M $CuSO_4$; **b)** 0,02M $CuSO_4$; **c)** 0,04M $CuSO_4$; **d)** 0,08M $CuSO_4$

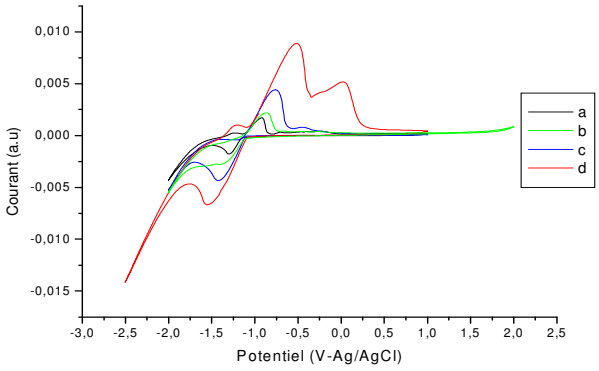


Fig 7: Cyclic voltammetry of the FTO glass: **a)** 0,01M $ZnSO_4$; **b)** 0,02M $ZnSO_4$; **c)** 0,04M $ZnSO_4$ **d)** 0,08M $ZnSO_4$

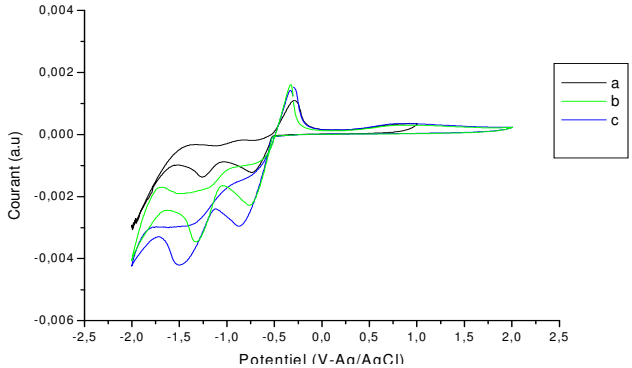


Fig 8: Cyclic voltammetry of the FTO glass: **a)** 0,01M $SnSO_4$; **b)** 0,02M $SnSO_4$; **c)** 0,04M $SnSO_4$

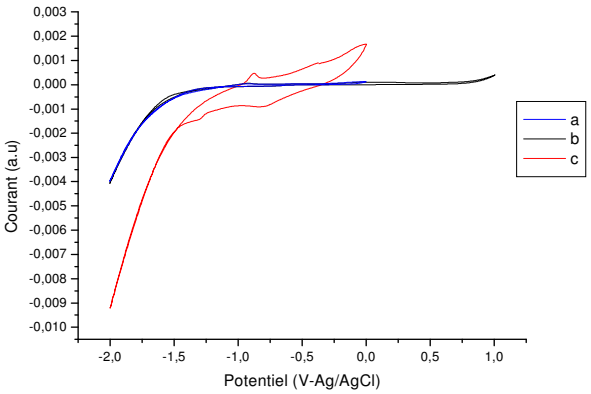


Fig 9: Cyclic voltammetry of the FTO glass: **a)** 0,01M $Na_2S_2O_3$; **b)** 0,02M $Na_2S_2O_3$; **c)** 0,04M $Na_2S_2O_3$

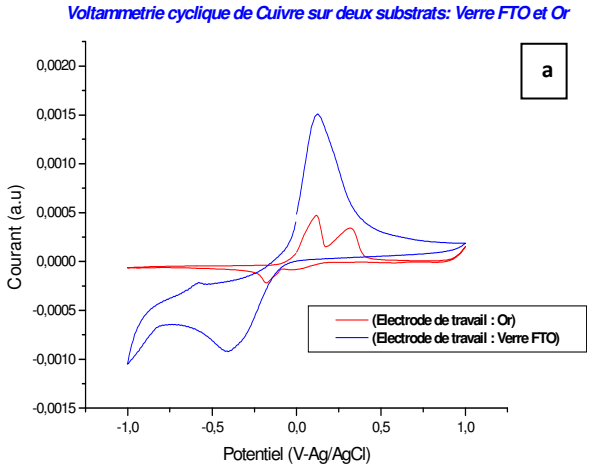
The cathodic electrochemical behavior is practically the same for each of the four elements on the gold electrode or on the FTO substrate. A difference is observed in the case of copper where less sharp peaks are observed, it can be explained by an overlap of two peaks which have been highlighted with the gold electrode. In the anodic part, the electrochemical behavior is different on both substrates FTO glass and gold.

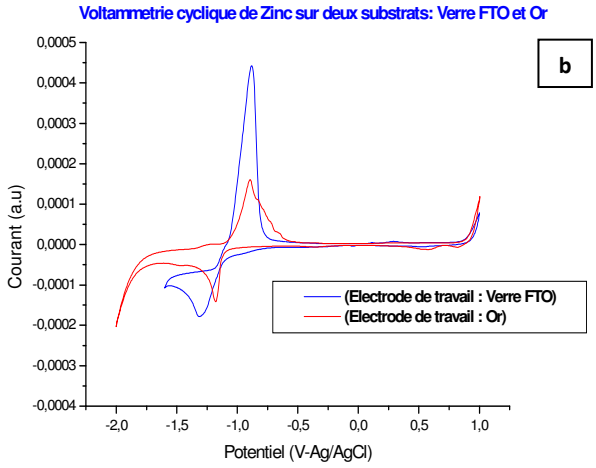
The variation of the concentration influences the intensity of the peaks, the intensity of the peack increases with the concentration.

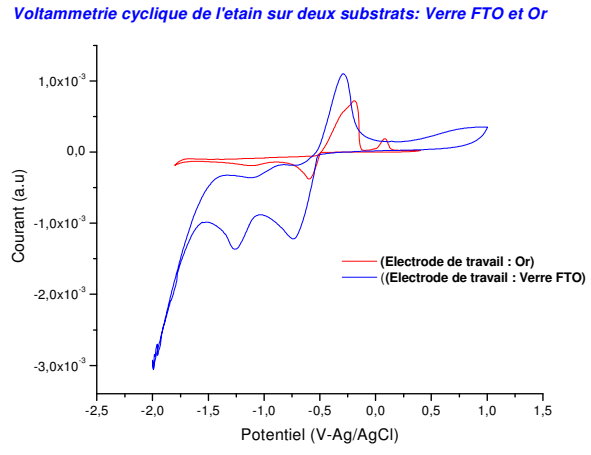
c. Comparison between the two substrates used: Gold and FTO/glass

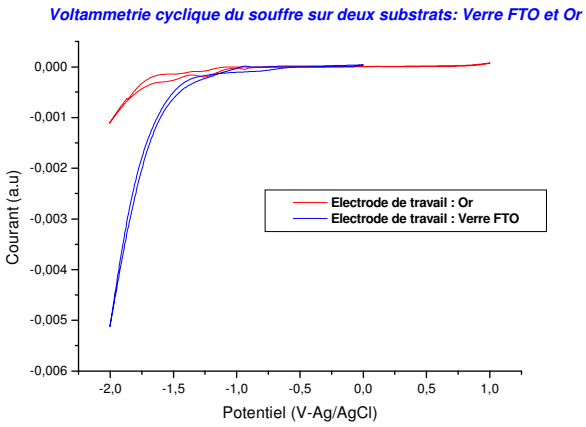
➢ Cyclic voltammetry of simple element : Copper, Zinc, Thin and sulfur

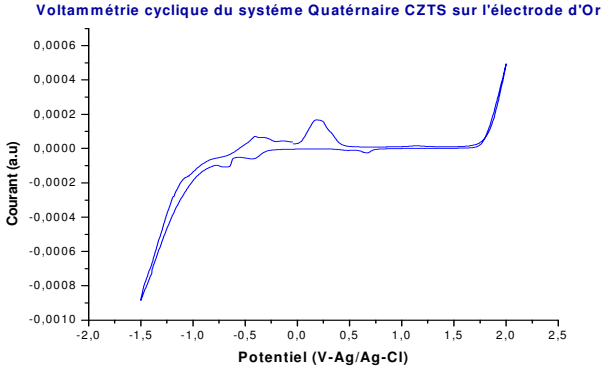
To study the behavior of elements in front of the substrates used solutions, the figure below shows a comparative study of the Golden-based substrate and the FTO glass substrate used for the four elements: Copper, Zinc, tin and sulfur.

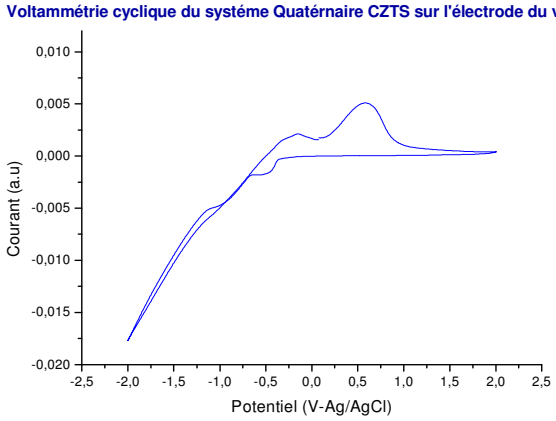












b

a

According to the results obtained, we find that for the same concentration the peaks obtained for the glass substrate FTO have larger areas than in the case of the electrode of gold, however for the two substrates, the resulting curves represent generally the same shape, and the peaks of oxidations and reductions are on about the same potential.

The Cyclic voltammetry of copper present two redox peaks for the gold substrate, however, the reaction occurs in two steps:

$Cu^{2+} + 1e^- \longleftrightarrow Cu^+$

$Cu^+ + 1e^- \longleftrightarrow Cu^0$,

While on the glass substrate the reaction pass through a single step: $Cu^{2+} + 2e^- \longleftrightarrow Cu^0$, the second reduction peak was at -200mV for Gold, and it happened at -511mV for the FTO glass.

For zinc, the two curves have kept the same oxidation peak, while the reduction peak has spent from -1,3V to -1,4V.The reaction goes in a single step.

For tin, the cyclic voltammetry on Gold has two peaks of oxidations and two peaks of reductions, for the FTO glass, reduction takes place in two steps and oxidation happens in one step. The reduction in gold is done at -450mV And -800mV, and reduction on the glass is carried out at - 500mV and -870mV. The behavior difference may be explained by the presence of tin on the deposit substrate in the case of the FTO substrate.

➢ **Cyclic voltammetry of the quaternary system CZTS:**

Figure 11 shows the voltammogrames obtained from a 0.5M lactic acid solution containing the elements of the matrix CZTS and 0.2M tri-sodium citrate as complexing agent at a scan rate of 20mV/s for both substrates studied: Gold and the FTO glass.

According to the results obtained for the two substrates: Gold and FTO Glass, we find that the curves represent generally the same shape and with a slight shift in peak potential of oxidations and reductions, also the peaks obtained for the FTO glass have larger areas and smoother than in the case of the gold electrode.

III.2 Effect of the concentration of the complexing agent on the properties of the deposited films:

To study the effect of concentration of the complexing agent on the structural properties of the CZTS deposited films, Electrodeposition was performed from a lactic acid solution containing 0.5M 0.02M $CuSO_4$, 0.01M $ZnSO_4$, 0.01M $SnSO_4$, 0.02M $Na_2S_2O_3$ and various concentrations of the complexing agent $Na_3C_6H_5O_7$ (0.02M, 0.1M and 0,2M), the pH is adjusted to 5 to 5.5 using 20% ammonia. The thin films were deposited at -1.05V vsAg / AgCl at room temperature for 20min, and then the deposit films were annealed at 250 ◦ C for 30min.

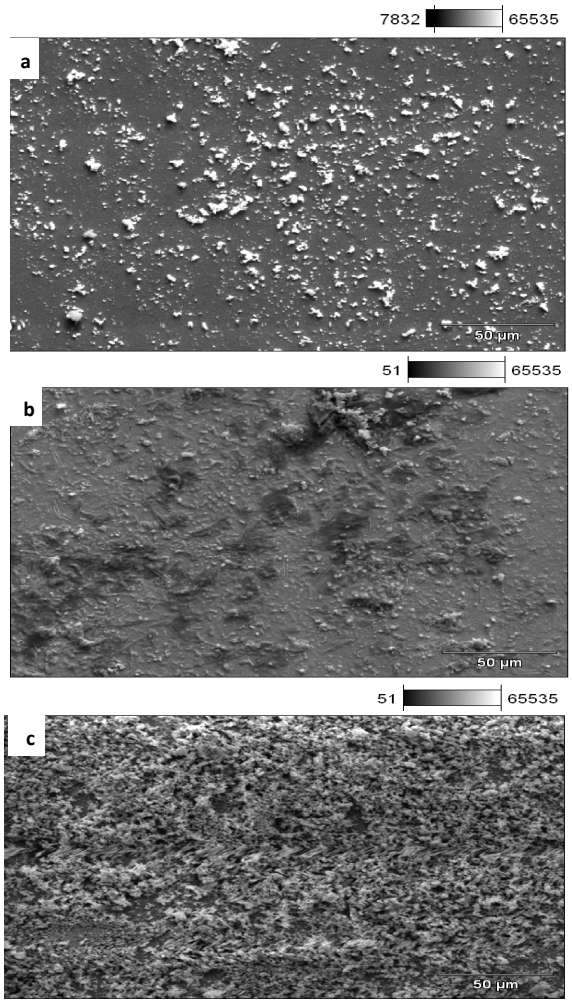


Fig 12: The SEM images of the CZTS layers on FTO glass to 250 ° C and at various concentrations of complexing agent: **a)** 0,02M $Na_3C_6H_5O_7$ **b)** 0,1M $Na_3C_6H_5O_7$; **c)** 0, 2M $Na_3C_6H_5O_7$;

The observation of the surfaces of the films obtained by scanning electron microscope is used to check the homogeneity, grain shape and aggregates.

SEM images of the films deposited at different complexing agent concentrations are shown respectively in figure 13.

The surface of the deposited film in 0.02M $Na_3C_6H_5O_7$ presents a homogeneous and dense background consisting of small white grains. At the concentration of 0.1M and 0.2M $Na_3C_6H_5O_7$ the surface of the deposited film becomes more dense, homogeneous, smooth and compact when increasing concentration.

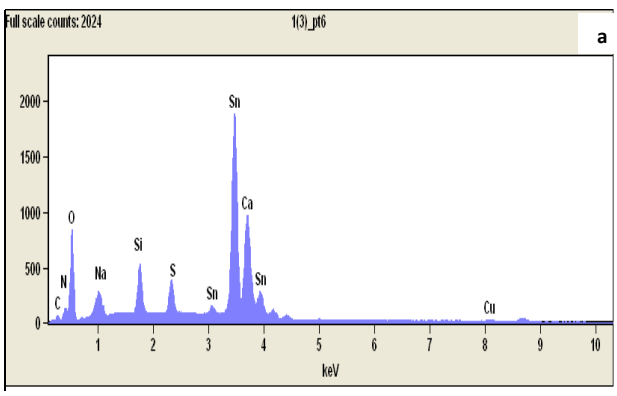


Fig 13: FTO glass spectrum without deposit ion

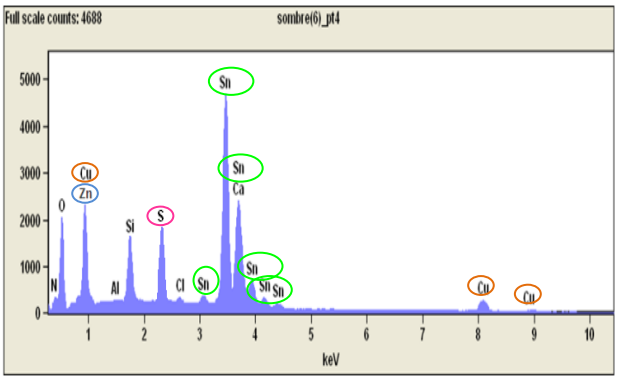


Fig 14: FTO glass spectrum after electrodeposition from a Solution lactic acid compound 0.02M $CuSO_4$; 0.01M $ZnSO_4$; $SnSO_4$ 0.01;0.02M 0.2M $Na_2S_2O_3$ and $Na_3C_6H_5O_7$, and annealing at 250 ° C for 30min

The spectrum produced by the SEM gives an idea (qualitative) on the chemical composition of the studied surface.

Figure N°13 shows the chemical composition of the FTO conductive glass used before deposition, the specter shows the presence of tin which comes mainly from the conductive layer, and silicium which comes from the glass itself.

The spectrum in Figure N°14 shows the presence of the constituent elements of matrix Cu_2ZnSnS_4 with different intensities, the tin which is present in many places means that comes in different forms, copper and zinc and sulfur with a largest peak.

IV. Conclusion

In conclusion, we have successfully synthesized thin films of CZTS by deposition of the four elements electrochemically from an electrolyte solution composed of 0.5M lactic acid, 0.02M$CuSO_4$, 0.01M $ZnSO_4$, $SnSO_4$ 0.01M, 0.02M $Na_2S_2O_3$ and disodium citrate as complexing agent $C_6H_5Na_3O_7$, the deposited films were annealed.

The results showed the effect of the concentration of the complexing agent on properties of absorbent layers on the FTO substrate / glass, the study of structural properties was carried out by SEM analysis surfaces.

Thin films CZTS having a smooth surface, with a dense and uniform topography on the FTO glass substrate were obtained after annealing at 250 ◦C for 30min with a concentration complexing agent of 0.2M. The spectrum of the chemical composition of the deposited films showed the presence of all constituent elements of the matrix CZTS.

It is a primary study to be much more developed in studying the electrodeposition on different substrates use the comparative method which enables the confirmation of the identification of some deposits. The work will been riched by further annealing studies at different temperatures and using other surface analysis for evaluate the qualitative aspect and access the quantitative aspect.

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