PROPERTIES OF PASSIVE FILMS FORMED ON TIN IN SODIUM SULFIDE AND SODIUM HYDROXIDE SOLUTION BY EIS

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ABSTRACT

Passive films formed anodically on tin, in 0.5 M NaOH and in 0.5 M Na_2S have been characterised by electrochemical impedance spectroscopy (EIS) and cyclic potentiodynamic polarization. The observation of the film formed at surface was done by scanning electron microscopy. In bothes cases the semiconductor properties of the passive films were investigated by Mott Schottky plots. The two passive films exhibit n-type semiconductor behavior. It was seen the differences is found concerning thickness of the space charge region and the second in the concentration of donors.

Keywords: SnS, SnO, Passivation; Electrochemical impedance spectroscopy; Semiconductor properties.

NOMENCLATURE

Insérer ici la liste des variables utilisées dans un tableau à 2 colonnes,centré et avec bordures supprimées. Dans la mesure du possible, les 2 colonnes seront d'égale longueur. Les symboles utilisés doivent obéir aux règles internationales.

Symboles :

D diametre de l'échantillon,m	Csc Capacité de la charge d'espace
T température, K	R_{el} resistance de l'electrolyte
v vitesse de balayage, V/s	R_{gb} resistance de grain boundary
C_{dl} capacité,F/cm^2	E_{fb}, potentiel de la bande plate,Volt
V tension,V	N_D concentration d'électrons
C concentration,mol/l	R_p resistance de polarisaion Ω/cm^{-2}

1. INTRODUCTION

Tin is interesting to study since it exhibits two oxidation states, and a special interest has been directed toward understanding the passivation process, which is still a topic of debate in terms of oxidation products [1.2]. SnS and SnO have received much interest due to its applications in optoelectronic [3]. The formation of has been reported within the active potential domain in alkaline medium. The mechanisms of tin passivation are somewhat contro- versial but most contributions agree that, upon anodic polarization. The potential must be controlled and the current does not exceed a critical value to preclude the competitive oxygen evolution followed by peeling of films. So, the deposition potential is selected from the polarization curves and the potentiostatic technique we employed differs slightly

Electrochemical impedance spectroscopy (EIS) has been widely used to study and characterise passive films anodically formed on pure metals [4,5].

2.Experimental

SnO and SnS film must be well adhered to the substrate and the electrochemical deposition is an economic technique with controlled growth rate and good area uniformity. Polycrystalline Sn disks (Merck, extra pure) of 0.5 cm diam., used as substrates, are encapsulated in glass holders with epoxy resin. The experiments are performed in a glass cell using a three-electrode configuration; a saturated calomel electrode (SCE) and a platinum electrode are used as reference and auxiliary electrodes respectively. The temperature is maintained at 20 ± 1°C using a thermostated bath. The polarization curves, the film growth and the impedance measurements are carried out with a PGZ 301 potentiostat (Radiometer analytical). The chemical plating bath consists of NaOH and Na_2S (0.1 M) . Prior to electrochemical study, the electrode is polished to a mirror finish down to 3 µm with Al_2O_3 polishing disks and thoroughly rinsed with water.

3. Results and discussion

Thin films preparation by electrochemical route has shown increasing interest owing to low energy consumption. Because of its amphoteric nature, a variety of oxides and sulfides are involved according to the potential-pHdiagram [6].
The SnO and SnS grow this complex and Fig. 1 show the cyclic polarization curve of a freshly polished Sn-electrode in alkaline solution.
As expected, the curve displays two anodic peaks followed by plateau region preceding the oxygen evolution.

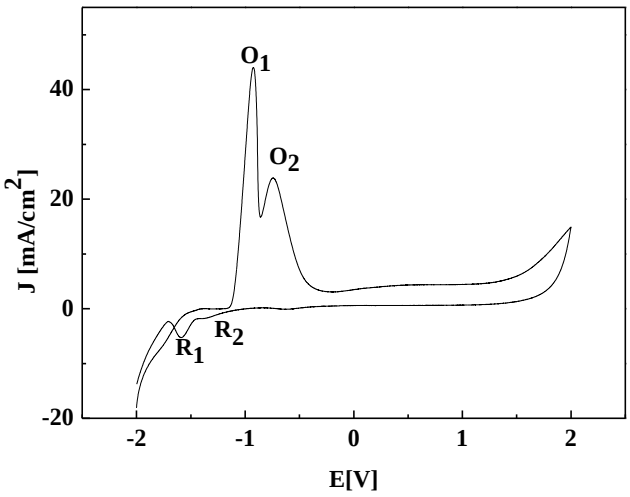

Fig.1. Cyclic voltammetry in 0.1 M NaOH of a freshly polished Sn electrode at a scan rate of 0.01 V s^{-1}.

Impedance measurement

The first case is Nyquist plots obtained at dark and under illumination for SnS sulfide tin immersed in Na_2SO_4 solution are observed in fig. 2 . the present diagram show one depressed semi-circle in the complex impedance plane, whose nature confirms the predominance of the bulk effect; which would be considered as the capacitance of the double layer between metal and the film . In bothes cases, the associated capacitance to this layer has value equal to 0.000 558F/cm^2 under illumination and 0.001490 F/cm^2 at the dark, these value are higher than the value of the usual double layer capacitance [7], meaning that the film is non-homogeneous and

more heterogeneous under illumination and that mechanism processes of tin sulfide in alkaline medium is controlled by charge and matter transfer. Its clear that R_p value is affected by the intensity light, a consequence it value of R_{pdark} is higher than the value of R_{plight} .

The shape of the diagrams obtained at dark is not different from this obtained under illumination, it can be concluded the process is not modified by intensity light. Fitting of the spectra was done by an equivalent electrical circuit.

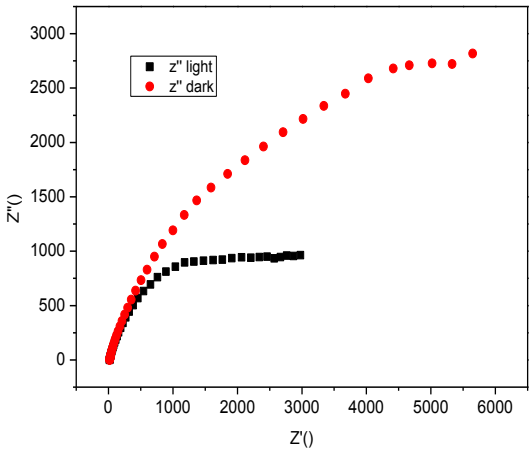

Figure.2. Complex impedance plots of SnS film formed at -1 V in Na_2SO_4 (0.1 M) solution.

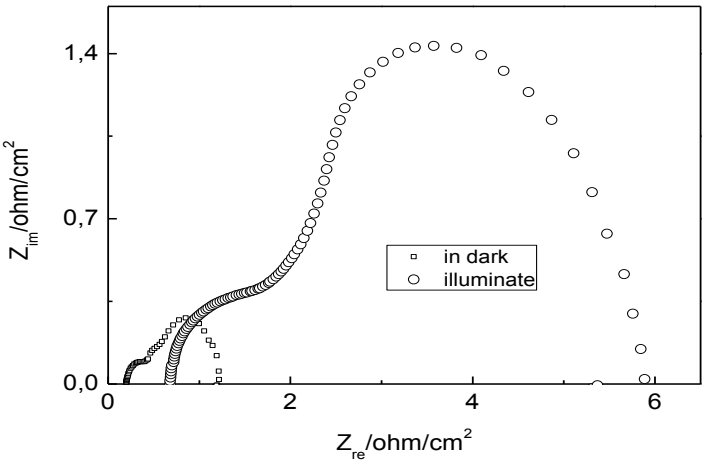

Figure 3. Complex impedance plots of SnS film formed at -1 V in Na_2SO_4 (0.1 M) solution.

The second case SnO, EIS measurement is done at the open circuit potential in alkaline medium to quantify the contributions of the electrolyte, bulk and grain boundaries. The Nyquist diagram of the junction SnO/NaOH (Fig.3) reveals two overlapped semicircles whose centers are localized below the abscissa axis, indicating that the charge transfer occurs via two successive steps. The valus (R_{ct}= 0.34 kΩ cm^2,C_{dl} =88µF/cm^2) while the second one is due to grain boundaries contribution (R_{gb}= 0.44 kΩ cm^2,C_{dl} =25µF/cm^2) [8]. CPE is proposed to account for the non-ideal capacitive behavior of the double layer which can be due to a roughness of electrode,

surface states with the gap region and non-uniform current distribution. The slight offset near the origin is due to the electrolyte resistance (R_{el}= 190 Ωcm^2, NaOH 0.1 M) because of the high molar conductivity of OH^- .

Photoelectrochemistry properties

The semi-conducting properties of SnO and SnS are elucidated from the capacitance(C) measurements.

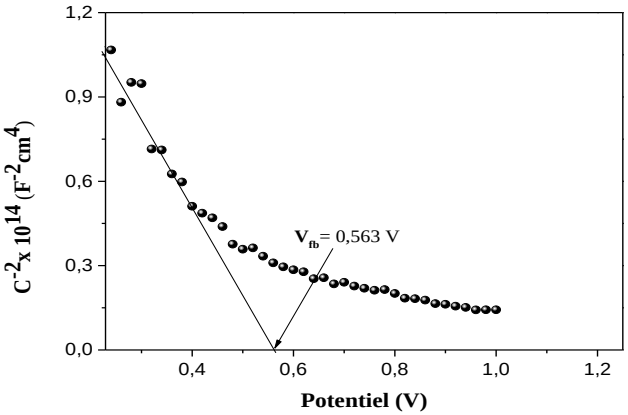

Figure.4 Mott–Schottky plot of the system SnS film/Na_2SO_4 (0.1 M).

The flat band potential (V_{fb}) and the electrons concentration (ND) of the film are extracted from the Mott–Schottky relation:

The flat band potential (E_{fb}) and the electron concentration (N_D) of the film are extracted from the Mott–Schottky relation:

$$C^{-2}_{SC}= [2/ e\varepsilon\varepsilon_o S^2 N_A] \times (E-E_{fb})$$

The intercept of linear plot to C^{-2}_{sc}= 0 and the slope give respectively a potential E_{fb} of 0.56 V and a density N_A of 9.75×10^{20} $cm^{-3}$for SnS.

The intercept of the plot with the potential axis and the slope give respectively a potential V_{fb} of -0.09 V and a density N_D of 1.45×10^{18} cm^{-3} (Fig. 8).

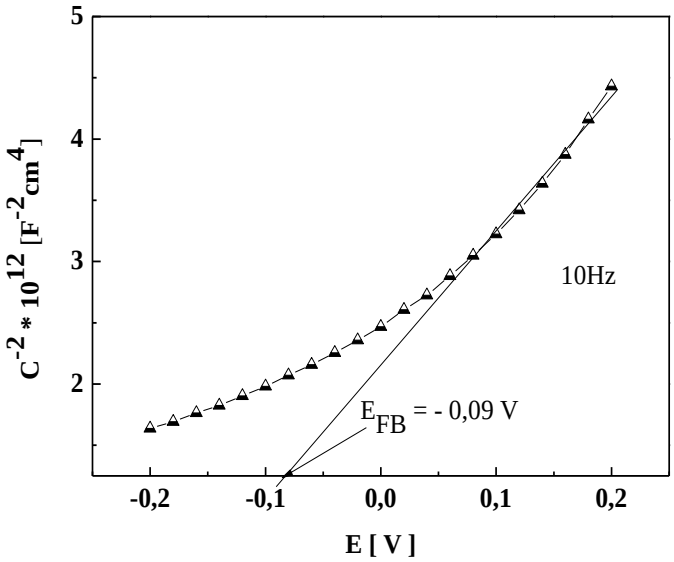

Figure.5 Mott schottky representation of the interfacial capacitance of SnO

5. Conclusions

- The electrochemical behavior of Sn electrode in an alkaline medium is described with in a large potential range covering both the active and passive regimes.
- At Open potential the value of polarization resistance obtained by EIS for SnO is higher than obtained by SnS meaning the SnS has better corrosion resistance than SnO.
- The SnS film is more heterogenous than the SnO.
- the charge transfer occurs via two successive steps for SnO and one step for SnS.
- The E_{fb} value should give rise to a large band bending at the semiconductor film/interface.

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