Electrochemically Deposited Thermoelectric Binary bismuth selenium thin films

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Introduction

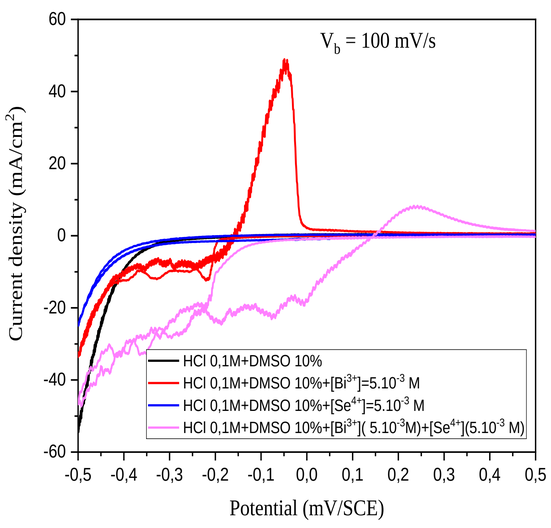
Compounds bismuth chalcogenides are solicited in many applications, such as electrochromic materials, optical coatings and photocatalysis. These compounds are presented generally under Bi_2X_3 forms, where X is O, S, Se, Te.

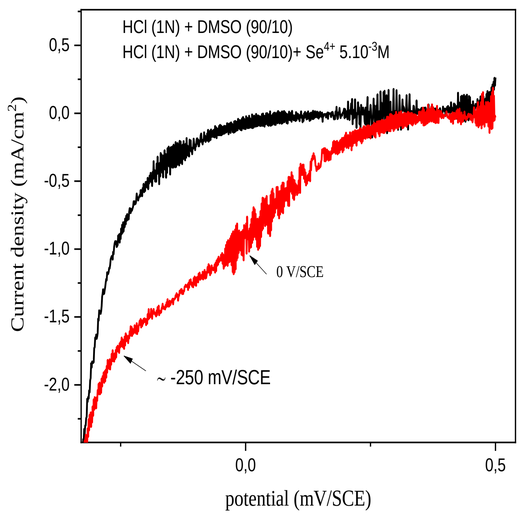
Bi_2Se_3 is a thermoelectric material, with a potential application in thermoelectric, optical photoconductive and electrochemical hydrogen storage devices. Bi_2Se_3 films can be obtained by several techniques, such as vapor deposition (PVD) , molecular beam epitaxial (MBE) and hydro-thermal methods. Electrodeposition could be a good alternative to obtain Bi_2Se_3 films.

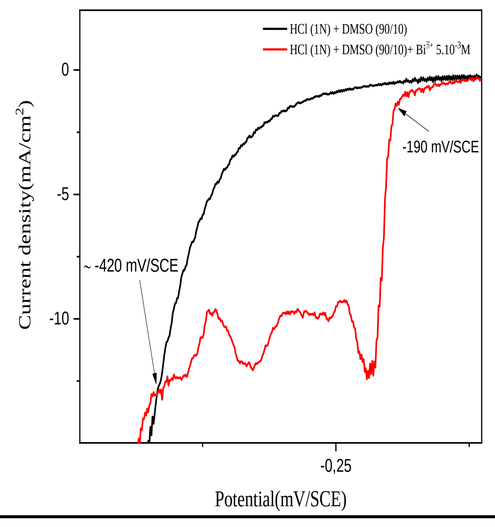
Conditions

Cyclic voltammetry was performed with a classical three electrodes, Pt. as a working and counter electrode, while saturated calomel electrode was taken as reference.
All experiments were performed at 30^0C with a Voltalab PCZ 301 potentiostat/galvanostat.
The Films were electrodeposited on FTO
The capacitance measurements were realized at a frequency of 1 kHz in a 0.1 M Na_2SO_4 solution.

∴ POLARIZATION CURVES



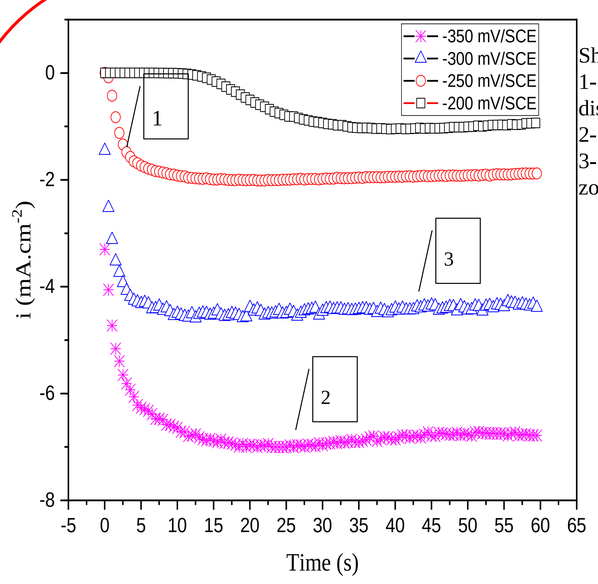




Theoretical potential for the electrodeposition of binary Bi-Se is fixed between -190 to less than -250 mV/SCE

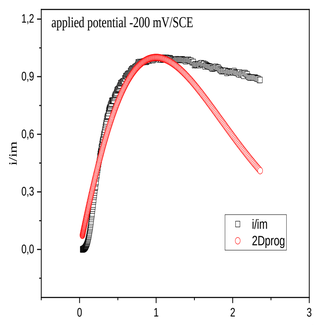
Colors of the obtained films varies from gray (-200, -250 mV/SCE), to dark for -300 and -350 mV/SCE

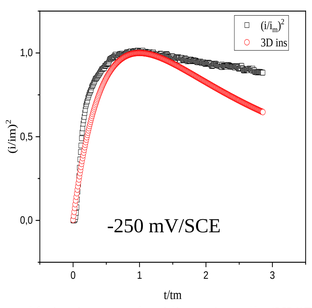
∴ Chronoamperometric curves



Shape of chronoamperometric curves :
1- decrease of the current density, attributed to he discharge of the double layer.
2- A random nucleation
3- thickening of the formed films, the current in this zone is governed by pure diffusion

The growth mode depend on the applied potential.





Dans le cas d'une nucléation instantanée (NI 2D) : $\frac{i}{i_m} = \frac{t}{t_m} exp\left[-\frac{1}{2}\left(\frac{t^2-t_m^2}{t_m^2}\right)\right]$

Dans le cas d'une nucléation progressive (NP 2D) : $\frac{i}{i_m} = \left(\frac{t}{t_m}\right)^2 exp\left[-\frac{2}{3}\left(\frac{t^3-t_m^3}{t_m^3}\right)\right]$

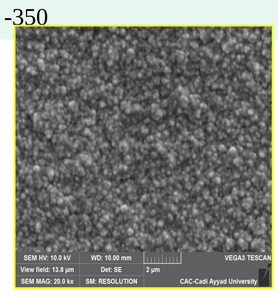
-Pour la nucléation instantanée tridimensionnelle (NI 3D): $\left(\frac{i}{i_{max}}\right)^2 = \frac{1,9542}{\left(t/t_{max}\right)}\left[1 - exp\left(-1,2564\left(\frac{t}{t_{max}}\right)\right)\right]^2$

-Et pour la nucléation progressive tridimensionnelle (NP3D) : $\left(\frac{i}{i_{max}}\right)^2 = \frac{1,2254}{\left(t/t_{max}\right)}\left[1 - exp\left(-2,3367\left(\frac{t}{t_{max}}\right)^2\right)\right]^2$

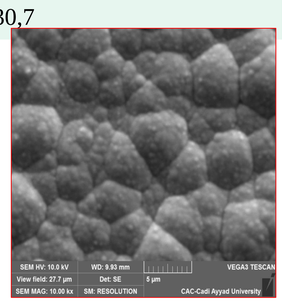
∴ EDX + SEM

Increasing applied potential increases amount of Bismuth

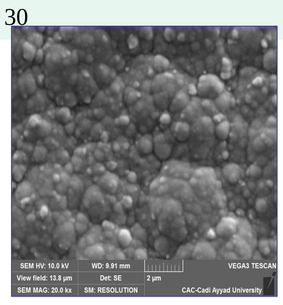
Applied potential (mV/SCE)	Atomic percentage of Se	Atomic percentage of Bi	Ratio Se/Bi
-200	21,8	35,9	1,65
-250	23,3	37	1,58
-300	40,2	28,6	1,4
-350	30,7	30	1 (presence of oxygen)



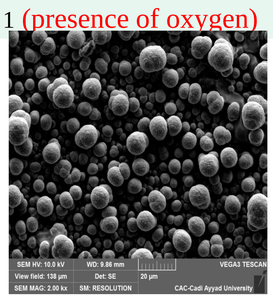
-200 mV/SCE



-250 mV/SCE

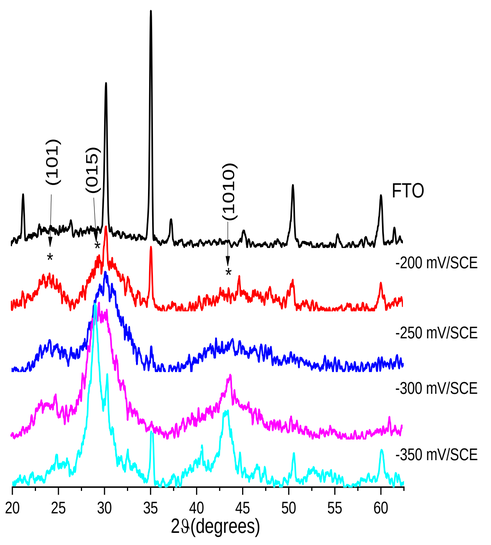


-300 mV/SCE

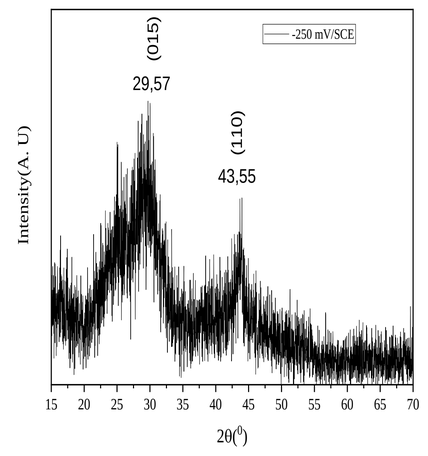


-350 mV/SCE

∴ X – ay diffraction

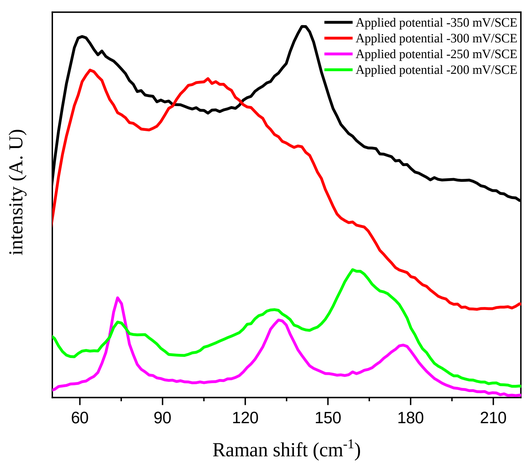


Increasing applied potential, increases thickness of the formed film. But the formed film less than -300 mV/SCE peels off



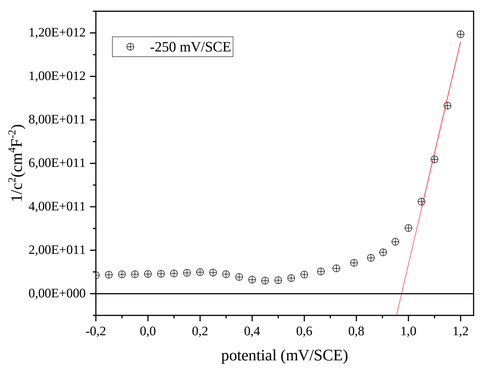
Grazing X- Ray diffraction show that the formed film at -250mV/SCE is closely Near to stoichiometric Bi_2Se_3.

∴ Raman shift



Peaks relatives to film obtained at -250 mV/SCE showed a Bi_2Se_3 profile.

∴ Mott Schottky plots



Mott Schottky studies were performed for films obtained at -250 and -200 mV/SCE

Applied potential(mV/SCED	Nd*10^{18}	$E_{(flat band)(v/CSE)}$
-250	1,1	0,97
-200	0,6	0,97

$\varepsilon_r(Bi_2Se_3)=25$

Conclusion :

- Atomic Ratio %Se/%Bi increases with increasing applied potential.
- XRD and grazing incidence XRD revealed that the films obtained at -200 and -250 mV/SCE consists of Bi_2Se_3. This results is confirmed by Raman specroscopy
- The growth mode depend on the applied potential.
- The obtained films are n type semiconductors and the number of carriers is about $10^{18}cm^{-3}$