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Physical characterization of tetraethylammonium [tris(1,3-dithiole-2-thione-4,5-dithiolato) stannate], $[Et_4N][Sn(dmit)_3]$ thin film

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Abstract – Thin films with approximately 70 nm thickness were obtained by electrodeposition of $[Et_4N][Sn(dmit)_3]$ from solution and were investigated by Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy. The results showed a dimensionality effect on the vibrational properties and loss of integrity of the octahedral structure of the anion $[Sn(dmit)_3]^{2-}$. The films obtained were extremely smooth with root mean square (RMS) roughness of a few nanometers.

Metal complex-based molecular materials are promising candidates for electrochemical sensors [1]. This application, as others, involve surface processes, which justifies the studies of these materials as thin films. The electrodeposition of $[Et_4N][Sn(dmit)_3]$ was performed at room temperature with galvanostatic control, using a constant current density of $1\mu A.cm^{-2}$, and with potentiostatic control deposition at 0.8V during different times. A thin film of gold was evaporated onto mica freshly cleaved substrate (2.0 x 2.1cm) and used as working electrode.

Light brown thin films were synthesized with potentiostatic control onto the substrates with root mean square (RMS) roughness about 3nm. The films showed a growth mode called Stranski-Krastanov, which forms quasi-bidimensional clusters later the completion of a few layers (indicated by arrow in Figure 1). An atomic profile was collected along the depth of the film by XPS using an argon beam. Table 1 shows the [S]/[Sn] atomic ratio at different depths. The highest ratio on the surface indicates that some rings left the anion octahedral structure of $[Sn(dmit)_3]^{2-}$. XPS analysis also indicates that tetraethylammonium is not present. Changes in vibrational modes assigned to dmit rings show the effect of dimensionality on the physical properties of the material (Figure 2).

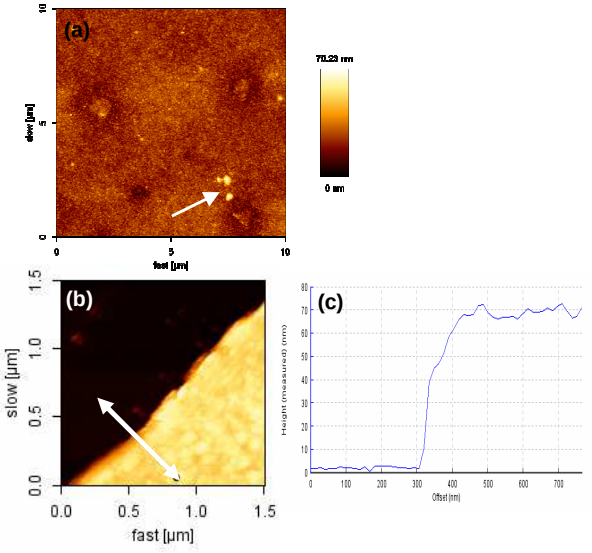

Figure 1: Topographic AFM images of $[Et_4N]_2[Sn(dmit)_3]$ thin film with 10 x 10µm^2 (a), 1.5 x 1.5 µm^2 of a risk intentionally caused to assay the thickness of thin film (b) and cross section of the arrow drawn on the image (c).

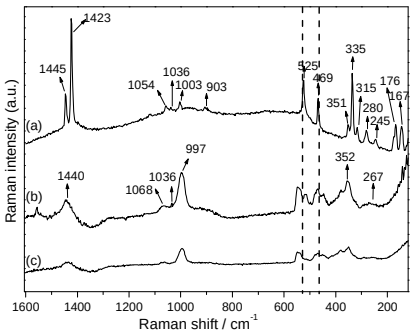

Figure 2: Raman spectra of $[Et_4N]_2[Sn(dmit)_3]$. Powder form (a); Electrodeposited thin films on evaporated gold substrate with different thickness, 919nm (b) and 178nm (c).

Table 1: Relative concentrations (atom %) of $[Et_4N]_2[Sn(dmit)_3]$ thin films at different thickness, obtained from survey scan of XPS spectra.

Core level	Relative concentration (atom %)			
	surface	2min sputt.	4 min sputt.	9 min sputt.
C 1s	60.35	48.04	42.66	42.21
O 1s	10.39	2.71	2.52	2.39
S 2p	28.22	45.55	49.21	45.39
Sn $3d_{5/2}$	1.03	3.69	5.60	7.01
Relative ratio				
[S]/[Sn]	27.04	12.34	8.79	6.48

References

[1] P. Cassoux, Coord. Chem. Ver. 185 (1999) 213.

CNPq, FAPERJ, Antonio Gerson Bernardo da Cruz