Tin oxide thin films: electronic properties and growth mechanism under electrochemical control

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Sn(IV) oxide is one of the most studied metal oxides due to its wide applications ranging from electrochemistry to optics, solar cells or gas sensor. We have recently developed an electrochemical method to obtain SnO_2 nanoparticles containing metal catalytic centers, that may result in an enhanced sensitivity of the material as gas detector [1]. SnO_2 displays n-type semiconducting properties, and the presence of oxidizing and reducing agents is known to have dramatic effects on the electronic properties of the material surface [2].

Despite the high interest of these oxides because of the close relationship between its electrochemical behavior and its applications, only a few studies have been recently reported regarding the electrochemical behavior of these oxides. Some results in citric acid media at different pH have been reported [3] and more extensive results giving information about this system can only be found in earlier works [4]. All these studies were done on polycrystalline tin and, to our knowledge, there is no fundamental research on tin single crystals that supports the reported results. Following previous work of our lab in the growth of iron oxide films under electrochemical control [5], we have started a characterization of tin oxides in borate buffer solution.

In order to investigate quantitatively the electronic properties of the semiconductor material, and the mechanism responsible for the gas-sensing properties of tin oxide, we have studied the electrochemical behavior of tin electrodes in a borate buffer solution at pH = 7.5. Regarding the understanding of the basic mechanisms of sensing, some advantages of anodic oxide films in solution, compared to nanoparticle-based materials in air are: (1) The layer formation and the change in its electronic properties are controlled externally by the potential applied to the sample. (2) The measurements versus a true reference electrode in solution allow quantitative results. (3) Ideal contact to semiconductor provided by metal substrate. (4) Changes in surface morphology can be followed by in situ SPM, further using a single crystal to take advantage of the high resolution of these techniques.

The results that will be presented include the assignment of the oxidation / reduction peaks in the voltammogram (figure 1a, and b) , and correlation with electrochemical impedance data in the significant potential regions (see fig. 1c). This allows the characterization of the electronic properties of the oxide layer formed at different anodic potentials, and to sketch the electronic energy diagram of the complex interphase metal / oxide / solution in every case. Our data suggests the buildup of an energy barrier at the surface (located presumably at the oxide / solution interphase) that strongly conditions the electrochemical behavior of the oxide layer (e.g. reduction potentials). Such energy barrier may be related to the sensing properties of SnO_2 when exposed to oxidizing and reducing agents.

In order to extend these systematic studies on polycrystalline tin to better controlled surfaces, we have developed a chemical method to obtain atomically flat terraces on Sn{100} single-crystals (see figure 2). The procedure involves a solution that etches tin anisotropically, thus allowing both sensitive electrochemical studies and the direct visualization of the electrode processes using STM as used previously to image the Iron oxide thin film [5].
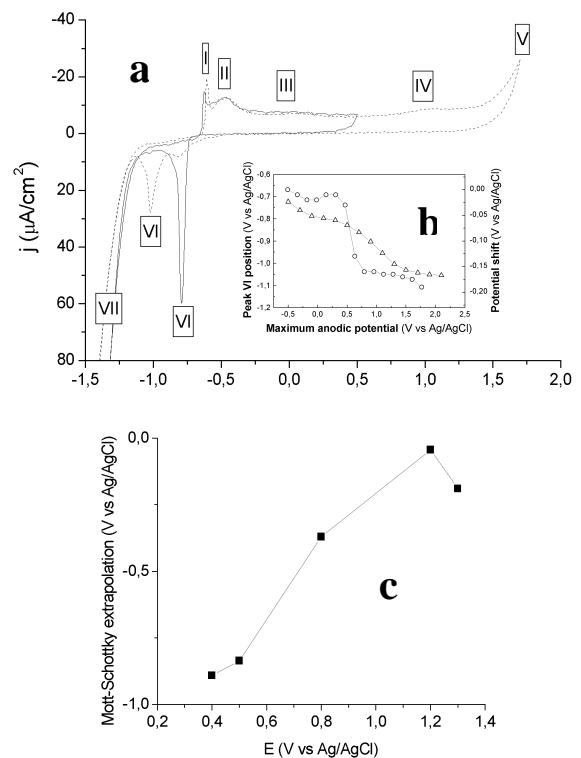
Figure 1. (a) Cyclic voltammograms of a tin electrode in a borate buffer solution at pH = 7.5. Scan rate 15 mV/s. It is observed that the position of peak VI shifts when scanning up to different potentials: (——) 0.5 V; (---) 1.7 V; (b) Peak VI position (△) and hydrogen evolution potential (for log I = -3.7) shift (○) with respect to the oxidation potential applied after oxidation during 10 s, scan rate 15 mV/s; (c) Extrapolation of Mott-Schottky plots from electrochemical impedance data with respect to the oxidation potential applied.
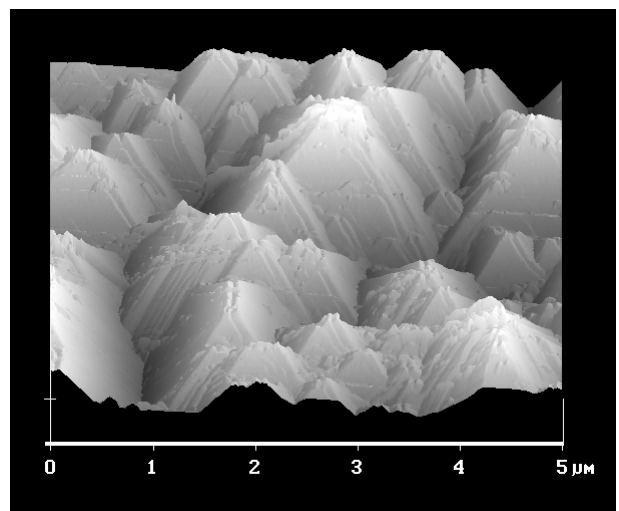
Figure 2. AFM image of the etched atomic facets of Sn(100) surface after chemical treatment.

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