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The influence of defects on the conduction in photoelectrodes used for water splitting

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The influence of the crystalline structure and the presence of defects can drastically modified the conductivity of materials. The photoactivity of the nanostructured films is also affected by these properties. The present paper investigates the characteristics of WO_3 thin films obtained by Spray Pyrolysis Deposition. Structural and electrical analysis was involved for evaluating the possibility of using WO_3 flims as a photoelectrode in a photoelectrochemical cell (PECC).

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1. Introduction

The importance of “smart” materials able to create systems that can support the production of renewable energy, grows each year. Such a material must have some particular properties characteristics for the specific application. The activity of a photoelectrode is represented by the interface and some of the incerface properties are related to the bulk material. It is known that the ability of a semiconductor system to generate hydrogen and oxygen by water photoelectrolysis is critically depending upon the interfacial characteristics between the semiconductor and the electrolyte solution, [1-3].

Tungsten trioxide is a semiconductor which has the required properties for a photoelectrode in a photoelectrochemical cell (PECC). The WO_3 layers have a wide range of applications due to their electrical and optical properties, particularly photolysis, electrochromic devices, and sensors have attracted considerable scientific and technological attention. To exploit the semiconductive properties of the material in a photon to electron device with a high efficiency, and to achieve a rapid response, a nanoscale particulate structure with a large surface area is desired. The aim of the PECC presented in this paper is to produce hydrogen via water splitting using only the solar radiation, [4, 5].

2. Experimental

2.1 Materials

TCO (transparent conducting glass, F doped SnO_2 coated glass – Libbey Owens Ford TEC 20/2.5 nm) was used as a substrate for WO_3 deposition.

The precursor $(NH_4)_2WO_4$ was obtained by mixing WO_3 powder (99.8%, Alfa Aesar) with ammonium solution (25%, J.T. Baker) at the average temperature of 60 °C.

2.2 Preparation of WO_3 thin films

The SPD (spray pyrolysis deposition) method was used for obtaining thin nano and mezostructured layers.

The deposition temperature was 270 ºC for WO_3 and air was the carrier gas. A post – annealing process was performed at 350 ºC for WO_3 films, in air, for improving the structural quality of the films.

2.3 Films characterization

The XRD measurements (Bruker D8 Advance Diffractometer) were used for the evaluation of the crystal structure of the films.

The I-V impedance and Mott-Schottky measurements (the current-voltage curves in dark) was performed using a DC Source Meter (Keithley, model 2400).

The morphology of the nanocomposite structure is studied using a Scanning Electron Microscope (SEM, Jeol JSM-5800LV).

3. Results and discussion

The X-ray diffraction spectra (Fig. 1 and 2) proves the importance of the annealing treatment for improving the crystalline structure and confirm the formation of WO_3 monoclinic structure, according to JCPDS 72-0677.

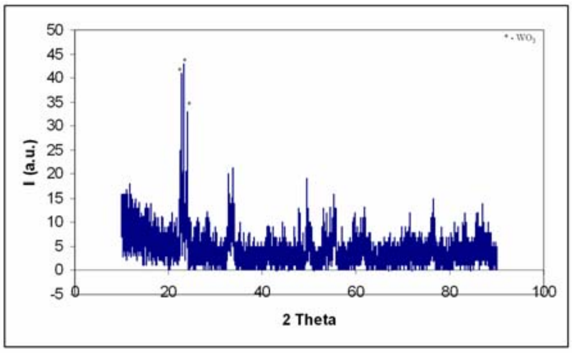

Fig. 1. XRD pattern of non-annealed WO3 film.

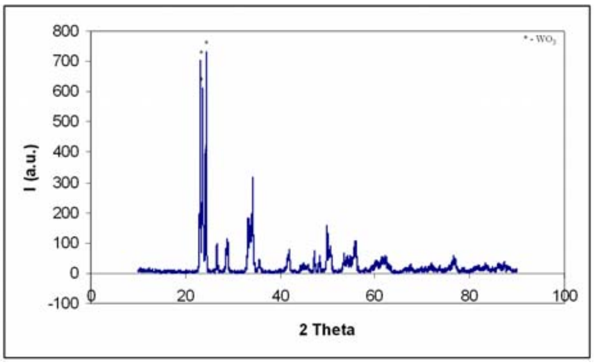

Fig. 2. XRD pattern of annealed WO3 film.

The SEM analysis (Fig. 3) shows that the film obtained from $(NH_4)_2WO_4$ exhibits a porous, well distributed structure. This type of morphology is important in the interface process where a large contact area, between the electrolyte and the films, is needed. Considering the characteristics of a photoelectrode, it is essential to have WO_3 porous films for increasing the efficiency of water splitting in a PECC system.

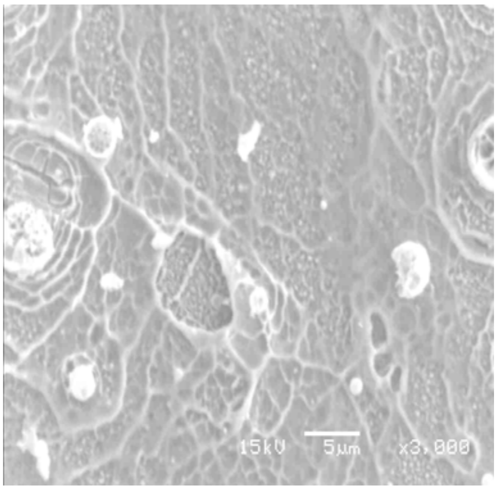

Fig. 3. SEM picture of WO_3 film.

The annealing treatment plays an important role also in the conductivity of the samples (Fig. 4 and 5).

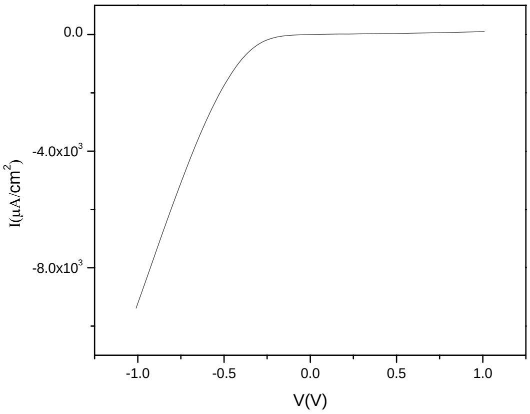

Fig. 4. I-V characteristics of WO_3 non-annealed films.

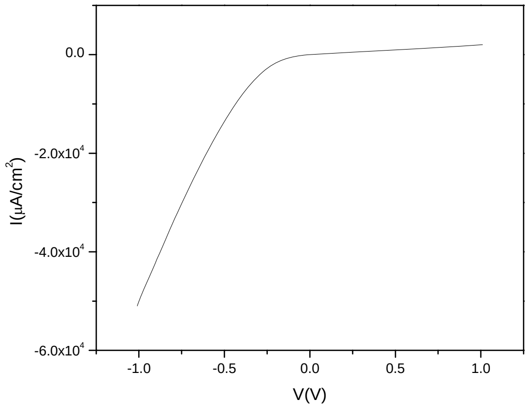

Fig. 5. I-V characteristics of WO_3 annealed films.

The conductivity of tungsten oxide films is governed by the non-stoichiometry of WO_3 as an n-type semiconductor and from oxygen vacancies:

$$O_o^x \Leftrightarrow V_o^x + (1/2\ O_2)_g \qquad (1)$$

where O_o^x represents the neutral oxygen atom in an oxide site and V_o^x represents the neutral oxygen vacancy with two trapped electrons which gives an donor level in the gap, [6].

If temperature increases, the donors are successively ionized generating free electrons (e^-) in the conduction band:

$$V_o^x \leftrightarrow V_o^{2+} + 2e^-, \qquad (2)$$

where V_o^{2+} represents an oxygen vacancy doubly ionized; the total equilibrium for carrier generation is:

$$O_o^x \leftrightarrow V_o^{2+} + 2e^- + (1/2O_2)_g. \qquad (3)$$

The annealing process is responsible for the stabilization of the structure by decreasing the number of oxygen vacancies until a determined equilibrium. But, if the annealing period is too long, the electrical properties of the films decrease.

$$2V_o^{2+} + O_2 \leftrightarrow 2O_o^x + 4e^- \qquad (4)$$

To measure the donor density of the film (influencing the conduction), the impedance spectrum is recorded as a function of a DC bias**.** The introduction of a dielectric material, like tungsten oxide, between two conducting plates (TCO glass and graphite) forms a capacitor. The equivalent circuit of the structure was fitted according to the impedance spectrum (Fig. 6). The donor density was calculated using the Mott – Schottky equation (Eq. 5) and correspond to the expected value (2×10^{18} cm^{-3}) considering the film application as a photoelectrode.

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{e\varepsilon_0\varepsilon_r N_D A^2}\right)\left(V - V_{fb} - \frac{kT}{e}\right) \qquad (5)$$

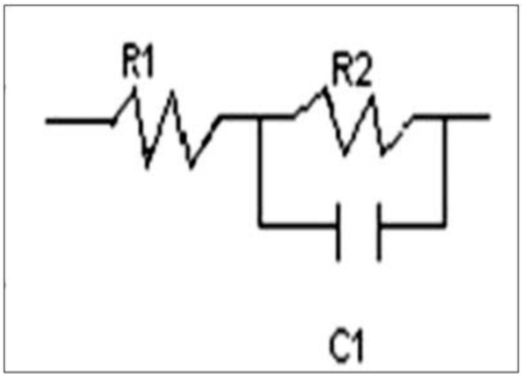

Fig. 6. Impedance spectrum of dense WO_3 recorded in dark, at room temperature and the equivalent circuit.

4. Conclusions

When the defect level concentration increases, the donor orbitals overlap and lead to the formation of bands, which lower the gap required for carrier ionization. For high defects concentration the “defect band” broadens sufficiently so that the gap disappears. Such a “defect band” model can be applied to the conductivity results that we obtain on WO_3 where the defect are surface oxygen vacancies. So, according to the model of “defect band” the activation energy for electron generation decreases as the density of vacancies increases. This occurs with decreasing oxygen partial pressure and drop to zero when the WO_3 sample is annealed in vacuum.

The main effect of the annealing is the removal of the recombination sites (traps) from the electronic structure. This effect is even more important for the porous structure, and can be ascribed to longer diffusion/drift path for the photogenerated carriers in the porous network, i.e., the probability of hitting a recombination site increases.

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