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High crystalline tungsten trioxide thin layer obtained by SPD technique

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Abstract

A nanostructured layer of tungsten oxide, WO_3, was prepared by a spray pyrolysis deposition (SPD) method using $(NH_4)_2WO_4$ precursor. The films were investigated in order to determine the electrical behaviour (impedance, Mott–Schottky and *I–V*) and the morphological characteristics (SEM). The XRD analysis reveals that tungsten oxide is present in monoclinic phase but the orthorhombic phase is also expected to be present in the structure of WO_3 crystals. Changes in conductivity of the WO_3 films have been observed after immersion in water.

Keywords: Films; Surface; Electrical conductivity; TiO_2; Fuel cells

1. Introduction

Considering the ecological problems threatening our society and our way of life (especially our comfort) it is certain that some measures need to be taken. The augmentation of toxic gas in atmosphere, the green house effect and the increase of industrial activity are sufficient motifs to undertake actions in this direction. The consumption of oil is increasing year after year and the deposit of fossil fuel decreases in the same way. Oil needs to be replaced by another fuel, non-polluting, abundant and cheap. An important candidate with good combustion properties is represented by hydrogen. In this respect, hydrogen has established its potential and can work as effective and possibly as the best substitute for oil and coal.

Tungsten oxide is a material with a large potential for use in many practical applications such as "smart" electrochromic windows, switchable devices (displays or mirrors), gas sensors and catalyst for many reactions.[1–3] Tungsten oxide can be considered as a photocatalytic semiconductor where photocatalysis is the generally accepted term for a process in which light and a catalyst bring about or accelerate a chemical reaction. In semiconductor photocatalysts, no energy is stored; instead there is an acceleration of radiation by a photon-assisted process.[4]

WO_3 films have been prepared by thermal evaporation, chemical vapour deposition, sputtering, sol–gel, and spray pyrolysis. Each preparation method provides different advantages depending on the device type and area, film properties and costs. Most of the above mentioned methods require, post-annealing steps in order to optimise the properties of the devices. At device operation conditions, it is possible to have different polymorphs such as monoclinic (>17–330 °C), orthorhombic (330–740 °C) and tetragonal (>740 °C) WO_3.[5–7] Tungsten oxide is the most investigated and used material for electrochromic device in which coloration and bleaching can be reversibly obtained by an electrochemical process. Although the WO_3 coloration mechanism has been intensely studied in the last 30 years, no complete information is yet available.

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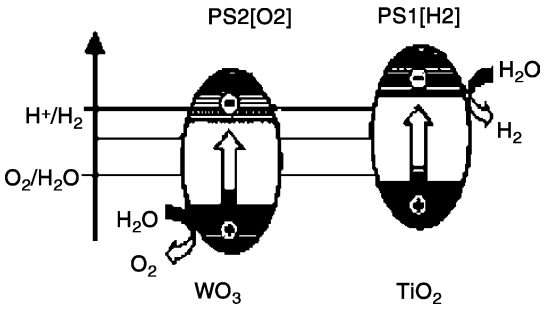

Fig. 1. The Z-tandem photoelectrochemical cell.[4]

In this study we investigate the behaviour of tungsten oxide from electrical and morphological point of view considering that future work will be concentrated on obtaining a Z photoelectrochemical tandem cell (see Fig. 1). This cell uses the solar energy to decompose water according to the following reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2, \quad E = 1.23\,V \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2HO^-,$$

$$E^0(\text{pH } 7) = -0.41\,V \text{ versus NHE} \tag{2}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-,$$

$$E^0(\text{pH } 7) = +0.82\,V \text{ versus NHE} \tag{3}$$

where NHE is a reference electrode (called sodium hydrogen exchange electrode).

This potential is equivalent to the energy at a wavelength, of approximately 1008 nm. Therefore, it should be possible to decompose water with visible light of wavelength shorter than 1008 nm, if the light energy is used effectively in the electrochemical system.[8–10] In natural photosynthesis of green plants, carbohydrate and O_2 are formed from CO_2 and water using the so-called Z-scheme reaction composed of two photo-excitation centres and many redox mediators under visible light.[11]

Although many researchers have investigated water splitting by solar light irradiation, any useful and applicable method has not been developed yet. Because water is transparent, it cannot be decomposed by visible light alone. It can be decomposed by irradiation alone only with UV-light shorter than 190 nm.[12,13] In our case the photoelectrochemicall cell will be formed using two oxides (see Table 1):

- tungsten oxide, is the photocathode responsible for oxygen formation;
- titanium oxide, is the photoanode responsible for hydrogen formation.

Table 1
Photosyntetic cell[13,15,16]

Band type	Reaction type	Overall reaction
Valence band of WO_3	$4H^+ + H_2O \Rightarrow O_2 + 4H^+$	$2H_2O \Leftrightarrow 2H_2 + O_2$
Conduction band of TiO_2	$4H^+ + 4e^- \Rightarrow 2H_2$	

2. Experimental

The TCO (transparent conducting oxide) glass was used as a substrate for WO_3 deposition. Pieces of 5 cm × 5 cm TCO were cleaned by successive immersion in ethanol and acetone using an ultrasonic bath and dried under N_2 gas.

The SPD (spray pyrolysis deposition) method was used in order to obtain thin nanostructured layers. 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 an average temperature of 60 °C (see reaction (4)). The deposition temperature was 350 °C and the inert carrier gas was N_2 (see reaction (5)).

$$WO_3 + 2NH_4OH \xrightarrow{60\,^\circ C} (NH_4)_2WO_4 + H_2O \tag{4}$$

$$(NH_4)_2WO_4 \xrightarrow{350\,^\circ C} WO_3 + 2NH_3 \uparrow + H_2O \uparrow \tag{5}$$

Post-annealing process was performed at 350, 450 and 500 °C in air for improving the quality of the films.

The *I–V*, impedance and Mott–Schottky measurements (the current–voltage curves in dark) are performed using a dc Source Meter (Keithley, model 2400) and a HF Frequency Analyser (Solartron Schlumberger, model 1255), respectively.

XRD analysis was performed using Bruker D8 Advance Diffractometer.

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

3. Results and discussion

3.1. SEM and XRD analysis

The SEM analysis (see Fig. 2) reveal the existence of inhomogeneities concerning the sample annealed at 500 °C compared with the samples annealed at 350 and 450 °C. The reason of this morphological imperfection may be due to the decomposition (varying in rate with temperature) and the time between deposition sequences.

The room temperature crystallographic structure of WO_3 is derived from the ReO_3 structure with the corner shared octahedra tilted, and the tungsten atoms distorted from their symmetrically located positions within the oxygen octahedra, to form zig-zag chains with alternating short and long W–O bond distances. Upon reduction of WO_3, oxygen vacancies are formed, which are compensated by either crystal shear planes (CS) or pentagonal column structures (PC). The CS planes are formed by the edge-sharing of neighbouring octahedral.[14]

The XRD analysis reveals a higher crystalline structure for the annealed sample (see Fig. 3) compared with the non-annealed sample (see Fig. 4). Considering these aspects the following analysis and conclusions concern the sample

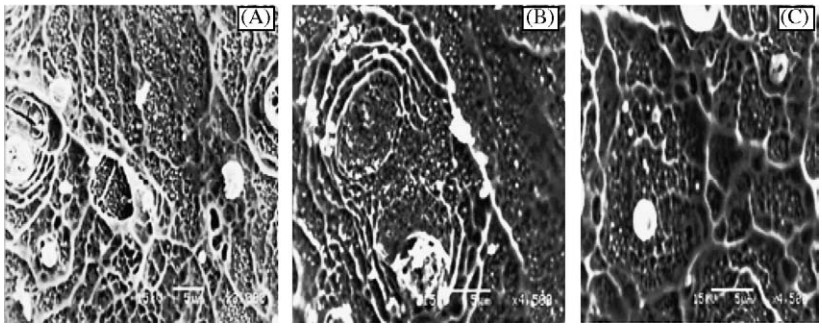

Fig. 2. SEM images (5 μm) of sample annealed at: (A) 350 °C; (B) 450 °C; (C) 500 °C.

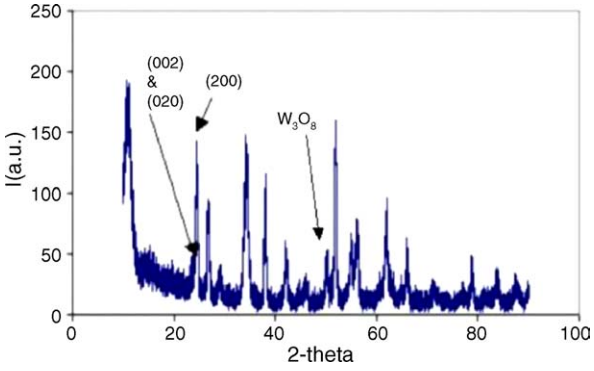

Fig. 3. X-ray diffraction pattern for WO_3 thin layer for the sample annealed at 500 °C.

annealed at 500 °C. The stoichiometry of the WO_{3-x} films, could not easily by assigned by XRD (see Fig. 4) analysis. Moreover, several non-stoichiometric tungsten oxide phases have been reported in literature and all of them exhibit very similar patterns.[14] Consequently, assigning the stoichiometry of the WO_{3-x} phases comprehensively from XRD data alone was a rather difficult task.

The tungsten oxide has a monoclinic structure but an orthorhombic phase is also expected to be present in the crystal and the non-stoichiometry can be related with the formation of W_3O_8, $W_{17}O_{47}$ or $W_{18}O_{49}$ compounds. The monoclinic structure (the majority compound) of WO_3 is characterised by three distinct XRD peaks that have been reported at $2\theta = 23.14°$, 23.60°, and 24.40° corresponding to $d = 0.385$, 0.375, and 0.364 nm. These three peaks are

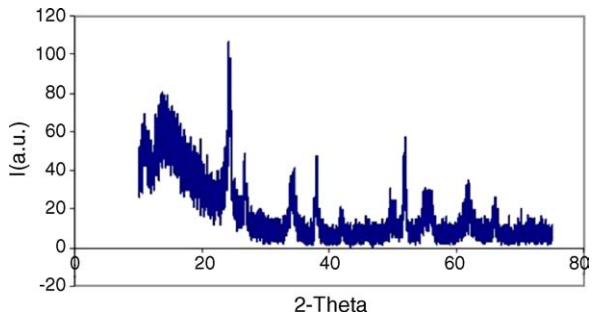

Fig. 4. X-ray diffraction pattern for WO_3 no-annealed layer.

due to the monoclinic (0 0 2) (0 2 0) and (2 0 0) planes, respectively.

The tungsten oxides consist of WO_3 octahedra arranged in various corner-sharing or edge-sharing configurations. In thin films, however, it is most likely that the octahedra are ordered hexagonally in crystallites with size depending on the fabrication route and deposition temperature.

The monoclinic phase requires a large unit cell (containing eight tungsten atoms). Now it is clearly what is the effect of annealing on the crystal structure of the tungsten oxide having in view the chemical and technological parameters involved in the thin films preparation. The XRD analysis has evidentied that the intensity of peaks increase like a consequence of the increasing in the degree of crystallinity for the annealed films at 500 °C. This is due to the fact that all phases are subjected to microstresses during the solid-phase transformation.

3.2. Impedance, Mott–Schottky and I–V analysis

The impedance spectroscopy measurement (see Fig. 5) was performed in order to determine the apparent electrical behaviour of the film annealed at 500 °C as a function of potential (and not temperature) under depletion condition and it is interpreted using the Mott–Schottky relationship (6). The introduction of a dielectric material, like tungsten oxide, between two conducting plates (TCO glass and graphite) lead to a capacitor. The value of the capacitance depends on:

- the size of the plates;
- the distance between the plates;
- and the properties of the dielectric.

A new problem can come about: what is the donor density in the film and how does this determine the conductivity of the film annealed at 500 °C. To measure the donor density, the impedance spectrum is recorded as a function of a dc bias using the Mott–Schottky formula. The impedance spectrum is a semicircle and it is characteristic to an equivalent circuit formed by a capacitance shunted by a Faraday type resistance.

The equivalent circuit gives numerical values of the space charge capacitance as a function of the dc bias and this can be analysed using The Mott–Schottky equation for an n-type

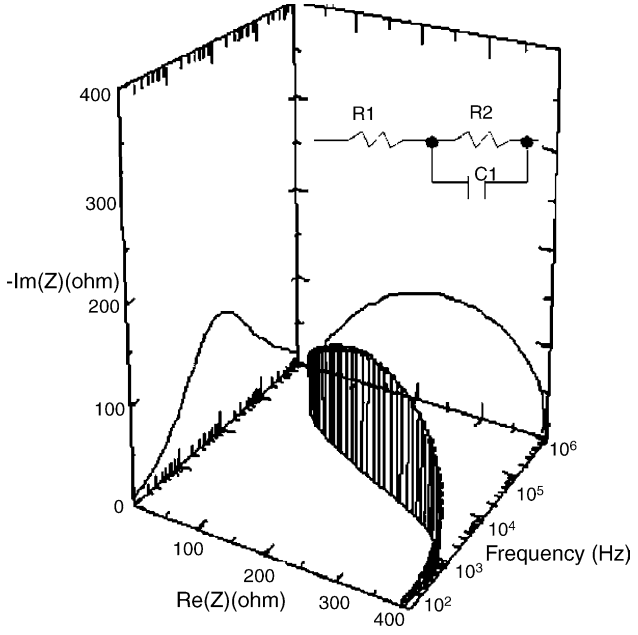

Fig. 5. Impedance spectrum of WO_3 annealed film recorded in dark, at room temperature and the equivalent circuit.

semiconductor:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{e\varepsilon_0\varepsilon_r N_D A^2}\right)\left(V - V_{fb} - \frac{kT}{e}\right) \quad (6)$$

where C_{sc} is the differential capacitance of the space charge region, N_D the donor density, ε_0 the permittivity of vacuum, ε_r the relative dielectric constant of WO_3, A is the surface area of the semiconductor contact, V the electrode potential, V_{fb} the flat band potential and k, T, e have the usual meaning. The donor density obtained is rather low, 1.69×10^{15} cm^{-3} and was calculated having in view the slope obtained from Fig. 6.

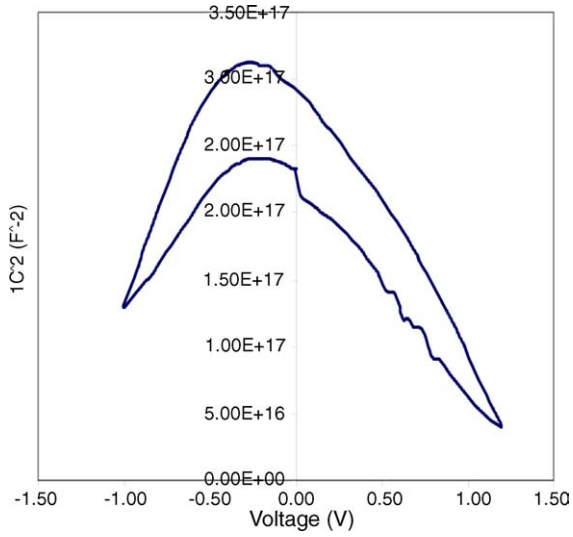

Fig. 6. Mott–Schottky measurements of a WO_3 layer annealed at 500 °C.

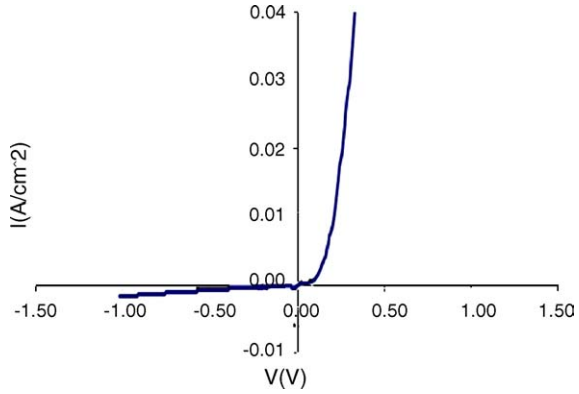

Fig. 7. *I–V* analysis of WO_3 annealed films before immersion in water.

One of the most attractive aspect of impedance spectroscopy as a tool for investigating the electrical properties of materials is the direct connection that often exists between the behaviour of a real system and that of an idealized model circuit consisting of discrete electrical components (the symbols have usually meaning).[17,18] Any material that will be electrode in a fuel cell has a geometrical capacitance $C_g = C_\infty = C_1$ and a bulk resistance. Beside $R_2 = R_\infty$ and $C_1 = C_\infty$, one often finds parallel R_2, C_1 give a response associated with a heterogeneous materials.

After a succinct overview on electrical behaviour concerning the variation of impedance function of frequency (between 1 MHz and 100 Hz) the *I–V* measurement must clarified the electrical resistivity of the WO_3 films.

The current versus voltage analysis in dark indicate a lower electrical resistivity of the annealed sample (see Fig. 7) and a decrease of the conductivity (see Fig. 8) after immersion in water. As Fig. 7 shows it is possible to obtain thin WO_3 conducting layers annealed at 500 °C by the SPD technique. Contrary, if the same annealed films are immersed in water and dried 12 h at 35 °C the electrical resistivity are changed (Fig. 8) but the morphology of the films remain unchanged, indicating a possible reaction at the surface layer. It is not totally clear what type of reaction is responsible for the

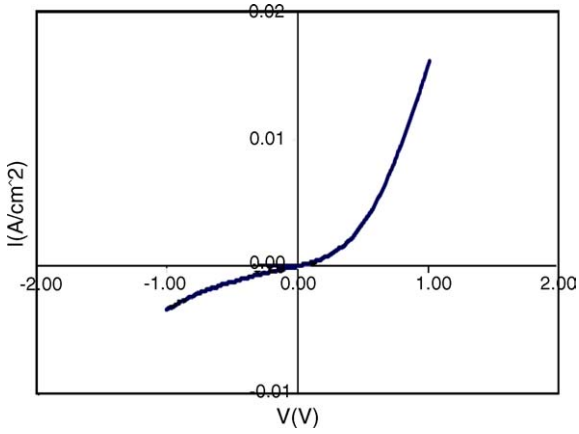

Fig. 8. *I–V* analysis of WO_3 annealed films after immersion in water.

changes in electrical resistance of the films. We suppose that the conductivity of tungsten oxide films is governed by the non-stoichiometry of WO_3 considered as an n-type semiconductor and we assume that the non-stoichiometry originates from oxygen vacancies. In this approach the changes in electrical resistivity is closely related to the oxygen vacancies equilibrium:

$$O_o^x \Leftrightarrow V_o^x + \left(\frac{1}{2}O_2\right)_g \quad (7)$$

where O_o^x represents the neutral oxygen atom in an oxide site and V_o^x represents the neutral oxygen vacancy.

However, the electrical properties are not drastically changed because the bulk conductivity remains one of the most important aspects of tungsten oxides. In fact there are many other parameters to take into account in order to establish the conductivity of WO_3 films, in particular the grain size with the barrier at the grain boundaries should also play an important role. We suppose that the most important phenomenon under these experimental conditions is the formation of oxygen vacancies as a consequence of the non-stoichiometry characteristic for this oxide.[19] A large amount of studies have reported that it is almost impossible to obtain stoichiometric WO_3 films. The catalytically properties of tungsten oxide in water splitting are also a consequence of the oxygen vacancy activity on the hydroxyl species. Water can be chemisorbed and/or physisorbed (in which case it is located between the clusters and bound by hydrogen bonds). Due to the chemisorbed H_2O, long and short W–O bonds arise (conforming with the chemisorptions theory applied on metal oxides), the short ones being called W=O bonds. The oxygen vacancy diffuses into the interior of the column, and some of the H_2O leaves the films. The diffusion of the oxygen vacancy may be favourable along the grain boundaries in the interior of the columns.

Annealing can diminish the oxygen vacancy concentration, but this structural defect cannot be totally eliminated. Analyses of the tungsten oxide phase diagram have confirmed the non-stoichiometry of this oxide at high temperatures (400–500 °C).[19]

4. Conclusions

SPD is an efficient method for obtaining high quality thin layers. As precursor $(NH_4)_2WO_4$ was used. The thermal decomposition at the surface of the TCO glass makes the formation possible of nanostructured tungsten oxide films. An annealing process is involved in order to assure a good crystalline structure of the films. XRD analysis demonstrates that the final product is WO_3 but also other oxide phase can be detected, possible because of temperature variation. It is encouraging that the prepared samples show good electrical properties. We suppose that the conductivity of tungsten oxide films is governed by the non-stoichiometry of WO_3 originating from oxygen vacancies. Also the morphological aspects of WO_3 layer are unchanged after 12 h of immersion in water proving that the films have a high chemical stability. Theoretically, if the tungsten oxide, WO_3, and titanium oxide, TiO_2, are stable in water and if these oxides can be excited by sunlight the development of a photoelectrochemical cell becomes possible.

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