The influence of the annealing process on the properties of WO₃ photoelectrode used in a photoelectrochemical cell (PECC)

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Abstract: The structural (Raman spectroscopy), electrical (Current-Voltage analysis) and photoelectrical (Photoconduction analysis) properties of the tungsten trioxide films annealed in air at different temperature are reported. The influence of the thermal post-treatment on the morphology of the films and the role of oxygen vacancies on the WO₃ opto-electronic properties has been discussed and linked with possible applications in hydrogen production in a PECC.

1. Introduction

Photocatalytic systems for the generation of oxygen and hydrogen by sunlight irradiation, using semiconductors electrodes and redox couples, is a goal and a subject of active research as one of the ways for solar and chemical energy storage.

Many different semiconducting materials have been used as photocatalysts for water decomposition to hydrogen and oxygen. Among them, metals oxides have been found to give the best activity and stability in a variety of organic and inorganic photocatalytic reactions and during long-time irradiation. In the systems reported so far, most of the materials that were used are wide band gap semiconductors, which use mainly ultraviolet light (λ < 400 nm) to achieve the photoexcitation and charge separation. Silver chloride was reported to have high efficiency as a photoanode in water splitting process, [1-5].

Technological and scientific interest on tungsten oxide has stimulated many works in the past few years. In particular WO₃ present a variety of interesting properties: this oxide is a well known electrochromic material and many investigations have been recently performed for testing its sensing properties, [6-8]. Grimes have reported the electrochemical anodisation as an appropriate method to obtain different metal oxide, among them the WO₃ with nanoporous structure, [9].

Thin films of metal oxides may be prepared by a number of methods, the spray pyrolysis deposition (SPD) offering the possibility of controlling film morphology by varying numerous experimental parameters, such as the precursor and the deposition conditions.

Furthermore, it may be possible to induce structural ordering in the oxide films during the thermal-treatment process, by varying the annealing temperature and/or time. Unfortunately, the high-temperature treatments, required to form well-crystallised films, can induce morphological disorders.
such as cracks or holes. The addition of complexation agents has also an important role on the crystal formation and stability, [10-12].

We have already described the synthesis of WO₃ thin film with a high crystalline structure, [13]. Such a film exhibits particularly promising photoelectrochemical properties, considering the possibility of development of a photoelectrochemical cell (PECC) where the WO₃ photoanode and platinum contraelectrode are used for water splitting under visible light.

2. Experimental

The 5 x 5 cm² TCO (transparent conducting glass, F doped SnO₂ coated glass – Libbey Owens Ford TEC 20/2.5 nm) was used as a substrate for WO₃ deposition. Samples of TCO were cleaned by successive immersion in ethanol and acetone using an ultrasonic bath and dried with N₂ gas.

The SPD (spray pyrolysis deposition) method was used in order to obtain thin nano- or mezostructured layers and optimized deposition parameters:
- 250°C deposition temperature;
- 1 bar pressure of carrier gas (N₂);
- 35 cm distance between the spraying source an substrate;
- 20 deposition sequences.

The WO₃ films were obtained from (NH₄)₂WO₄ ammonium solutions at a precursor concentration of 0.03 M, as already reported, [13].

Considering the deposition temperature and the polymorphic changes, at 450°C, the annealing process was performed at two different temperatures, below 400°C, Table 1.

Table 1. Different thermal post-treatment of WO₃ films.

| Sample | a       | b   | c   |
|--------|---------|-----|-----|
| Annealing temperature [°C] | Without annealing | 300 | 350 |

Raman spectra are recorded in a backscattering mode, using a set of notch filters to remove Raleigh scattering, and a Spex 340E monochromator equipped with an 1800 grooves/mm grating. The morphology of the samples was examined using a Jeol JSM-5800LV scanning electron microscope (SEM).

The I-V in dark was performed on solid state with graphite contacts using a DC Source Meter (Keithley, model 2400). Photocurrent experiments were performed in solutions of 0.0005 M HCl, under a 0.5 V bias, using as light source a ThermoOriel halogen lamp (200 W, model 50034), a Spectra Pro-50 monochromator (Acton Co.) and a DC Source Meter (Keithley, model 2400).

3. Results and discussions

One of the most important properties of a photoelectrode is related to a high crystalline structure that can work under sunlight irradiation. During deposition, dislocation centered on the edge of the shear plane in the crystal body appears due to the pyrolysis process. Since the oxygen vacancies concentration is higher close to the surface, their passivation during thermal treatment is expected.
The thermal energy during annealing induces little structural modifications, recorded as a shift of the maximum peaks for the samples b and c comparing with a (Figure 1. and Table 2). The different value of the maximum peaks for not-annealed and annealed samples indicates the vacancies (of oxygen) as possible defects that are passivated during annealing.

Table 2. Recorded wavenumber [cm\(^{-1}\)] from Raman spectra of WO\(_3\) samples.

| Sample | W-O-W bending mode | W-O-W stretching modes |
|--------|---------------------|------------------------|
| Standard, [14] | 275 (4.512 eV) | 719 (1.726 eV) | 808 (1.535 eV) |
| a | 273.908 (4.530 eV) | 717.503 (1.729 eV) | 805.706 (1.540 eV) |
| b | 274.539 (4.420 eV) | 718.332 (1.727 eV) | 807.404 (1.537 eV) |
| c | 275.222 (4.509 eV) | 719.075 (1.725 eV) | 808.011 (1.535 eV) |

Increasing the annealing temperature the oxygen migration into the lattice is favored and the obtaining structure is close to the perfect lattice (standard values).

The SEM images (Figure 2) show that the WO\(_3\) films exhibit a porous morphology regardless the annealing temperature. This type of morphology is important in the interfaces process where a large contact area, between the electrolyte and the films, is required. 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.

Figure 1. Raman spectra of WO\(_3\) films derived from ammonium tungstate precursor.

Figure 2. SEM images of WO\(_3\) samples.
Light texture modification can be observed for all samples. During the thermal treatment the film surface wrinkled due to the presence of agglomerates crystallites and the roughness decrease.

The annealing step is generally involved in order to improve the quality of the crystallographic structure, and consequently the electrical properties of the films. The I-V analysis (Figure 3) proves the increasing conductivity of the sample annealed at 350°C (sample c), comparing with the samples a and b. Moving an ion through the lattice under the driving force of an electric field needs sufficient thermal energy to pass over an energy barrier, the intermediate position between lattice sites.

When mobile electrons or holes are present, even in small concentrations, their relatively high mobility, several orders of magnitude larger than ionic mobility, gives an appreciable contribution to the overall conductivity. The improvement of the conductivity of sample c comparing with sample a and b can be explained due to improvement of the crystalline structure and diminution of the traps influence in electronic bands. There is a suitable equilibrium between the defects concentrations (oxygen vacancies) present in the lattice structure of the annealed film at 350°C and the electrons-holes recombination rate.

The aim of a photoelectrode like WO₃ is represented by the sensitivity during sunlight irradiation and the band absorption domain (preferable in VIS). The photocurrent analysis (Figure 4) shows that the sample a gives no response to the light excitation and, consequently, don’t have the required properties to work as photoelectrode. For the annealed samples the maximum absorption peak is at 320nm and the photocurrent value is higher for the sample c comparing with sample b. The explanation consists in the fact that WO₃ is an n-type semiconductor and the decreasing of the electrons-holes recombination affect not only the electrical properties (confirmed by the I-V curves) but also the opto-electrical properties after the annealing treatment.

![Figure 3. Current – Voltage (I-V) analysis of WO₃ annealed at different temperature.](image)

![Figure 4. Photocurrent measurements of WO₃ films in acid electrolyte at 0.5V bias.](image)
4. Conclusions

Tungsten trioxide films with porous morphology were obtained using SPD technique. The thermal post-treatment in air have an important influence on the structural, electrical and optical properties of the films. The not-annealed sample presents low conductivity properties and non-sensitivity to light excitation. The annealing process is responsible for the stabilization of the structure by decreasing the number of oxygen vacancies until a determined equilibrium. The main effect of the annealing is removing recombination sites (traps) from the electronic structure. When the defect level concentration increases, the donor orbitals overlap and lead to the formation of bands which lessens the gap required for carrier ionization. Increasing the annealing temperature up to 350°C, a lower electrical resistivity and a good photoexcitation response are obtained, comparing with the not-annealed sample.

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