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Influence of annealing and processing conditions on nano-structured thin films of tungsten trioxide

S. Touihri [a], A. Arfaoui [a], K. Boubaker [a,*], H. Essaidi [a], J.C. Bernède [b]

[a] Unité de physique des dispositifs à semi-conducteurs, Faculté des sciences de Tunis, Université de Tunis El Manar, 2092 Tunis, Tunisia
[b] LUNAM, Université de Nantes, Moltech Anjou, CNRS, UMR 6200, FSTN, 2 Rue de la Houssinière, BP 92208, Nantes F-44322, France

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ABSTRACT

Transition metal oxides represent a novel class of compounds which have attracted a considerable interest in the recent literature. Among these materials, tungsten trioxide has shown great potential due to photo-oxidation of water with visible light, high photocurrent with nano-crystals and good sensing properties towards several gases. The purpose of this study is to investigate the influence of conditions of heat treatment on properties of WO_3 thin films prepared by thermal evaporation under vacuum. Physico-chemical properties of WO_3 thin layers for different heat processing conditions were determined by X-ray diffraction XRD, microprobe electronics and scanning electron microscopy (SEM). Optical measurement yielded transmission and reflection measurements. The study of the physicochemical properties of thin layers of thermally post-treated tungsten trioxide showed that layers processed under vacuum have an unidentifiable structure than those annealed in air and crystallized under different crystallographic structures depending on processing temperature. Layers annealed in oxygen had monoclinic crystalline structures. It has been recorded that crystallinity and transmission of these films were drastically improved.

1. Introduction

Tungsten trioxide is a common n-type semiconductor. It is widely used in the fields of catalysis, photocatalytic [1,2] and electro-chromic systems [3–6] for the production of smart windows, chemical sensors for detection of polluting gases such as H_2S [7,8], NO_x [9–11], NH_3 [12,13] and monitoring H_2 gas concentration to ovoid explosions in embedded system [14]. Due to its rich yellow color and relatively low price, it is also used as a pigment in ceramics and painting designs. Depending on oxidation state, the conductivity of tungsten oxides monitors insulating, semiconductor or even superconductors patterns, particularly in the case of WO_2–WO_3 complex oxides. All of these crystalline oxides differ not only in terms of composition but also regarding their structure. These two parameters have a deep influence on sensitivity, selectivity and chemical sensors stability [15]. Other applications of the sensors range from detecting to quantifying gases and vapors in the food processing technologies: such an example is ethanol (C_2H_5OH) where it can be in the form of vapor or liquid [16]. They are also used as an optical detector in UV radiation [17].

2. Experiment

2.1. WO_3 layers elaboration

WO_3 crystalline films were obtained by deposition via secondary vacuum thermal evaporation (Joule effect)

* Corresponding author.
E-mail address: mmbb11112000@yahoo.fr (K. Boubaker).

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under pressure of about 10^{-5} Pa. Layers were obtained from WO_3 powder provided by Aldrich with 99.99% purity and were deposited on 2.5×1 cm^2 glass. They are cleaned ultrasonically for 10 min in alcohol as well as in cold water to remove all impurities of organic substance and/or mineral, and finally dried under nitrogen or argon flux. After primal fabrication, a programmed heat processing under high vacuum, air and oxygen flow has been carried out inside a tubular oven. Processing conditions have been managed by a Hermann Moritz programmed system. Finally, thin films were annealed under temperatures of about 673, 723 and 773 K for a period of 1 h.

2.2. Characterization techniques

In order to optimize sample's quality, structural analysis was carried out using an X-ray diffraction technique (PANalytical X Pert PROMPD), utilizing an anticathode copper tube powered by a current of 40 mA at 45 kV tip voltage. Emission line corresponds to a Cu Kα monochromatic radiation (λ=0.15405 nm). Topography of all obtained WO_3 films was performed via scanning electron microscopy (SEM) and analysis electron probe microanalysis (EPMA). On the other hand, the optical transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were recorded using a Schimadzu UV 3100 double-beam spectrophotometer, within a (250–2500 nm) wavelength range.

3. Achieved analyses and discussion

3.1. Structural analyses

X-ray diffraction analysis had shown that the structures before heat treatment were amorphous (Fig. 1). Thin tungsten trioxide annealed under vacuum at 673–723 K crystallized in unknown forms while layers treated at 773 K crystallized in monoclinic structures with formula $W_5O_{14}(WO_{2,8})$ (ASTM: 41-0745) (Fig. 2). Fig. 3 shows diagrams obtained with different annealing temperatures of T_R=673, 723 and 773 K in air. Fig. 3(a) shows a main peak at 2θ=24.243° for layers annealed at T_R=673 K, followed by some less intense peaks characterizing the monoclinic structure of WO_3 [18].

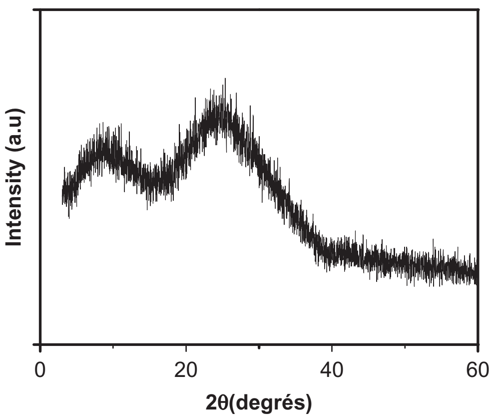

Fig. 1. X-ray diffractogram of as-prepared WO_3 films on glass substrate.

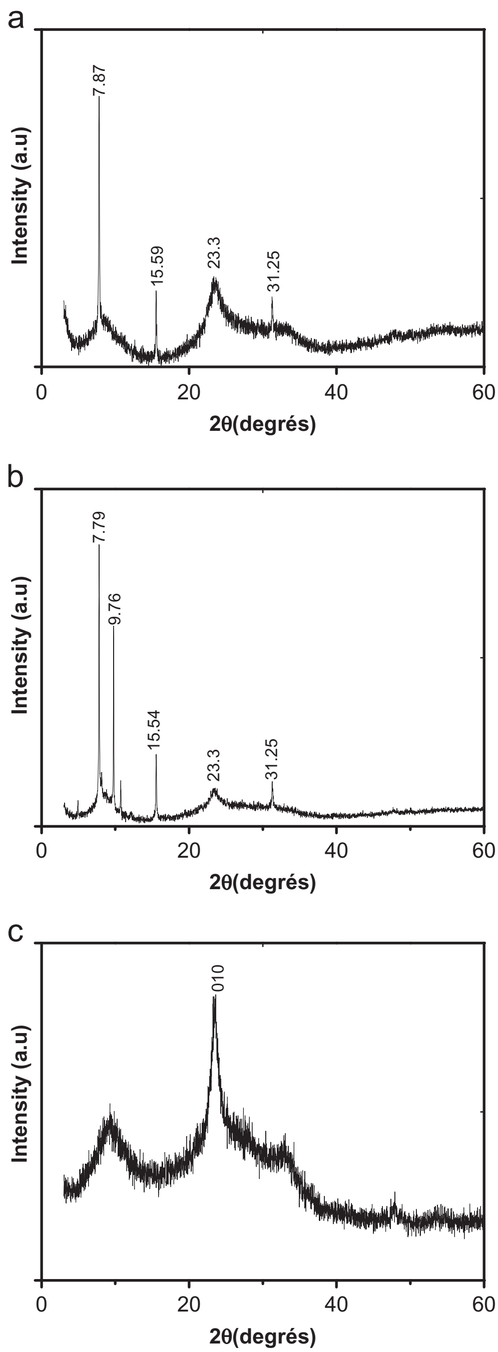

Fig. 2. X-ray diffractogram of WO_3 films annealed in vacuum at different temperatures: (a) 673 K, (b) 723 K and (c) 773 K.

However, at T_R=723 K various other peaks appear with significant intensity that reflect a good crystallization. By identifying the structure, it appears as Tetragonal W_4O_{11} ($WO_{2.75}$), similar to the layers annealed at T_R=773 K, (JCPDS formula: 89-8764). The effect of increasing annealing temperature is to shift the structure from monoclinic to tetragonalphase, with an induced oxygen deficit. The most suitable annealing temperature for obtaining stoichiometric WO_3 layers is 773 K. X-ray diffraction analysis