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An easy method for the room-temperature growth of spongelike nanostructured Zn films as initial step for the fabrication of nanostructured ZnO

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ABSTRACT

Spongelike nanostructured zinc films were grown by room temperature sputtering processes and pure wurzitic zinc oxide nanostructured films were obtained by a subsequent thermal annealing process. This method allowed growing films with a thickness of a few micrometers with a relatively short deposition time. A study on the influence of the process parameters on the morphology of the films was carried out. The radio frequency power applied to the cathode appeared to be the main factor in order to achieve nanostructures with different morphological features. The physical and chemical characteristics of the nanostructured ZnO obtained with the method herein described make it suitable to be used as photoanode in Dye-sensitized Solar Cells.

1. Introduction

Zinc oxide is a wide band-gap semiconductor, characterized by a high electronic mobility [1] and a low electron-hole recombination probability [2]. These properties make ZnO suitable for the fabrication of different kinds of devices, like Dye-sensitized Solar Cells (DSCs) [3], gas sensors [4,5], and optical devices (e.g., light-emitting diodes) [6], just to cite some examples. With reference to DSCs, several ZnO-based photoanode architectures have been suggested so far [7], in order to provide an alternative to the widely used TiO_2 nanoparticle-based photoanodes. One-dimensional ZnO nanostructures, nanowires (NWs) for instance, have been extensively studied [3] because of the presence of a direct path for the electrons through the NW, which allows for a higher electron transport if compared to nanoparticle (NP) structures [8], where the conduction occurs by means of the electron hopping between the NPs [9]. Moreover, their high surface-to-volume ratio still allows the absorption of a high amount of dye molecules. In spite of these advantages, the photocurrents and the efficiencies of the ZnO–NW cells are still lower than those of TiO_2–NP DSCs [8]. To overcome this problem it is crucial to optimize the architecture of the ZnO-based photoanodes to be used in DSCs. Many papers report on the synthesis of thin ZnO or Zn nanostructures performed by means of different techniques. Most of them exploit high temperature vapor-phase processes [9–15], often using catalyst particles [16], and chemical synthesis routes requiring the presence of a sacrificial template [17,18]. Precipitation methods may introduce chemical contamination in the synthesized materials and sometimes (e.g., in the case of hydrothermal synthesis) they exhibit slow kinetics [19]. The aim of this work is to provide a simple way of depositing nanostructured Zn films at room temperature with a thickness of a few micrometers, and to show how it is possible to obtain nanostructured ZnO films with a simple thermal treatment on Zn films.

Zn films were synthesized by the RF magnetron sputtering technique. The advantages of using such a method for the deposition of nanostructured zinc films are numerous: low temperatures (usually ranging from room temperature to a few tens of degrees Celsius) can be used to achieve porous structures [20], no catalysts are required and, additionally, it is easy to implement the sputtering technique in industrial environments, allowing large-area substrates to be covered. The drawback in using this method is that a thermal oxidation process is required after Zn deposition, in order to create ZnO nanostructures. However, the temperature used during oxidation of Zn is much lower than that employed within high temperature vapor-phase processes. In this work, spongelike nanostructured zinc oxide films with an open structure, particularly suitable for dye sensitization, were synthesized by thermal oxidation of nanostructured zinc sputtered at room temperature.

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2. Experimental details

2.1. Film preparation

Zinc films were deposited on silicon substrates and on glasses coated with fluorine-doped tin oxide (FTO) by the RF magnetron sputtering technique. FTO-coated glasses are commonly used as transparent conductive substrates for the fabrication of DSC photoanodes. Substrates were cleaned in ultrasonic bath with acetone (10 min) and ethanol (10 min), and dried under direct nitrogen flow. The vacuum chamber was pumped down to a pressure ranging from about 8×10^{-6} Pa to about 6×10^{-5} Pa. A zinc target, with a purity of 99.99% and a diameter of 101.6 mm, was fixed on the cathode, placed at about 8 cm from the substrate holder. Argon (5.0 purity) was used as sputtering gas. The plasma discharge was created by applying a RF voltage at a frequency of 13.56 MHz between the target and the grounded substrate holder. Depositions were carried out in different conditions: in particular the influence of gas pressure, gas flow and RF power on the quality of the samples was tested. Each film was grown at room temperature, i.e., no intentional heating was supplied to the substrates.

Table 1 reports the parameters used to deposit the zinc nanostructured films.

After the deposition by sputtering, the films were placed on a hot plate at 653 K for 60 min in ambient air, in order to oxidize the zinc and obtain zinc oxide nanostructured layers.

2.2. Characterization

Field Emission Scanning Electron Microscopy (FESEM) was performed with a ZEISS SUPRA 40 microscope. Nanostructured films were analyzed both in cross-section and top view, at an operating voltage of 5 kV. The BET (Brunauer–Emmett–Teller) specific surface area of the ZnO sample was evaluated from N_2 sorption isotherms (Quantachrome Autosorb1) through a multipoint method within the relative pressure range of 0.1–0.3 P/P_0. X-ray Photoelectron Spectroscopy (XPS) was performed on zinc films with a PHI 5000 VersaProbe — Physical Electronics, equipped with an Ar ion gun for sample surface cleaning and depth profile measurements. The surface of each sample was cleaned with a 1 minute sputtering process (beam energy: 2 keV) in order to remove the native oxide, although the morphology of the samples did not allow it to be completely removed. High resolution spectra were acquired on $Zn2p^{3/2}$, $Zn2p^{1/2}$ O1s, and C1s peaks. In particular, carbon peak, used as a reference for the shift of the other peaks, was acquired before surface cleaning, because no significant amount of this element was found to be present below the first layers of the sample surface. The shift was evaluated as the difference between the binding energies of the carbon peak of each sample and of the reference carbon peak (centered at 284.6 eV). The peaks were fitted with Gaussian curves and the Shirley method was used to create the baseline with the Fityk 0.9.3 software. For thicker films, X-ray Diffraction (XRD) patterns were acquired with a PANalytical X'Pert MRD PRO diffractometer in Bragg–Brentano configuration, while for thinner films a PANalytical PW3020 set-up was used in a parallel beam geometry with a fixed angle of incidence $\omega = 1.5°$. Both the instruments were equipped with a Cu K_α radiation source ($\lambda = 1.54056$ Å).

3. Results and discussion

3.1. Morphological analysis

Different process conditions (reported in Table 1) were adopted to investigate their effects on Zn film growth. Fig. 1a and b shows the FESEM cross-section images of the zinc films deposited at high power (100 W), at different gas flow and pressure values (samples T1 and T3, respectively), while the FESEM top views of the same samples are shown in Fig. 1c and d. For a fixed deposition time (60 min) the thickness of the films grown at high power ranged between about 1.4 μm and 4.3 μm. The thickness values were vastly different because of the deposition conditions adopted for the growth of the films, and their variation was consistent with the mechanisms of growth involved in a sputtering process [21,22].

In all the deposited films there was evidence of nanostructures characterized by the same spongelike morphology, compatible with the results of the study proposed by Jankowski and Hayes [23], a study that can be considered as an integration to the Thornton model [24], which is, in turn, an extension of the model proposed by Movchan and Demchinshin [24]. This model, also known as "structure zone" model, predicts three structural zones as a function of the ratio T/T_m, where T is the substrate temperature and T_m is the coating-material melting point. Zone 1 consists of tapered crystals separated by voided boundaries. Zone 2 consists of columnar grains separated by distinct and dense intercrystalline boundaries. Zone 3 is composed of equiaxed grains with a bright surface. Thornton introduced a transition region, the so-called Zone T, standing between Zone 1 and Zone 2, characterized by a more fibrous morphology. Jankowski and Hayes introduced an additional zone corresponding to what they defined a stable "spongelike" morphology, between Zone T and Zone 2. This zone can be obtained at a substrate temperature lying in a range centered at $T/T_m \sim 0.5$, where surface diffusion still dominates but the onset of faceting that plays the dominant role in Zone 2 occurs. In the case of zinc, that has a low melting temperature (~690 K), the substrate temperature required for obtaining a value of 0.5 is ~350 K. The substrate temperature can increase by tens of degrees Celsius during sputtering

Table 1
Process conditions used for growing all the analyzed zinc samples, and results from the calculation of the lattice constants obtained from the XRD patterns. Calculations were not applicable (n.a.) to all the samples since only T1, T4, th1, th2 and th3 were analyzed by XRD.

Sample name	Ar flow	Pressure	Power	Time	Thickness	Calculated lattice constants		Percent deviation from database lattice constants[a]	
	(sccm)	(Pa)	(W)	(min)	(nm)	a (Å)	c (Å)	on a (%)[b]	on c (%)[c]
T1	40	0.67	100	60	2820	2.66	4.94	−0.2	−0.001
T2	40	0.36	100	60	1750	n.a.	n.a.	n.a.	n.a.
T3	10	2.67	100	60	1350	n.a.	n.a.	n.a.	n.a.
T4	10	0.67	100	60	4260	2.66	4.94	−0.2	−0.001
T1*	40	0.67	100	2	65	n.a.	n.a.	n.a.	n.a.
T4*	10	0.67	100	2	130	n.a.	n.a.	n.a.	n.a.
th1	10	0.67	20	60	415	2.67	4.96	0.2	0.003
th2	10	0.27	20	120	65	–	–	–	–
th3	10	2.67	20	60	185	2.67	4.96	0.2	0.003

[a] The reference lattice constant parameters from the Joint Committee on Powder Diffraction Standards (JCPDS) database—International Center for Diffraction Data, 1998, PCPDFWIN v.2.01 (card number 65-3358).
[b] Percent deviation was calculated with the formula: $(a-a_{db})/a_{db}*100$ where a_{db} is the lattice constant parameter from database[a].
[c] Percent deviation was calculated with the formula: $(c-c_{db})/c_{db}*100$ where c_{db} is the lattice constant parameter from database[a].