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Tin oxide thin layers obtained by vacuum evaporation of tin and annealing under oxygen flow

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Abstract

Tin dioxide layers have been prepared by vacuum evaporation of tin on ordinary glass substrates. Thickness of the deposited tin layers was 500 or 1000 Å. Enrichment in oxygen was ensured by a thermal annealing at temperatures between 300 and 500 °C, for 1, 2, 4, 6, 8 and 10 h. The layers were characterized using X-ray diffraction, environmental scanning electron microscopy and EDX analysis and conductivity by the 4 point method. Oxygen enrichment of these films during annealing at high temperature induces the formation of the nanocrystalline tin oxide.

Keywords: Tin dioxide; Photovoltaic cells; Annealing; Vacuum evaporation; Nanocrystalline

1. Introduction

Thin tin dioxide layers present a large industrial interest because of their particular properties such as type n semiconductor character, a high optical transmission in the field of the visible range, a high reflectivity in the infra-red as well as a good chemical resistance. Consequently they can be used to constitute transparent and chemically stable thermal barriers. These crystalline coatings are also used for the design of chemical sensors and photovoltaic cells [1–3]. Indeed, it is possible to obtain films having an amorphous or a crystalline structure depending on the processes and the conditions of their developments. These differences in the structure influence electric and optical properties of the layers as well as their chemical stability [4]. Different routes of manufacturing have been developed: sputtering [5], chemical vapor deposition (CVD) [6], pyrosol process [7–9], electrodeposition [10,11], thermal oxidation [12] or dip coating [13,14]. The different manufacturing parameters (deposition technique of precursor compounds, conditions of synthesis and operation parameters) influence in an important way the properties: morphological (sizes of the grains, dimensions of the aggregates), optical (transparency, index of refraction, absorptivity, transmissivity or reflectivity in the various fields of the electromagnetic spectrum) and electrical (electric conductivity, density of charge carriers, quantum containment) of the oxide formed. Devers et al. [15] have shown that annealing, in air for 2 h at 270 or 300 °C, a tin film with a thickness of some nanometers obtained by electrodepositing induces the formation of SnO_2 (mainly amorphous). The volume fraction of this oxide increases either with annealing time or annealing temperature.

Considering these preliminary experiments, the present work deals with tin layers with a thickness of 500 or 1000 Å on ordinary glass substrates. Then these layers are oxidized under oxygen flow by thermal treatment at different temperatures, 300, 400 and 500 °C, during various times. The aim of this investigation is to follow the transformation kinetics of tin into tin dioxide and to evaluate the resistivity of these layers versus the annealing time. Let us mention that the principal goal of this process is to obtain transparent films having a good electric conductivity, for

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the design of nanocrystalline photovoltaic cells free from organic materials or other pollutants.

2. Experimental procedure and results

2.1. Manufacturing of thin tin layers

Vacuum evaporation films are obtained with a well-defined thickness ranging from 50 Å to more than 2000 Å with a high degree of accuracy, a perfect purity and a remarkable homogeneity. Used substrates are ordinary glass rectangular plates (2 cm/5 cm/2 mm). They are introduced in an evaporator ALCATEL, model ATP150 provided with three different crucibles, an adjustable substrate with manual mask, a thickness measuring device MAXTECH TM 350-asf 140 and a powder supply system SDL-G2-HR 10-250.

Thin tin layers with a thickness of about 500–1000 Å are manufactured by evaporation under a high vacuum reaching a value of 10^{-7} Torr onto glass substrates. Both the substrates (ordinary glass) and the material to be evaporated (tin) are first carefully cleaned in solvents and acids. Indeed, the physicochemical properties of the layers obtained are strongly dependent on the conditions of preparation of the substrate and those of evaporation and preparation of material.

2.2. Annealing in oxygen flow

Oxidation of our layers was carried out in a continuous pipe of mark BL Barnstead/Thermolyne (tube furnace 21100) under oxygen flow.

Processing parameters are on the one hand the thickness of the layer and on the other hand the annealing conditions (temperature, time and oxygen flow). Oxidation of the metallic layers is carried out at 300, 400 and 500 °C during different times in a continuous tube under constant oxygen flow.

2.3. X-ray diffraction

X-ray diffraction data were collected using an X-ray diffractometer Philips PW1820, of $\theta-2\theta$ ranging (Bragg–Brentano geometry). Diffraction experiments were carried out using the K_α copper radiation ($\lambda = 1.5404$ Å) and a nickel filter with a fixed low incidence angle (1.5°), in order to limit the investigated depth.

2.4. Environmental scanning electron microscope (ESEM)

The observations have been performed with an FEI XL 30 FEG ESEM INSA, Lyon, France. ESEM is equipped with both secondary and backscattered electron detectors, and an EDAX Phoenix energy dispersive spectrometer (EDS). The EDS system is used to identify the major elements present in a sample in concentrations greater than about 1 wt%.

3. Results and discussion

Directly after elaboration, tin coatings are reflective. After annealing in an oxygen flow they become transparent with a low opacity. This opacity decreases when the time of annealing increases. This time of annealing influences the nature of the phases and the structures which are formed in the layer.

3.1. Structural and morphological features

3.1.1. X-ray diffraction

X-ray diffraction is used to investigate the progressive transformation of tin into tin dioxide during annealing under an oxygen flow of a 500 or a 1000 Å thick tin coating.

In order to show the main transformations submitted to the tin evaporated layer before and after annealing at different temperatures and under different times we gather all obtained patterns in Figs. 1–3.

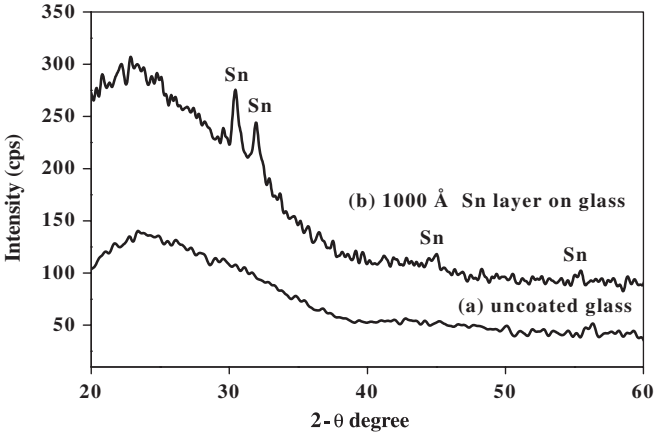

Fig. 1. Diffraction spectrum: (a) uncoated glass, (b) 1000 Å Sn layer deposited by vacuum evaporated.

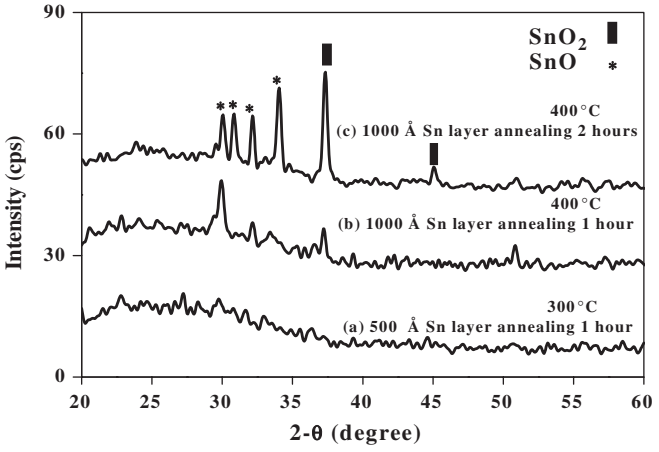

Fig. 2. Diffraction spectrum: (a) for a 500 Å tin layer annealed at 300 °C for 1 h; (b) for a 1000 Å tin layer annealing at 400 °C for 1 h and (c) for a 1000 Å tin layer annealing at 400 °C for 2 h.