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ScienceDirect
Thin Solid Films 515 (2007) 8632–8636
www.elsevier.com/locate/tsf

Initial growth of SnO_2 thin film on the glass substrate deposited by the spray pyrolysis technique

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Available online 1 April 2007

Abstract

Spray pyrolysis of di-*n*-butyltin(IV) diacetate (DBTDA) has led to the deposition of [200]-oriented SnO_2 film on a glass substrate. In order to clarify growth mechanism of the preferential orientation the sprayed SnO_2 thin film has been investigated by using the atomic force microscopy and the X-ray photoelectron spectroscopy. The results have suggested that the sprayed solution forms the SnO_2 small particles on the glass substrate and they spread overall relatively soon. At the very early stage each particle grows with almost the same rate and only its density increases with no change in a surface roughness.

Keywords: SnO_2 thin film; Spray pyrolysis; Preferential orientation; Nucleation; Film growth; AFM; XPS

1. Introduction

Tin(IV) oxide (SnO_2) is an n-type semiconductor material with wide band gap energy, high donor concentration and large mobility [1]. The material is transparent in the visible and reflective in the infrared regions. Thus, the SnO_2 thin films have been utilized as transparent electrodes in sophisticated electronic devices [2–4]. The material also has an advantage in availability of constituent atoms different from ITO (indium tin oxide).

We have reported a deposition of highly oriented SnO_2 thin films on a glass substrate from the organotin compounds by using a spray pyrolysis technique. The results indicated that the (200)- and (110)-oriented thin films were prepared from $(C_4H_9)_2Sn(OOCCH_3)_2$ (DBTDA) [5] and $(C_4H_9)_4Sn$ (TBT) [6], respectively. Two chemical species, O-Sn-O and Sn, relevant to deposition of the oriented thin films were produced in majority through the pyrolysis of DBTDA and TBT, respectively [7], with which the oriented growth can be attributed to a matching between the atomic configuration and each crystalline plane [8].

Spray pyrolysis, one of the well-known chemical techniques applied to form a variety of thin films such as noble metals, metal oxides and chalcogenide compounds, results in good productivity from a simple apparatus. The spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated substrate where the constituents react to form a chemical compound. The chemical reactants are selected so that products except the desired compounds are volatile at the temperature of deposition. We call this technique an SPD (spray pyrolysis deposition) method. One successful application of the technique is in the large-scale formation of CdS thin films for solar cells [9].

In the present study, we have observed initial growth stages of the SnO_2 thin film sprayed on a glass substrate by using the atomic force microscopy (AFM), and measured photoelectron signals from both the film and the substrate by using the X-ray photoelectron spectroscopy (XPS) to clarify the initial growth process of the [200]-oriented SnO_2 thin film.

2. Experimental

2.1. Formation of SnO2 thin film

Di-*n*-butyltin(IV) diacetate (DBTDA) (>95% purity) was used as a starting compound. It, with no further purification,

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doi:10.1016/j.tsf.2007.03.128

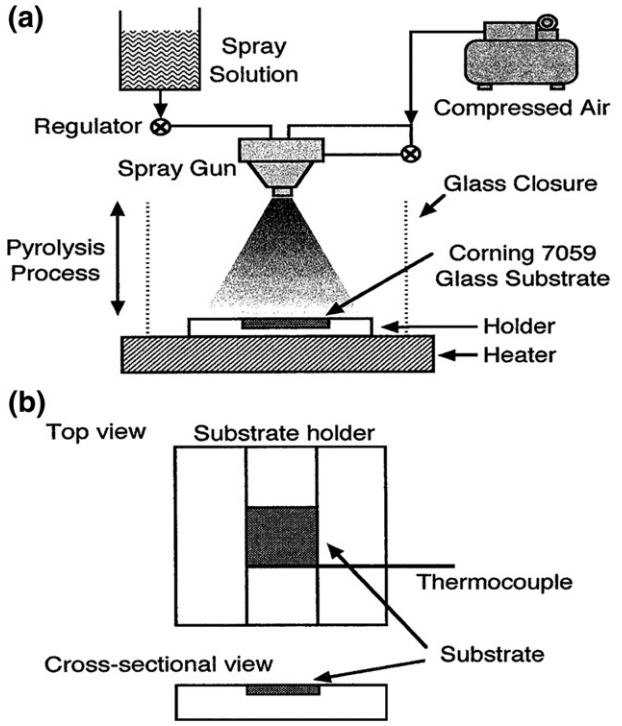

Fig. 1. Schematic drawings of (a) SPD apparatus and (b) substrate and holder.

was dissolved in a dehydrated ethanol. Apparatus used in the present study is illustrated schematically in Fig. 1a. The ethanol solution containing the starting compound was atomized by a pneumatic spraying system. The droplets were transported by the spraying onto a heated Corning 7059 glass substrate measuring 25 mm × 25 mm × 1 mm. Since a substrate temperature was lowered by the spraying air, the solution was atomized not consecutively but intermittently. It thus took several seconds for the next spray until the substrate temperature had recovered, although the period of one spray was 0.1 s. The substrate was mounted on a cordierite ceramic holder (Fig. 1b), and a sheath-type thermocouple was inserted between the substrate and the holder to control the substrate temperature. The spray pressure and distance were fixed to be 0.3 MPa and 450 mm, respectively.

2.2. Characterization of SnO2 thin film

Film thickness was determined by a stylocontact method (Dektak IIA, Sloan). The film thickness, however, of very thin films in a range of several nm was determined by the calculation as follows. In general, the film thickness of deposited film, D [nm] is proportional to a product of concentration, C [wt%] and a total volume, V [ml] of the spraying solution in the SPD method,

$$D = kCV \tag{1}$$

where k is a constant depending on the substrate temperature and determined from a relation between the total volume and the film thickness at the constant substrate temperature. The film thickness determined from Eq. (1), D is called as a calculated film thickness hereafter.

In order to investigate the initial film growth process, surface morphologies of the film were observed by using the

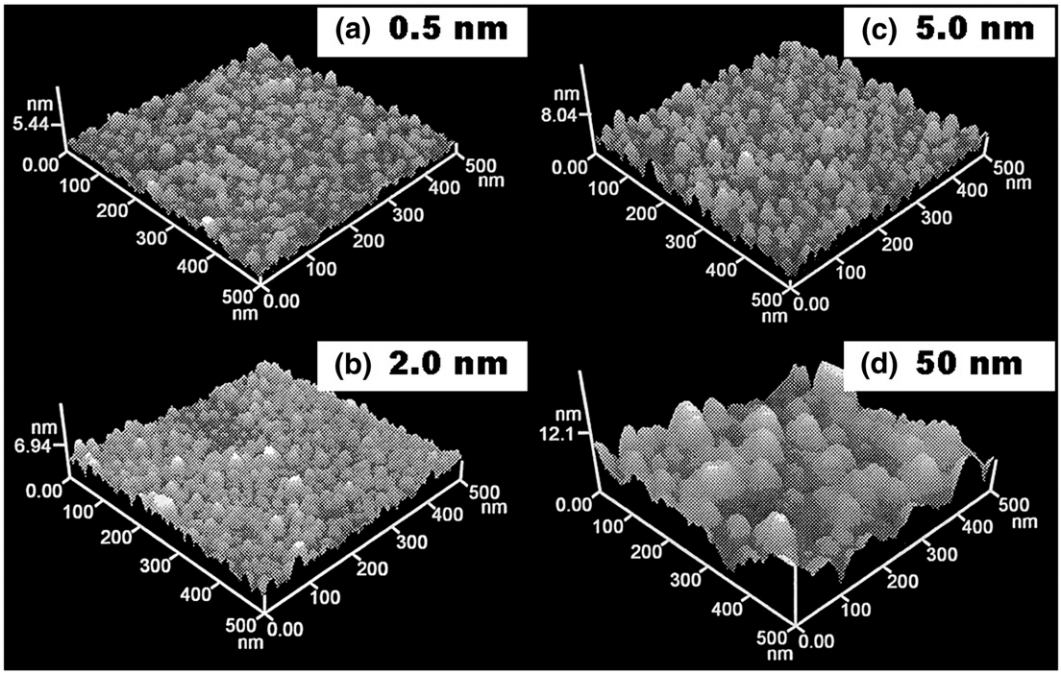

Fig. 2. AFM images of SnO_2 thin films. The calculated film thicknesses are (a) 0.5 nm, (b) 2.0 nm, (c) 5.0 nm and (d) 50 nm. The scan area is 500 nm × 500 nm. The substrate temperature is 475 °C and the DBTDA concentration is 2.0 wt%.