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Elaboration of tin oxide nano-islands through post-deposition thermal treatment

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ABSTRACT

Tin dioxide (SnO_2) films have been grown onto (006) sapphire substrates by sol–gel dip-coating using tin alkoxide solutions. It is shown, using transmission electron microscopy and atomic force microscopy, that the thickness of the layers is easily controlled with tin concentration. It can vary after the deposition process between few nanometers and few tens of nanometers according to the concentration of the precursor in the sol. A post-deposition thermal treatment forces the continuous precursor film to split into isolated islands. A decrease of the tin concentration in the precursor sol to 100 μM allows the formation of islands of a few nanometers (3 nm) in height and several tens of nanometers in diameter (30 nm). Such height value is very close to the Bohr radius of SnO_2.

1. Introduction

Nanostructured systems based on heteroepitaxial islands (noble metals, transition magnetic metals, functional oxides, etc.) grown onto oxide surfaces (MgO, ZnO, Al_2O_3, etc.) are attracting intensive interest due to both the fundamental significance and potential application in optics, electronics, spintronics, and magnetic data storage. In such nanosystems, the control of the interatomic structure, the shape, and the size of the islands are of prime importance in determining the overall physical properties.

The generation of crystalline metal oxides in the form of nanoparticles has attracted significant attention in the recent years. Among these oxides, with a band gap of 3.6 eV, tin dioxide (SnO_2) is of particular interest for its properties used for gas sensors, optoelectronics devices, dye base solar cells, photocatalyst, and electrochemical devices [1–3] such as secondary lithium battery electrode materials. It is assumed that SnO_2 shows improved sensing properties not only because of the increased surface area [4] but also because the grain size of the oxide gets smaller than the space-charge depth originating from surface chemisorbed oxygen species [5]. When the dimensions of nanocrystalline particles approach the exciton Bohr radius (2.7 nm), the effective bandgap energy of SnO_2 becomes more important [6]. Indeed, it is well-known that increasing the surface/bulk ratio by decreasing the grain size is crucial for achieving high-sensitivity in gas sensors and high-photocatalytic activity.

Oxide thin films are principally prepared through physical techniques such as molecular beam epitaxy [7] or pulsed laser deposition [8,9]. Originating from wet chemistry, chemical solution deposition processes, such as sol–gel processing [10–14] can be used to achieve epitaxial oxide thin films as a low cost alternative [15–19]. It is well-known that sol–gel grown thin films subjected to post-deposition thermal annealing are affected by a morphological instability, forcing the film to split into isolated epitaxial islands [15,19]. Taking advantage of this effect, self-patterned nanostructures can be generated [10,11].

SnO_2 thin films can be obtained by different techniques like chemical vapor deposition [20,21], sputtering methods [22–24], spray pyrolysis [25,26], electron beam evaporation [27], pulsed laser ablation [28,29] or molecular beam epitaxy [30]. As compared to these techniques, the sol–gel dip-coating technique is able to produce homogeneous SnO_2 films with crystallites very regular in size and offers also advantages such as low cost, low temperatures processing and precise control of stoichiometry [31–41].

In a previous study [41], SnO_2 films were grown onto (006) sapphire substrates by sol–gel dip-coating. We found that heat treatment between 500 °C and 1300 °C revealed the presence of two growth mechanisms in both xerogels and thin layers. Up to 1100 °C, grain growth is governed by surface diffusion, while beyond this temperature evaporation–condensation predominates and induces fast grain

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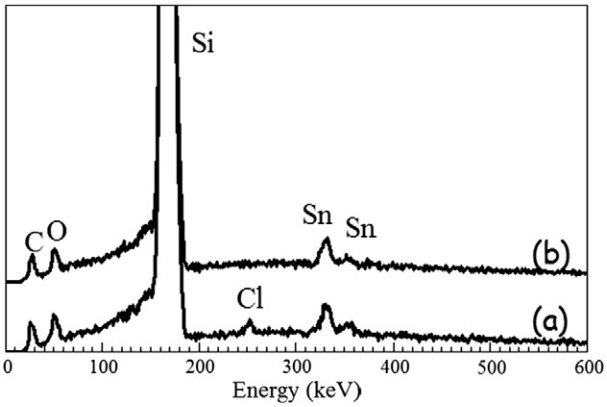

Fig. 1. EDS analysis of (a) a raw SnO_2 material and (b) a layer annealed at 500 °C. The thin films were grown on Si wafer (peak labeled Si) and for the EDS analysis the sample was covered with a carbon layer (peak labeled C).

growth. This behavior was observed for nano- and micro-powders [42,43]. For temperature higher than 1100 °C, thin films split into textured isolated islands. For temperatures higher than 1300 °C, the SnO_2 phase dissociates into SnO(g) and O_2(g): $SnO_2(s) \rightarrow SnO(g)$ and $1/2O_2(g)$. Even under high-oxidizing atmosphere, we were not able to avoid this sublimation process and the maximum temperature value that we can use is 1300 °C. In general manner, it is well-known [15,17–19,44–46] that islanding and texturation through post-deposition thermal treatment are concomitant processes. Thus the limitation of the useable temperature hinders the formation of epitaxial islands through this process. Nevertheless we have shown that thermal treatment at 1300 °C promotes a strong texturation into quite thick SnO_2 films [41].

Starting from the results previously published [41], the aim of this paper is to evidence the influence of the initial tin concentration into the precursor solution onto the microstructure of the elaborated film. In particular, we will show how the choice of very low concentration values result after convenient thermal treatment at moderated temperature on the formation of nanosized tin oxide disconnected islands well-dispersed onto the substrate surface.

2. Experimental details

Two types of precursors are frequently used in sol–gel techniques: metal alkoxides or metal salts. In the case of tin oxide, it turns out that the use of tin alkoxide is hindered by its expensive price and its extreme reactivity toward hydrolysis [47,48]. SnO_2 thin films were hence prepared on sapphire substrates by sol–gel dip-coating from two different precursors i.e. (1) $SnCl_2 \cdot 2H_2O$ salt and (2) tin(IV) isopropoxide isopropanol $Sn(OC_3H_7^i)_4 \cdot {}^iC_3H_7OH$. In the first system, the SnO_2 precursor solution was prepared from tin chloride by dissolving $SnCl_2 \cdot 2H_2O$ in pure ethanol [41]. The obtained solution was refluxed for 24 h. During the deposition of the film the presence of Cl^- ions can affect the growth rate [49]. The elaboration of pure SnO_2 then requires eliminating Cl^- ions. A chemical analysis was performed by EDS (energy dispersive X-ray spectroscopy) before and after thermal annealing of the films (Fig. 1) by using the emitted X-rays in a S260 Cambridge Instruments Scanning Electron Microscope equipped with a tungsten filament electron gun and a PGT Synergie4 spectrometer with a germanium diode. The spectral resolution is 112 eV at 15 kV on the line of manganese. Before thermal annealing, the films contain the following elements: O, Sn, Cl (Fig. 1a). After a thermal annealing at 500 °C, the films are free of Cl (Fig. 1b).

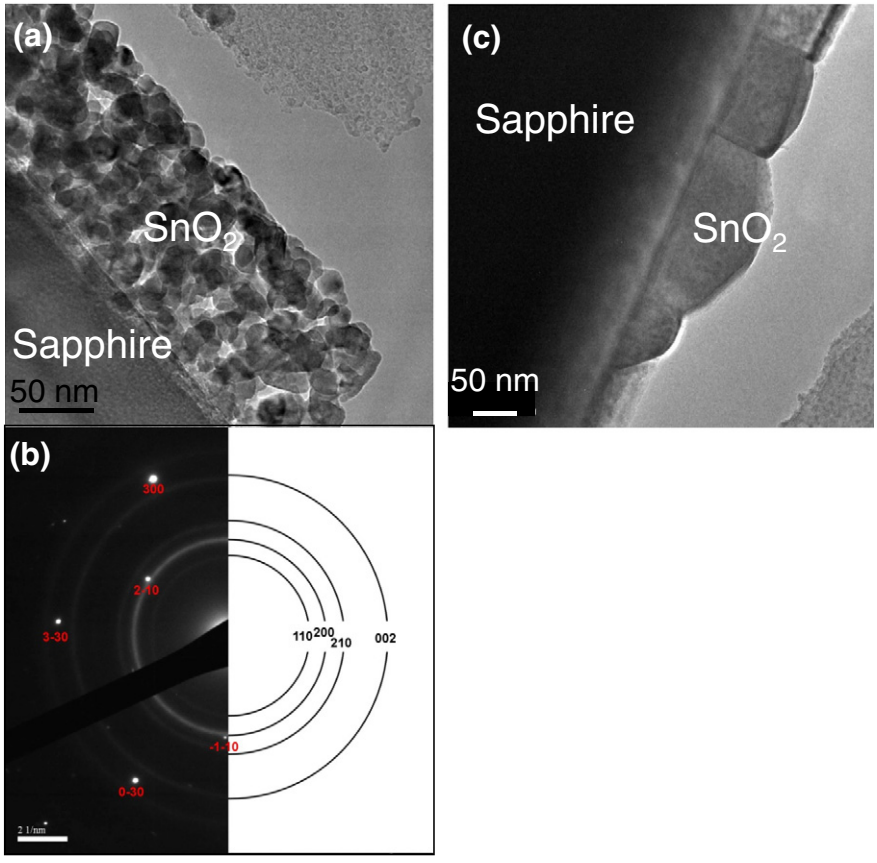

Fig. 2. TEM cross-sections of SnO_2 layers on sapphire with a concentration of Sn = 0.5 M treated for 1 h at (a) 800 °C and (c) 1250 °C, (b) diffraction pattern of a TEM plane-view of the sample (a).