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High-resolution transmission electron microscopy investigation of nanostructures in SnO_2 thin films prepared by pulsed laser deposition

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Abstract

Pulsed laser deposition (PLD) was used to grow nanocrystalline SnO_2 thin films onto glass substrates. The nanocrystallites and microstructures in SnO_2 thin films grown by PLD techniques have been investigated in detail by using X-ray diffraction and high-resolution transmission electron microscopy (HRTEM). The PLD process was carried out at room temperature under a working pressure of about 2×10^{-6} mbar. Experimental results indicate that thin films are composed of a polycrystalline SnO_2 and an amorphous SnO phase. In particular, the presence of such an amorphous SnO phase in the thin films greatly limits their practical use as gas-sensing devices. HRTEM observations revealed that SnO_2 nanocrystallites with tetragonal rutile structure embed in an amorphous SnO matrix, which are approximatively equiaxed. These approximatively equiaxed SnO_2 nanocrystallites contain a high density of defects, such as twin boundaries and edge dislocations. The grain growth of SnO_2 thin films may be discussed in terms of the coalescent particle growth mechanism.

Keywords: SnO_2 thin film; Microstructure; Nanocrystallite; Pulsed laser deposition

1. Introduction

The microstructural evolution of tin dioxide (SnO_2) thin films has been studied exhaustively and this topic has recently gained even greater importance due to the interest in controlling particle size in nanostructured materials [1–7]. Moldovan et al. [3] have used analytical and simulation methods to characterize the growth law and morphology of two-dimensional growth by grain-rotation-induced grain coalescence in polycrystalline microstructures. Leite et al. [5] reported on experimental evidence indicating that the crystal growth process took place in a colloidal nanocrystal system at room temperature. This crystal growth process is based on grain rotation among neighboring grains, resulting in a coherent grain–grain interface, which, by eliminating common boundaries, causes neighboring grains to coalesce, thereby forming a single larger nanocrystal. With the continuous breakdown of sizes and the increased demand on performance for optical, electronic, and magnetic devices, the control of thin film structures is becoming increasingly significant. Many efforts have been devoted to investigation of the growth mode [8,9], to the formation of crystallographic structures [10,11], and to the kinetic morphology evolution of island ensembles [12,13]. SnO_2 is widely employed in gas-sensing applications because of its excellent response to different pollutant gases [14]. Under a nanostructured form, the nanocrystalline SnO_2 thin films have been shown to exhibit better gas-sensing performance than their micro- and/or macro-structured counterparts [15]. Therefore, the investigation of the micro- and nanostructure characteristics of SnO_2 thin films, by means of X-ray diffraction (XRD) and high-resolution transmission electron microscopy

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(HRTEM) [16,17], is an essential step toward a better understanding of how the growth conditions influence the thin film nanostructure which, in turn, determines the film sensing performance. In this context, the pulsed laser deposition (PLD) technique stands out by its unique features, such as its extremely high instantaneous deposition rate and the highly energetic ablated species, that permit the growth of nanostructured thin films exhibiting unprecedented properties [18].

In this paper, we report on an HRTEM investigation of nanostructures of SnO_2 thin films prepared by PLD. Experimentally, PLD deposition under vacuum is found to produce thin films that are composed of both a polycrystalline SnO_2 phase and an amorphous SnO phase. HRTEM observations revealed that the SnO_2 nanocrystallines with tetragonal rutile structure are embed in an amorphous SnO matrix, and tend to be approximatively equiaxed. These approximatively equiaxed SnO_2 nanocrystallites contain a high density of defects, such as twin boundaries and edge dislocations. The grain growth of SnO_2 thin films may be discussed in terms of the coalescent particle growth mechanism.

2. Experimental

SnO_2 thin films were prepared by the PLD method [17]. Sintered cassiterite SnO_2 bulk was used as the target. The circular target consisted of a high-purity commercial SnO_2 (99.8%) disk. The size of the target was about $\varnothing 15\,\text{mm} \times 4\,\text{mm}$, and they were installed to minimize contamination. The laser was a KrF excimer laser producing pulse energies of 350 mJ at a wavelength of 248 nm, and the duration of every excimer laser pulse was 34 ns. The laser energy was deposited onto the target in a high-vacuum chamber through a UV-grade fused silica window using a UV-grade fused silica lens. During the experiment, the laser was operated at a repetition rate of 10 Hz at an incident angle of 45° to the polished sintered cassiterite SnO_2 target, which was rotating at a rate of 15 rpm to avoid drilling. The fluence was set at about $5\,\text{J/cm}^2$ per pulse, with a total of approximately 150,000 laser pulses. The growth rate was estimated to be about 0.3 nm/s (or 1 μm/h) and the final as-deposited thin film thickness was about 4 μm. The ablated substance was collected on a glass slide, which was mounted on a substrate holder 2.5 cm away from the target. The high vacuum in the deposition chamber was achieved using a cryopump. The base pressure prior to laser ablation was about 1×10^{-6} mbar, and the working pressure during laser ablation was about 2×10^{-6} mbar. All deposition processes were carried out at ambient temperature.

XRD patterns were recorded at a scanning rate of 0.05°/s in the 2θ range from 15° to 65° using a *Philips X'pert* diffractometer with Cu $K\alpha$ radiation (1.5406 Å), reflection geometry, and proportional counter. The nanocrystallite quality of the SnO_2 thin films was characterized using high-resolution observation of the microstructural evolution of SnO_2 nanoclusters, which were performed using a JEOL-2010 transmission electron microscope (HRTEM), with a point-to-point resolution 1.94 Å, operated at 200 kV.

3. Results and discussion

Figs. 1a and b show XRD patterns of the cassiterite SnO_2 bulk and the as-prepared SnO_2 thin films, respectively. All reflections can be indexed with tetragonal cell of SnO_2, and all cell parameters are close to $a = 4.737$ Å, and $c = 3.185$ [19]. The SnO_2 average sizes were calculated using the Scherrer formula: $D = K\lambda/\beta \cos\theta$, where D is the diameter of the nanoparticles, $K = 0.9$, $\lambda(\text{Cu}K\alpha) = 1.5406$ Å, and β is the full-width at half-maximum of the diffraction lines. XRD results show that the average grain size of the as-prepared nanocrystalline SnO_2 is about 12 nm. The

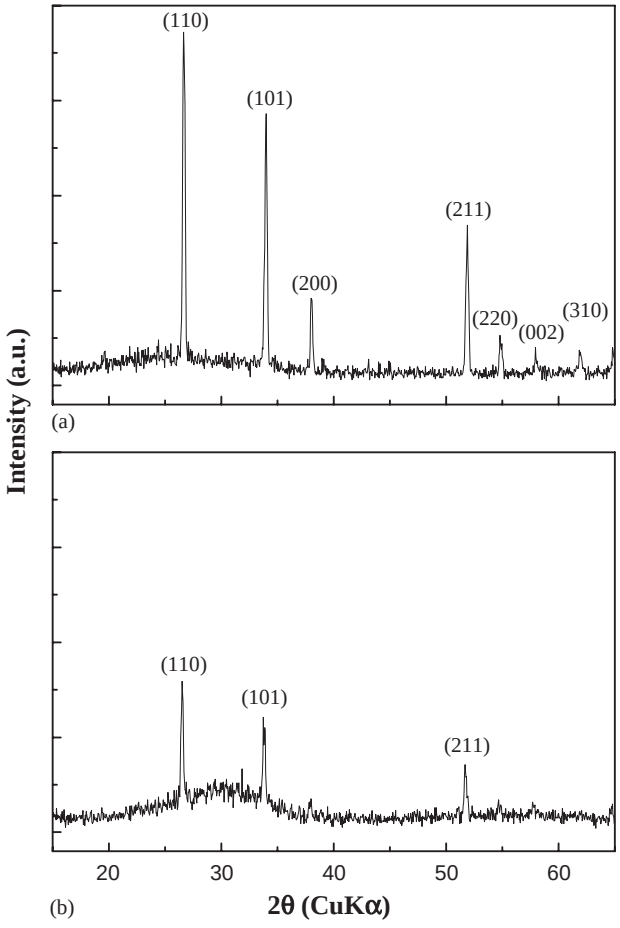

Fig. 1. XRD patterns of SnO_2: (a) SnO_2 bulk material and (b) as-prepared SnO_2 thin film.