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Synthesizing SnO_2 thin films and characterizing sensing performances

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ABSTRACT

SnO_2 thin films were grown on silica glass substrates using the pulsed laser deposition (PLD) method, and their structures, electric properties, and sensor performances were examined to investigate the sensing mechanism of thin-film gas sensors. Single-phase SnO_2 films with rutile-type structures were obtained at 650 °C. All the SnO_2 films had many columnar grains, and the grain size increased with film thickness. Measurements of the Hall coefficient at room temperature revealed that the Hall mobility of the films was independent of the film thickness. In contrast, the sensing performances of the films for NO_2 and H_2 gases respectively in an air atmosphere drastically improved for film thicknesses under 100 nm. These results for the film properties and sensing performances of SnO_2 thin films are discussed in terms of a space-charge layer formed on the columnar grains.

1. Introduction

SnO_2 has been applied in semiconductor gas sensors for many years [1]. These sensors are used for various purposes, such as detecting flammable gas in the home and office, detecting H_2, CH_4, and LPG to prevent leakage, and detecting CO to prevent incomplete combustion. Most commercially available SnO_2 gas sensors are either a bulk-ceramic or thick-film-type prepared using conventional ceramic techniques. Recently, the development of SnO_2 thick-film gas sensors composed of nanoparticles or nanostructures has been extensively studied in order to achieve high-performance gas sensing [2–4]. The gas sensing mechanism of SnO_2 ceramics and thick films has been investigated in relation to double Schottky barriers formed at grain boundaries [5,6]. The double Schottky barrier in association with the electronic state of the grain and accepter level of the grain boundary behaves as a potential barrier to electron transport [7,8].

Thin-film sensors have attracted a great deal of attention recently. Multifunctional sensing with a combination of various sensors and electric-power saving by using a film-type heater fabricated with microelectromechanical system (MEMS) technology are expected to be developed in the future. Research on thin-film-type sensors synthesized using a dry process and on small sensor devices applying the MEMS technology has been conducted [9–13]. Film-type SnO_2 sensors have been fabricated using chemical vapor deposition [14], sputtering [15], molecular beam epitaxy [16], and a pulsed laser deposition (PLD) [17] method. However, the structures and crystallographic orientations of thin films differ markedly from that of bulk ceramics and thick films, and the mechanisms of thin-film sensors are still to be clarified.

In the present study, SnO_2 thin films grown on glass substrates were prepared using a PLD method, and their structural, electric, and sensing properties were studied. Moreover, we examined the sensing mechanisms of SnO_2 thin films in terms of the thickness dependencies of the electric properties and the sensor responses.

2. Experimental

SnO_2 films were grown using a PLD method in a growth chamber with a backing pressure of 3×10^{-7} Pa. SnO_2 ceramics (4N) were used as the ablation target. Silica glass substrates were cleaned in ultrasonic baths of acetone and ethanol and placed in the growth chamber. A pulsed laser of the fourth harmonic generation of neodymium-doped yttrium gallium garnet (Nd:YAG, $\lambda = 266$ nm) with a 5-ns pulse width and 5-Hz repetition rate was focused on the target. The growth temperature was varied between 350 and 700 °C in O_2 pressure of 1×10^{-3} Pa. The thicknesses of the grown SnO_2 films were 40–400 nm.

The crystalline phases and lattice orientations of the SnO_2 films were identified from X-ray diffraction (XRD; 2θ–θ, and pole figure

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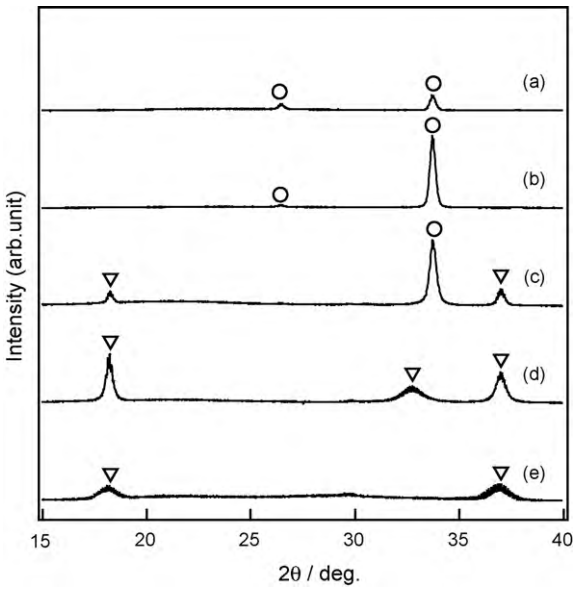

Fig. 1. XRD profiles of films grown at various temperatures: (a) 700 °C, (b) 650 °C, (c) 600 °C, (d) 500 °C, and (e) 350 °C. Open circles are diffraction peaks of SnO_2 phase (JCPDS: 01-071-5323). Open triangles are those of SnO phase (JCPDS: 01-072-1012).

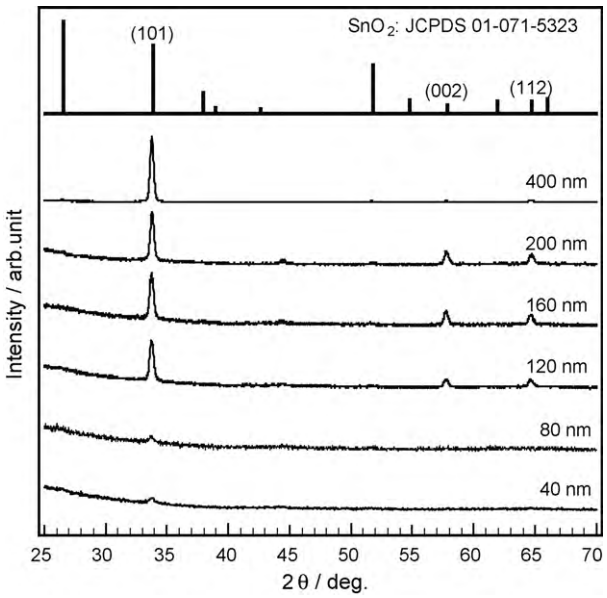

Fig. 2. XRD profiles of SnO_2 films of various thicknesses grown at 650 °C.

modes) with CuKa radiation. The thicknesses of the films were measured with a Dektak surface profiler. The cross-sections and surface morphologies of the films were observed by a scanning electron microscope (SEM) and an atomic force microscope (AFM), respectively. We used Hall coefficient measurement at room temperature to clarify the electric properties of SnO_2 films, i.e., resistivity without junction resistance, carrier concentration, and Hall mobility. Standard van der Pauw four-probe geometry was applied to the 8 mm × 8 mm square films, and electric contacts made of Al were formed using an evaporation method. Before measuring, we verified that the ohmic contact was good and the contact resistance between the films and the electrodes was low.

To evaluate the sensing performance of the films, the electric resistances of the films were obtained by two-terminal measurement using Au electrodes. Two rectangular electrodes placed 5 mm apart were used. The Au electrodes were sputtered on the surface of the as-grown SnO_2 films. The gas responses of the SnO_2 films to 1000-ppm NO_2 gas in air and 1% H_2 gas in air respectively at 350 °C were measured as a function of time. Air and the target gases were

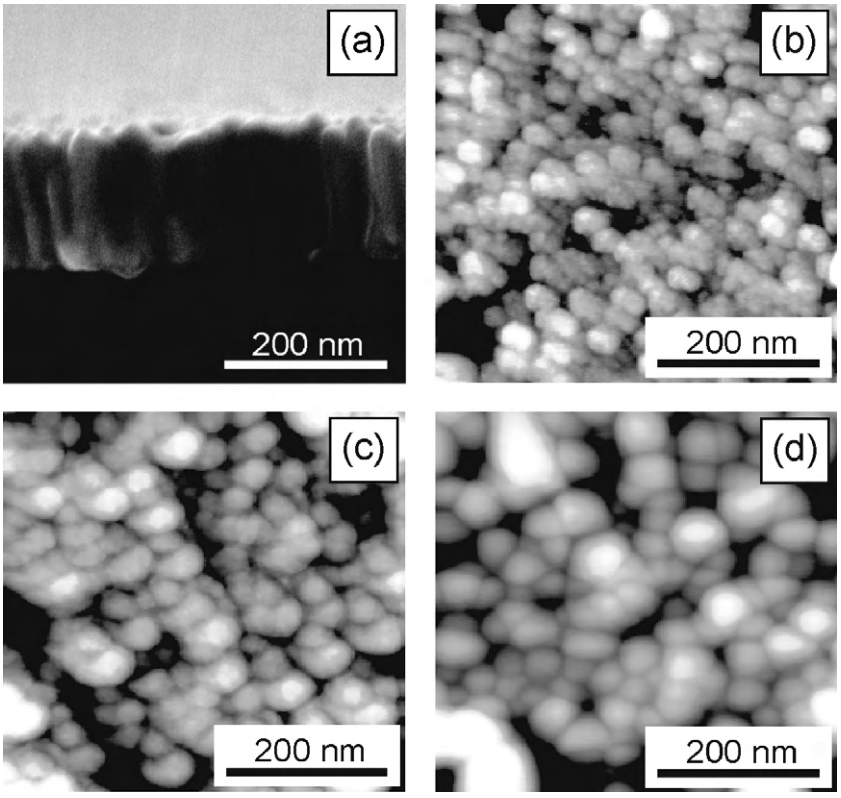

Fig. 3. Cross-sectional SEM image (a) and AFM images of SnO_2 film surfaces (b)–(d). (a) 200-, (b) 40-, (c) 120-, and (d) 200-nm-thick films.