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Structural, electrical and optical properties of sputter-deposited Nb-doped TiO_2 (TNO) polycrystalline films

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Abstract

Transparent conductive oxide (TCO) films of polycrystalline Nb-doped TiO_2 (TNO) were fabricated by post-annealing reactively sputtered amorphous films under H_2 atmosphere. Carrier transport properties of the H_2-annealed films were found to be strongly dependent on substrate temperature T_s and oxygen content in sputtering atmosphere. A minimum resistivity (ρ) of 9.5×10^{-4} Ω cm and an average visible transmittance of ~75% were obtained at T_s=RT and oxygen content of 10%. This ρ value is of the same order as those of epitaxial TNO films, indicating that polycrystalline TNO has sufficient potential as a practical TCO suitable for large-area applications.

Keywords: Transparent conductive oxide; Nb-doped TiO_2; TNO; Anatase; Sputtering; Polycrystalline films; Post-annealing

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1. Introduction

Use of transparent conductive oxides (TCOs) has been explosively expanded owing to the rapid growth of flat panel display (FPD) market [1]. In particular, sputter-deposited Sn-doped In_2O_3 (ITO) has been established as a practical TCO material because of its excellent resistivity ρ (~2×10^{-4} Ω cm) and visible transmittance (80–90%) [2]. However, indium has a shortage problem, stimulating researchers to seek new TCO materials free from indium.

Recently, we found that Nb- or Ta-doped TiO_2 epitaxial films grown on various single crystal substrates by pulsed laser deposition (PLD) exhibit low ρ (<3×10^{-4} Ω cm) and excellent internal transmittance (>90%) in the visible region [3–6]. This was followed by PLD growth of polycrystalline Nb-doped TiO_2 (TNO) films on glass, indicating ρ of 1.5×10^{-3} Ω cm and transmittance T_r of 60–80% [7]. Lower ρ value down to 5×10^{-4} Ω cm was attained by post-annealing PLD-grown amorphous films under pure H_2 atmosphere [8]. These are good demonstrations that TNO has sufficient potential as an ITO-alternative TCO material.

Practically, TCO films, including ITO, have been mainly fabricated by sputtering technique, which is suitable for low-cost and uniform coatings on large-area substrates. In order to establish TNO as a practical TCO material, thus, it is highly desirable to develop sputtering-based procedures for high-quality TNO films. Gillispie et al. succeeded in sputter-deposition of TNO epitaxial films on $SrTiO_3$ with ρ of ~3×10^{-4} Ω cm and T_r of >80%, which are comparable to those of epitaxial PLD films [9]. Moreover, we have achieved ρ ~ 1×10^{-3} Ω cm and T_r=60–80% [10], by applying the above-mentioned post-annealing technique to sputter-deposited TNO films.

In this paper, we report electrical, optical and structural properties of TNO polycrystalline films, prepared by post-annealing sputter-deposited amorphous films, as functions of sputtering conditions, such as substrate temperature T_s and oxygen partial pressure during amorphous deposition. By comparing these properties between sputter- and PLD-grown films, material parameters that govern the transparent conductivity of TNO will be discussed.

2. Experimental details

Polycrystalline TNO films were fabricated by post-annealing sputtered amorphous films, as follows. The amorphous TNO

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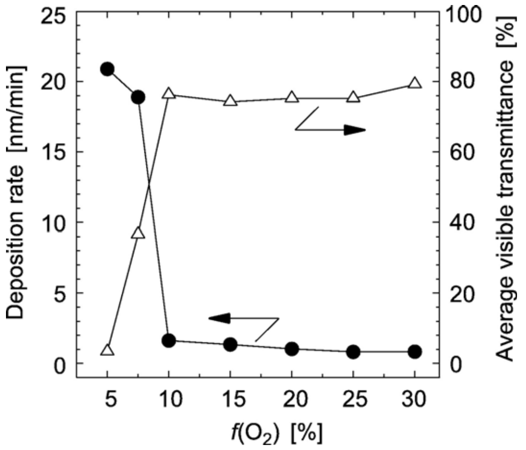

Fig. 1. Deposition rate (closed circle) and average visible transmittance (open triangle) of as-deposited TNO film (T_s=RT) as functions of $O_2/(Ar+O_2)$ flow ratio $f(O_2)$ during deposition of amorphous films.

thin films were deposited on heated (T_s=150°C) or unheated (T_s=RT) alkali-free glass substrates (Corning #1737) by reactive DC magnetron sputtering. A $Ti_{0.94}Nb_{0.06}$ alloy disk of 50 mm was used as the target. Base pressure below 5×10^{-4} Pa was established, prior to each deposition run. Film deposition was conducted in a mixture of Ar and O_2 with various $O_2/(Ar+O_2)$ flow ratio, $f(O_2)$, ranging from 5 to 30% under a total pressure of 1.0Pa. The DC power applied to the target was kept constant at 180 W during sputtering. Before the film deposition, the target surface was sputter-cleaned using pure Ar for 15 min in order to remove surface oxide layers and contamination, and was subsequently pre-sputtered for 10 min under the same condition as the film deposition. The typical deposition time and film thickness were 120 min and 120–150 nm, respectively. The as-deposited films were post-annealed in pure H_2 under the pressure of 1×10^5 Pa for 60 min in a rapid thermal annealing furnace, where the annealing temperature was raised to 600 °C at a rate of 10 °C/min.

Carrier transport properties, including resistivity (ρ), carrier density (n_e), and Hall mobility (μ_H), of the TNO thin films were determined using the van der Pauw method at room temperature. Structural properties were characterized by X-ray diffraction (XRD) using a diffractometer equipped with a two-dimensional detector (Bruker D8 Discover) and cross-sectional transmission electron microscopy (TEM). Surface morphologies of as-deposited and annealed films were observed by using an atomic force microscopy (AFM). Optical measurements were performed using a UV–VIS–NIR spectrophotometer in a wavelength region of 300–2300 nm.

3. Experimental results and discussions

3.1. Sputtering mode

Deposition rate (T_s=RT) and average visible transmittance (λ=400–800 nm) as functions of $f(O_2)$ are plotted in Fig. 1. The average visible transmittance T_{ave} over wavelengths ranging from 400 to 800 nm is defined by the following formula,

$$T_{ave} = \frac{\int_{400}^{800} T_r(\lambda)d\lambda}{400}, \tag{1}$$

where, $T_r(\lambda)$ is a transmittance at a wavelength λ (in nm unit). Increase of $f(O_2)$ from 5 to 10% causes steep decrease of deposition rate and sudden improvement of transmittance from 0 to 75%. This is due to the transition of sputtering mode from metallic sputtering mode to the compound sputtering one [11]. We henceforth discuss the properties of transparent TNO films deposited at $f(O_2)\geq10\%$.

3.2. Structural properties

θ–2θ XRD patterns of TNO films prepared at $f(O_2)$=10% on unheated (T_s=RT) and heated (T_s=150 °C) substrates are

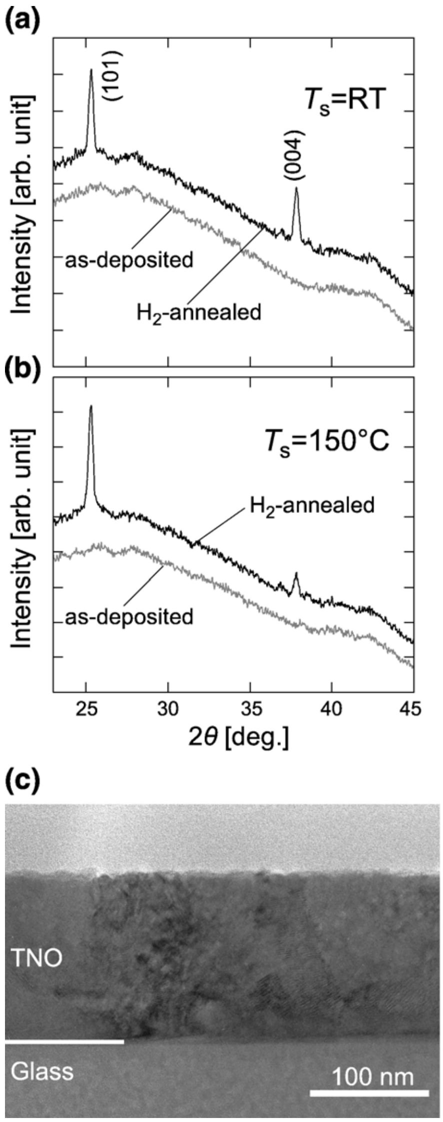

Fig. 2. X-ray diffraction patterns of as-deposited (gray lines) and H_2-annealed TNO films (black lines) deposited at $f(O_2)$=10% on (a) unheated (T_s=RT) and (b) heated (T_s=150 °C) substrates. (c) Cross-sectional TEM image of H_2-annealed films presented in (a).