

Low-temperature Fabrication of Transparent Conducting Anatase Nb-doped TiO₂ Films by Sputtering

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We present a low-temperature ($\sim 300^\circ\text{C}$) process for preparing transparent conducting anatase Nb-doped TiO₂ (TNO) polycrystalline films by sputtering. We first deposited amorphous films composed of an oxygen-rich bottom layer and oxygen-deficient top layer at room temperature. These films were then crystallized in a reducing atmosphere. The oxygen-rich bottom layer behaved as a seed layer during crystallization of the top layer, resulting in significant improvement of crystallinity and reduction of crystallization temperature. We obtained TNO polycrystalline films showing a resistivity of $6.4 \times 10^{-4} \Omega \text{ cm}$ and absorption below 10% in the visible region by post-deposition annealing at 400°C . The developed low-temperature process was applied to fabricating TNO films on plastics and glass with low glass-transition temperature. © 2008 The Japan Society of Applied Physics

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Transparent conducting oxides (TCOs) are among the key materials supporting optoelectronics technology, and sputter-deposited Sn-doped In₂O₃ (ITO) has been established as a practical TCO material because of its excellent resistivity ρ ($\sim 2 \times 10^{-4} \Omega \text{ cm}$) and transparency in the visible region. However, the development of new optoelectronic devices, including blue light-emitting diode, vertical cavity surface emitting laser (VCSEL) and solar cell, requires the advance of new TCOs with additional properties that conventional TCOs do not possess,¹⁾ such as high work function,²⁾ and durability against atomic hydrogen.³⁾

Recently, Nb-doped anatase TiO₂ (Ti_{1-x}Nb_xO₂; TNO) epitaxial films grown on SrTiO₃ or LaAlO₃ single-crystal substrates by using pulsed laser deposition (PLD) have exhibited low ρ ($\sim 2 \times 10^{-4} \Omega \text{ cm}$) and high internal transmittance ($>90\%$) in the visible region.⁴⁻¹⁰⁾ A characteristic feature of TNO is a high refractive index of ~ 2.4 , which plays an important role in the increase of plasma wavelength and suppression of electron scattering by impurities.¹¹⁾ An excellent transparent conductivity ($\rho = 4.6 \times 10^{-4} \Omega \text{ cm}$) and a visible transmittance of 60–80% have been achieved even in polycrystalline TNO films on glass, prepared by crystallizing amorphous films at high temperature ($>500^\circ\text{C}$),^{12,13)} demonstrating the sufficient potential of TNO as a next-generation TCO.

Sputtering, which is suitable for low-cost and uniform coating on large-area substrates, has been established as a standard technique for preparing TCO films. Thus, development of a sputter-based procedure for transparent conducting TNO films on glass is desirable. Furthermore, there is a strong demand for suppression of processing temperature, as this would allow the deposition of TNO films on plastics and thus substantially expand the application fields of TNO.

In this paper, we report the fabrication of sputter-deposited transparent conducting anatase TNO polycrystalline films on glass substrates at processing temperatures below 300°C . We used amorphous films with a double-layered structure, composed of oxygen-rich bottom and oxygen-deficient top layers. The films were annealed under

reducing atmospheres, where the bottom layer presumably behaved as a nucleation center during crystallization. The proposed low-temperature process was used to fabricate polycrystalline TNO films on polyimide and soda lime glass with a low glass-transition temperature.

Polycrystalline TNO films were crystallized from sputtered-deposited amorphous films on unheated non-alkaline glass substrates (Corning #1737). The substrate temperature during deposition was confirmed to be in the $70\text{--}80^\circ\text{C}$ range. As a target, we used a ϕ 2-in. disk of Ti_{0.963}Nb_{0.037}O_{2- δ} composition, which was heat-treated in an Ar-reducing atmosphere in order to introduce oxygen vacancies. The base pressure prior to each deposition run was $\sim 5 \times 10^{-5}$ Pa. Sputter deposition was performed in a mixture of Ar and O₂ at various flow ratios $f(\text{O}_2) = [\text{O}_2]/(\text{Ar} + \text{O}_2)$ under a total pressure of 1.0 Pa. The RF power applied to the target was kept constant at 120 W during sputtering. Before each deposition, the target surface was sputter-cleaned by pure Ar for 10 min, and then pre-sputtered for 5 min under the film deposition conditions. The as-deposited amorphous films were crystallized by annealing in a rapid thermal annealing furnace, where the temperature was raised at a rate of $100^\circ\text{C}/\text{min}$. The Nb content of the Ti_{1-x}Nb_xO₂ films was determined to be $x = 0.040 \pm 0.001$ by Rutherford backscattering spectrometry (RBS). Carrier transport properties were measured using standard Hall bar geometry. Structural properties were characterized by X-ray diffraction (XRD) and cross-sectional transmission electron microscopy (TEM).

In order to determine the crystallization temperature (T_{crys}) as a function of $f(\text{O}_2)$, we measured the ρ of amorphous films grown at different $f(\text{O}_2)$ in a heating-cooling cycle under pure hydrogen atmosphere (1 atm), as shown in Fig. 1(a). The temperature was first raised to 500°C at a rate of $3^\circ\text{C}/\text{min}$, held for 60 min, and then cooled to room temperature at $3^\circ\text{C}/\text{min}$. Each ρ - T curve in Fig. 1(a) exhibits an abrupt drop in ρ around $300\text{--}340^\circ\text{C}$, corresponding to a phase transformation from amorphous to polycrystalline anatase.¹²⁾ As seen from Fig. 1(a), T_{crys} tends to be suppressed with increasing $f(\text{O}_2)$. For example, the $f(\text{O}_2) = 5\%$ film shows $T_{\text{crys}} = 300^\circ\text{C}$, which is 40°C lower than that of $f(\text{O}_2) = 0.05\%$. The origin of this suppression of T_{crys} on increasing $f(\text{O}_2)$ is still an open question.

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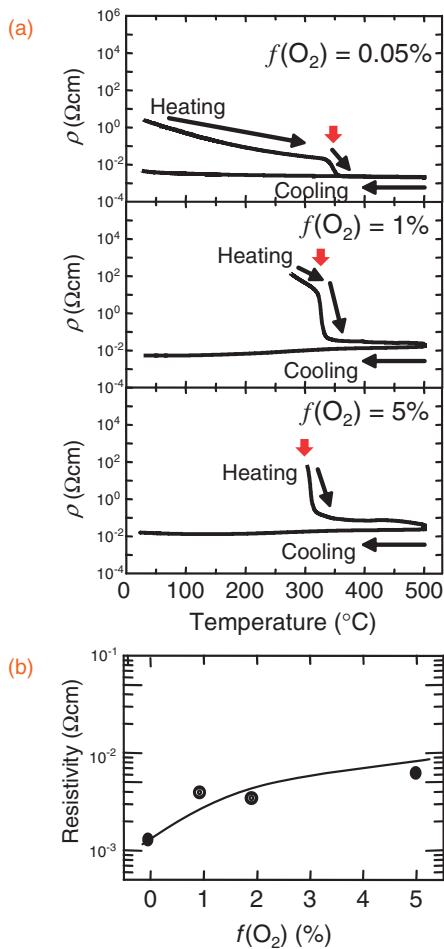


Fig. 1. (a) Resistivity of as-deposited films measured *in situ* during the heating and subsequent cooling treatments, and (b) resistivity as a function of $f(\text{O}_2)$. Red arrows in (a) are guides for eyes to indicate crystallization temperature. Note that the crystallization temperature reduces as the $f(\text{O}_2)$ is increased. Solid curve in (b) is also guide for eyes.

Figure 1(b) plots ρ against $f(\text{O}_2)$ for films annealed at 500°C in H_2 atmosphere. A clear trend of increasing ρ with increasing $f(\text{O}_2)$ is observed. Thus, there is a tradeoff between decreasing T_{crys} and pursuing low ρ . To overcome this difficulty, we propose here a novel process to crystallize an amorphous film with double-layered structure, composed of an oxygen-rich bottom seed layer [$f(\text{O}_2) = 5\%$] and oxygen-deficient top layer [$f(\text{O}_2) = 0.05\%$]. Here, we call the TNO films prepared at $f(\text{O}_2) = 0.05\%$ and $f(\text{O}_2) = 5\%$ as “oxygen-deficient” and “oxygen-rich”, respectively. This is because, according to recent X-ray photoemission spectroscopy (XPS) results, highly conductive films contain oxygen deficiency δ as $\text{Ti}_{1-x}\text{Nb}_x\text{O}_{2-\delta}$,¹⁴⁾ while insulating ones incorporate excess oxygen atoms around Nb dopants, which form deep impurity levels and suppress conductivity.¹⁵⁾ The oxygen-rich bottom layer with low T_{crys} is expected to act as a nucleation center, where crystallization of the top oxygen-deficient layer with higher T_{crys} is initiated.

We first deposited an oxygen-rich bottom layer with a thickness of 30 nm under $f(\text{O}_2) = 5\%$ atmosphere, and then grew a 200-nm-thick oxygen-deficient layer at $f(\text{O}_2) = 0.05\%$, as schematized in Fig. 2(a). Figure 2(b) shows a ρ - T curve measured for the double-layered amorphous film, revealing that crystallization begins around 300°C , which is

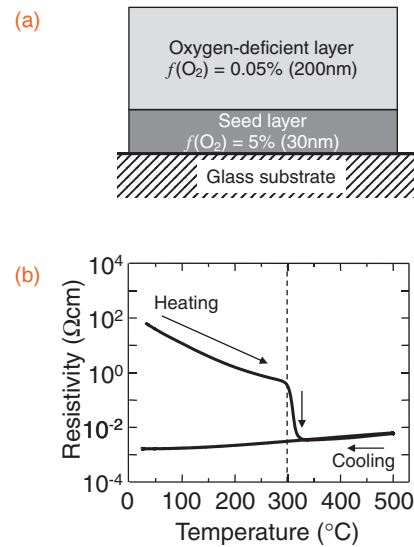


Fig. 2. (a) Structure of double-layer film. (b) Resistivity of double-layer films measured *in situ* during heating and subsequent cooling treatments.

identical to the T_{crys} of the bottom layer. This evidences that the crystallization process propagates from the bottom layer to the top layer at 300°C .

Figure 3 shows ρ values as functions of annealing temperature and annealing atmosphere [pure H_2 and vacuum (3×10^{-3} Pa)] for the above-mentioned double-layered films. Notably ρ is essentially independent of annealing atmosphere, proving that the incorporation of hydrogen into TNO is not responsible for the low ρ of crystallized TNO films. The optimum annealing temperature is spread over a wide range (300 – 400°C), and the lowest ρ of $7.0 \times 10^{-4} \Omega\text{cm}$ is obtained at 400°C in H_2 atmosphere. The annealed films, except for that prepared at 250°C , exhibit metallic temperature dependence ($d\rho/dT > 0$) and a temperature-independent carrier density of $\sim 1.2 \times 10^{21} \text{cm}^{-3}$, indicating that the films can be categorized as degenerate semiconductors. The Hall mobility was estimated to be $\sim 8 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K. We applied a similar process to a film with $\text{Ti}_{0.94}\text{Nb}_{0.06}\text{O}_2$ composition and attained a lower ρ ($6.4 \times 10^{-4} \Omega\text{cm}$) by annealing at 400°C in vacuum. These films exhibited high optical transmittance of 60–80% and absorption below 10% in the visible region.

Using the low-temperature process described above, we have attempted to deposit highly-conductive TNO films on polyimide and soda-lime glass with a low glass-transition temperature of 550°C . We obtained $\rho = 1.9 \times 10^{-3} \Omega\text{cm}$ on polyimide and $\rho = 7.0 \times 10^{-4} \Omega\text{cm}$ on soda-lime glass when annealing at 300 and 400°C , respectively, in H_2 atmosphere. The ρ value obtained for the soda-lime glass substrate is equivalent to that for non-alkaline glass. Here, we would like to point out a possibility that the seed layer might act as a barrier which blocks sodium or impurity diffusion from glass and plastic substrates. This barrier effect could explain why we obtained excellent conductivity even in TNO films on soda-lime glass.

The results in Fig. 1 signify that the crystallization temperature could be further reduced by using a more oxygen-rich seed layer. Indeed, we succeeded in decreasing the processing temperature to 250°C by using a bottom layer

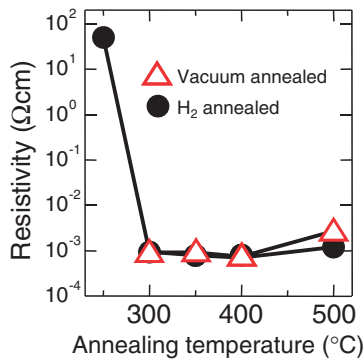


Fig. 3. Resistivity of double-layer films as functions of annealing temperature and annealing atmosphere. We first deposited an oxygen-rich bottom layer with a thickness of 30 nm under $f(\text{O}_2) = 5\%$ atmosphere, and then grew a 200-nm-thick oxygen-deficient layer at $f(\text{O}_2) = 0.05\%$, as schematized in Fig. 2(a).

prepared at $f(\text{O}_2) = 100\%$, although the ρ value obtained was somewhat higher: $\rho = 2.9 \times 10^{-3} \Omega \text{ cm}$.

The minimum ρ value of double-layer films, $7.0 \times 10^{-4} \Omega \text{ cm}$ (Fig. 3), is substantially lower than that of the single-layered film deposited at $f(\text{O}_2) = 0.05\%$, $\sim 9.8 \times 10^{-4} \Omega \text{ cm}$, annealed in 400°C (H_2 atmosphere). A comparison of the XRD patterns of the two films [Fig. 4(a)] reveals that this is due to the better crystallinity of the former. As discussed above, it is thought that the bottom layer with lower T_{crys} undergoes crystallization first. If this is the case, the bottom layer might act as a seed layer during the crystallization of the top layer, resulting in improvement of crystallinity. This improvement may be due to the reduced number of nucleation centers. As seen from the TEM images in Figs. 4(b) and 4(c), the single-layered film shows small grains of $\sim 50 \text{ nm}$ with inhomogeneous interior structure. This indicates that nucleation centers are distributed randomly inside the film. Meanwhile, the double-layered film is characterized by much larger grains with a more uniform crystalline lattice, supporting the scenario that nucleation starts from the bottom layer. The increase in grain size tends to suppress electron scattering at grain boundaries and thus also contributes to the suppression of ρ .

In summary, we have developed a low-temperature fabrication process for transparent conducting anatase Nb-doped TiO_2 (TNO) polycrystalline films on glass via crystallization of sputter-deposited amorphous films. Since the crystallization temperature decreased with increasing oxygen gas flow ratio $f(\text{O}_2)$, while the ρ value of the polycrystalline film was an increasing function of oxygen gas flow ratio, we proposed to use an oxygen-rich layer as a nucleation center for the oxygen-deficient top layer. The double-layered amorphous film, composed of $f(\text{O}_2) = 5\%$ bottom and $f(\text{O}_2) = 0.05\%$ top layers, was confirmed to undergo crystallization at 300°C . The polycrystalline film obtained showed a resistivity of $\rho = 7 \times 10^{-4} \Omega \text{ cm}$, which is lower than those of single-layered films, $\rho \sim 1 \times 10^{-3} \Omega \text{ cm}$. XRD and TEM measurements revealed that the use of an oxygen-rich bottom layer improved crystallinity and enlarged grains, resulting in suppression of ρ . By using the present low-temperature procedure, we have successfully fabricated TNO films on polyimide and soda-lime glass at a processing temperature of 300 and 400°C , respectively.

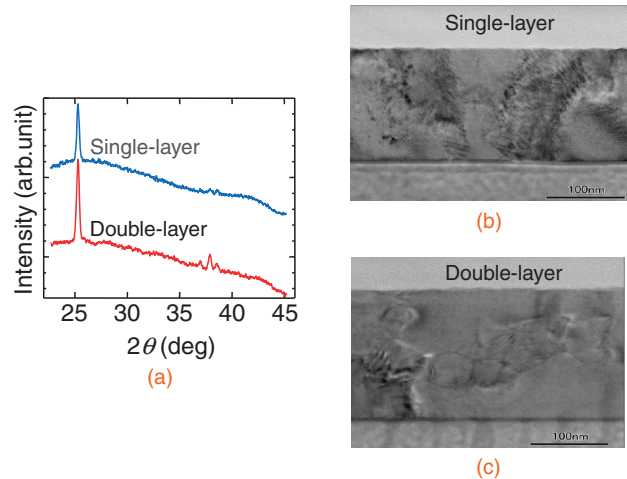


Fig. 4. (a) X-ray diffraction patterns of double-layered [$f(\text{O}_2) = 5\%$ for bottom (thickness of 30 nm), $f(\text{O}_2) = 0.05\%$ for top (thickness of 200 nm)] and single-layered [$f(\text{O}_2) = 0.05\%$] films (thickness of 200 nm). (b) TEM image of the single-layered film. (c) TEM image of the double-layered film annealed at 400°C in H_2 atmosphere.

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