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Full Length Article

Ageing effects on electrical resistivity of Nb-doped TiO_2 thin films deposited at a high rate by reactive DC magnetron sputtering

Davide Casotti[a,b,*], Valentina Orsini[a], Alessandro di Bona[b], Sandra Gardonio[c], Mattia Fanetti[c], Matjaž Valant[c,d], Sergio Valeri[a,b]

[a] Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, via G. Campi 213/a, 41125 Modena, Italy
[b] Consiglio Nazionale delle Ricerche, Istituto Nanoscienze, via G. Campi 213/a, 41125 Modena, Italy
[c] University of Nova Gorica, Materials Research Laboratory, Vipavska 11c, 5270 Ajdovščina, Slovenia
[d] Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, 610054 Chengdu, China

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ABSTRACT

We report on the long-term stability of electrical resistivity in Nb-doped TiO_2 thin films grown at a high rate by a reactive DC magnetron sputtering from metallic targets. The high deposition rate is obtained by an active control of the oxygen flow during the growth process. Film microstructure and preferential orientation of the crystallites are controlled by the total working pressure in the film growth process. After a heat treatment in vacuum, the film resistivity is in a $10^{-3}\,\Omega\,cm$ range and the optical transmission higher than 80% in the visible region. While the film is stable when kept under dry nitrogen, significant ageing has been observed when the material is exposed to air. In this case, the DC resistivity steadily increases and fractures form throughout the film. The ageing process is discussed in terms of the evolution of the film microstructure and/or the oxygen exchange through on the film surface. Oxygen uptake from ambient air is confined to a shallow surface region. It is possible that this mechanism triggers the formation/propagation of the fractures that predominantly contribute to the increase in film resistivity.

1. Introduction

The industry-standard transparent conductive oxide (TCO) materials, namely Sn-doped indium oxide (ITO) and F-doped tin oxide (FTO), beside their excellent electrical and optical performances [1,2], have some severe drawbacks for large-scale applications: low mineral reserve of indium [3–5], toxicity issues [6–8], charge recombination effects [9–12] and interfacial resistance between the nanoporous TiO_2 layer and TCO [10,12] in dye-sensitized solar cells applications. In the last twenty years, great attention has been put on titanium dioxide for its potential in many applications, *e.g.* as a catalyst for environmental applications [13,14], additive in food and personal products [15], wear-resistant material [16], anti-corrosion material [17], synthesis of organic compounds [18], pigment in paints [19], protection of cultural heritage [20,21], sensors [22], cancer therapy [23], photovoltaics [24], light emitting diodes [25] and as a TCO for flat panel displays and solar cells [26].

In 2005, Furubayashi proposed Nb-doped anatase (one of the polymorphs of TiO_2) as a novel TCO with potential capability to substitute ITO and FTO [27,28]. He obtained, by pulsed laser deposition, an epitaxial thin film with low resistivity ($2 \times 10^{-4}\,\Omega\,cm$) and high optical transmittance (> 90%) in the visible region [27,28]. Later on, several research groups have explored different deposition methods for Nb-doped titanium dioxide (TNO) deposition, *e.g.* chemical vapor deposition [26], sol–gel [29], electrospinning [30] and magnetron sputtering [31]. Among these techniques, magnetron sputtering was found to be attractive for device manufacturing because of its low cost, good reproducibility and large-area uniformity [32,33]. RF or DC variants of the sputtering technique have been successfully used for the TNO deposition using metallic alloy targets [34]; substoichiometric ceramic compound targets [35]; metallic composite targets [36–38] and elemental metallic targets [37]. For the metallic targets, the TNO films were obtained by operating in an oxygen-enriched (*i.e.* reactive) working gas [37,39]. A high deposition rate and the stabilization of the metal-oxygen stoichiometry of the deposited material have been obtained by operating the magnetron source in the so-called transition region using an active impedance control system [40,41].

In this work, we studied the long-term stability of TNO films grown

Abbreviations: FTO, F-doped tin oxide; ITO, Sn-doped indium oxide; PID, proportional–integral–derivative; TCO, transparent conductive oxide; TNO, Nb-doped titanium dioxide

* Corresponding author at: Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, via G. Saragat 1, 44122 Ferrara, Italy.
E-mail address: cstdvd@unife.it (D. Casotti).

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at a high-rate, impedance-stabilized, reactive, DC magnetron sputtering system equipped with two (Ti and Nb) metallic targets. The study focuses on the mechanism of ageing, linking the causes to the effects. The film characterization was systematically done under controlled ambient condition, since relevant modifications of microstructure, morphology and resistivity have been observed on films exposed to ambient air conditions. The most relevant ageing effect is the formation of fractures in the film. Oxygen incorporation into the film surface layers is proposed as the possible cause.

2. Experimental

Nb-doped anatase thin films (TNO) were deposited on SiO_2 substrates (600 nm of thermal oxide on (1 0 0) Si wafers) and on alkali-free Corning 1737 glass (1.1 mm thickness) by DC reactive magnetron sputtering from Ti and Nb targets (purity > 99.99%, 76.2 mm in diameter). The substrates were placed on a rotating sample holder (12 rpm) at an average distance from the targets of approximately 10 cm. During the growth process, the substrate temperature slowly increased from room temperature to about 60 °C. The working gas was an Ar + O_2 mixture with a variable composition. The Ar gas flow was 8 sccm, while the O_2 gas flow was varied in a 0.5–4 sccm range by a proportional–integral–derivative (PID) controller that actively monitors and stabilizes the Ti source discharge voltage to a fixed setpoint value by changing the O_2 gas flow [40]. The total working gas pressure was kept constant (0.27–1.1 Pa range) by a downstream butterfly valve. The PID changes the O_2 content of the feed gas in the 6–33% range. The O_2 partial pressure changes correspondingly. The TNO films were grown at constant DC power on the Ti and Nb magnetron source targets (11 W/cm^2 for Ti, 1.3–1.7 W/cm^2 for Nb). The deposition process is further detailed in Section 3.1. A series of film thicknesses ranging from 200 nm to 1 μm were deposited. To avoid atmospheric contamination, the films produced in the sputtering system were transferred to a glove box filled with dry nitrogen (residual H_2O and $O_2 \leq 2.0$ ppm) by means of a gas-tight transport manifold. The annealing process was done in a high vacuum oven (total residual pressure < 10^{-4} Pa) at 600 °C for 1 h. Oven loading and unloading operations were done under dry nitrogen flux by a load-lock transport manifold. Sheet resistance measurements were done inside the glove box by a collinear four-point probe equipped with W tips. The thickness of the films was monitored during the growth by a quartz microbalance and measured after the growth process by a stylus profilometer. Scanning Electron Microscope (SEM) imaging was performed by means of a field-emission scanning electron microscope equipped with secondary and backscattered electrons detectors at 5–10 kV beam voltage. The atomic composition of the deposited material was determined by an Energy Dispersive Spectroscopy (EDS) microanalysis system coupled to the SEM, equipped with a liquid nitrogen cooled Si(Li) detector. The EDS system was operated at 15 kV beam voltage. The Nb-to-Ti atomic ratio (*i.e.* the doping level) was assessed by the ratio between the area of Nb and Ti characteristic X-ray emission peaks (Nb $L_{\alpha,\beta}$ at 2.05–2.40 keV and Ti K_α at 4.30–4.74 keV) using a linear relationship: $Nb_{at}/Ti_{at} = k \cdot A(Nb_{L_{\alpha,\beta}})/A(Ti_{K_\alpha})$, where X_{at}, and $A(X_Y)$ (X = Nb or Ti; $Y = K_\alpha$ or $L_{\alpha,\beta}$) are the atomic fraction of X and the area of the X_Y X-ray emission line, respectively. The constant $k = 0.41$ has been determined by a series of Monte Carlo simulations implemented in the DTSA-II (Iona version) software, using the model "film on a bulk, homogeneous substrate" [42]. The relevant simulation parameters were: 15 keV beam energy, normal incidence, standard calibration Si(Li) detector, film thickness 200 nm, film density 3.78 g/cm^3, film composition $Nb_xTi_{1-x}O_2$ ($0 \leqslant x \leqslant 0.15$), substrate density 2.65 g/cm^3, substrate composition SiO_2. X-Ray Photoemission Spectroscopy (XPS) data were recorded in an ultra-high vacuum chamber using a non-monochromatized Mg anode X-ray source and a 125 mm radius hemispherical electrostatic analyzer with an angular acceptance of ± 8° around the sample normal direction. The overall energy resolution, mainly determined by the width of the Mg K_α line, is about 0.8 eV. X-ray diffraction patterns were acquired by an X-ray diffractometer in the Bragg-Brentano geometry, parallel beam optics with Göbel mirror, flat graphite monochromator, proportional counter and Cu anode X-ray source operating at 40 kV and 40 mA. Cathodoluminescence (CL) measurements were performed at room temperature in a field emission SEM. The beam-induced light emission was collected in the 300–750 nm range by a grating monochromator (resolution < 0.5 nm). Suitable beam voltage and current were chosen to avoid probe-related artifacts, namely, changes of the CL spectrum with irradiation time. In order to maximize the CL signal from the film and minimize that from the substrate, beam voltages of 3, 5 and 7 kV were used to measure films with 200, 400 and 1000 nm thickness, respectively. Optical transmittance spectra in the 300–1800 nm wavelength range have been measured with a single beam spectrophotometer. IR transmittance spectra in the 1800–4000 nm range have been measured by a Fourier-transform infrared interferometer. The samples for the optical transmittance measurements have been deposited on the alkali-free Corning 1737 glass and sealed in a gas tight cuvette filled with dry nitrogen. The transmittance spectra have been normalized to transmission of the cuvette plus Corning 1737 substrate.

3. Results and discussion

3.1. The film deposition process

The film deposition setup is shown in Fig. 1. The "double target" configuration (*i.e.* that with individual targets for the main material and for the dopant) allows to vary the doping level simply by changing the dopant target power, a feature that is not available in single target systems where the doping level is fixed by the composition of the target.

As expected for reactive sputtering, the deposition rate shows a hysteretic dependence on the oxygen content of the working gas [40]. It switches from a high value (30 nm/min in our system) at low O_2 content (called the "metal mode" condition) to a low value (1 nm/min or less) at O_2 content so high that the Ti target is fully oxidized (called the "compound mode" condition). No stable target operation can be set between these two limiting conditions. This instability, thoroughly studied by Berg [43], is due to the lower sputtering yield of the compound (*i.e.* the titanium dioxide) that forms on the target surface with respect to that of the "bare" target material. Hysteresis has two significant side effects on the film deposition: (i) it makes the stoichiometry (TiO_x) of the deposited material to switch abruptly from $x \cong 0$ (in

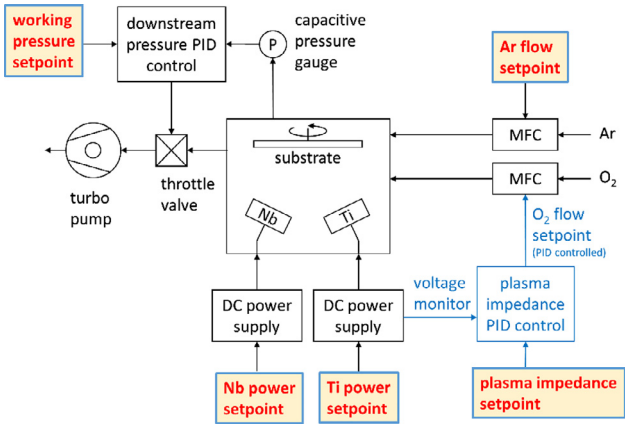

Fig. 1. Schematic of the reactive sputtering system used in this work. The working pressure is kept to a setpoint value by a downstream pressure control. The Ti discharge voltage is monitored by the PID controller, which in turns adjusts the oxygen flow fed to the process chamber in order to keep the monitored voltage pinned to the setpoint value. Argon is fed at a constant mass flow. The DC power of the Ti and Nb sources are set to specific constant values.