Materials Research Bulletin 74 (2016) 15–20

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Structural and electrical properties of Nb doped TiO_2 films prepared by the sol–gel layer-by-layer technique

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ARTICLE INFO

Article history:
Received 18 May 2015
Received in revised form 1 September 2015
Accepted 6 October 2015
Available online xxx

Keywords:
A: Thin films
B. Sol–gel chemistry
B. Optical properties
D. Defects
D. Electrical properties

ABSTRACT

Thin films of 5 and 10-layered sol–gel TiO_2 were doped with 1.2 at.% Nb and their structural, optical and electrical properties were investigated. The films crystallized only in anatase phase, as evidenced by X-ray diffraction and selected area electron diffraction analyses. High resolution transmission electron microscopy revealed nanosized crystallites with amorphous boundaries. Current-voltage measurements on metal-TiO_2–Si structures showed the formation of n^+–n heterojunction at the TiO_2–Si interface with a rectification ratio of 10^4. The effective donor density varies between 10^{16} and 10^{17} cm^{-3}, depending on film thickness. The sheet energy densities under forward and reverse bias are in the order of 10^{12} and 10^{10} cm^{-2} eV^{-1}, respectively. These values and the high specific resistivity (10^4 Ω cm) support the existence of compensating acceptor levels in these films. It was established that the conduction mechanism is based on space charge limited current via deep levels with different energy positions in the band gap.

1. Introduction

Titanium dioxide (TiO_2) is a large band-gap (3.20 eV for anatase phase) semiconductor extensively studied for development of novel environment- and energy-related processes such as photocatalysis for water purification [1], gas sensing [2], electrochromic material [3] or solar cells application [4–6]. The application range of TiO_2 can be extended by improving its properties through doping with transitional metal ions (e.g. Fe, Nb, V, etc.). Among these, Nb-doped TiO_2 (TiO_2:Nb) is one of the most studied transparent conductive oxides (TCO) and recommended as a replacement for the high-cost indium tin oxide (ITO) as electrode [7].

In Ref. [8] it has been shown that pulsed laser deposited (PLD) anatase TiO_2:Nb films on $SrTiO_3$ have low specific resistivity of order of 10^{-4} Ω cm. Higher specific resistivity of order of 10^{-1} Ω cm was obtained also by PLD on sapphire substrate [9]. Furubayashi et al. pointed out that higher values of specific resistivity in PLD TiO_2:Nb films deposited in sapphire are connected with rutile phase of these films [10]. Furthermore it has been shown that annealing in H_2 gas ambient of PLD TiO_2:Nb films is connected with crystallization and subsequent decrease of specific resistivity of these films from values in the 10^2 Ω cm range to values in the 10^{-4} Ω cm range [11]. The decisive role of annealing procedures, done mainly in vacuum, in decreasing of the specific resistivity has been established also in TiO_2:Nb films prepared by the sol–gel method [7]. All these results show that point defects generation and transformation in these films during the deposition and subsequent annealing steps determine the mechanism of electrical conduction. The elucidation of this role will contribute to the advancement of applications of TiO_2:Nb films as TCO materials and structures.

The aim of this work is to reveal the electrical conduction mechanism in sol–gel deposited TiO_2:Nb films and to characterise the role of deep levels related with point defects in these films. Additional information about the films properties was gained from structural, morphological and optical measurements.

2. Materials and methods

2.1. Sample preparation

The multilayered Nb-doped TiO_2 films with 5 and 10 layers (further denoted as 5TiO_2:Nb and 10TiO_2:Nb, respectively) on glass

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http://dx.doi.org/10.1016/j.materresbull.2015.10.009
0025-5408/

and Si substrates were obtained through the sol–gel method starting from tetraethylorthotitanate [$Ti(OCH_2CH_3)_4$], niobium ethoxide [$Nb(OCH_2CH_3)_5$] with ethanol (C_2H_5–OH) as solvent and 2,4-pentanedione acting as chelating agent. The solution was aged for 24 h before deposition. The doping percentage was set to 1.2 at.% Nb, as literature indicates that a low amount of Nb (below 6 at.%) leads to the best results for transparent conductive oxide applications. Thin films were dip coated using a 5 cm/minute extraction rate. A densification treatment at 300 °C for 30 min (heating rate 5 °C/minute) was applied after each deposition and a final thermal treatment at 450 °C for 1 hour using the same heating rate.

2.2. Measurement methods

The structure of the thin films was determined by X-ray diffraction (XRD) using an Ultima IV Diffractometer (Rigaku Corp., Japan), equipped with parallel beam optics and a thin film attachment, employing Cu Kα radiation (λ = 1.5405 Å), operating at 30 mA and 40 kV, over the range $5 < 2\theta < 90°$, at a scanning rate of 5°/min and at a fixed incident angle ($\omega = 0.5°$).

Surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on a Quantera SXM equipment, with a base pressure in the analysis chamber of 1.33×10^{-7} Pa. The X-ray source was the Al Kα radiation (1486.6 eV, monochromatized) and an overall energy resolution of 0.65 eV estimated by the full width at half maximum of the Au 4f7/2 line. In order to take into account the charging effect on the measured binding energies (BEs) the spectra were calibrated using the C1s line (BE = 284.8 eV, C—C(CH)n bonds) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure ($e^-$and Ar^+ ion beams) has been used to compensate the charging effect in insulating samples.

The conventional transmission electron microscopy (TEM) images and the selected area diffraction (SAED) patterns were recorded using a Jeol 200CX electron microscope and the high resolution images were obtained by a Topcon 002B electron microscope. Specimens for TEM observations were prepared by the conventional cross section method (XTEM) for all samples.

Ellipsometric measurements were carried out on a VASE-Woollam Spectroscopic Ellipsometer (SE) working in UV–vis spectral range. Information about the film thickness, d_f, surface roughness, d_{rough}, the optical constants n and k (beyond the scope of the present paper), and the optical band gap energy, E_g, values was gained from the SE data recorded in the 350–1700 nm spectral range and at three angles of incidence (60, 65, 70 °C). In order to check the film transparency, T, the transmission spectra of the studied films were measured in the 200–1700 nm spectral range and at normal angle of light incidence. Tauc–Lorentz model [12] was used to simulate the ellipsometric data of the films deposited on Si and glass substrates.

For the electrical measurements, MIS structures with the TiO_2:Nb films were formed by vacuum evaporation of Al contacts. For the front contact Al dots with a contact area of s=2.8 × 10^{-3} cm^2 were deposited onto films surface through a metal mask, while the Si back-side contact was continuous Al film. The current-voltage (I–V) characteristics were measured with a cycle sequence beginning from 0 V toward negative or positive voltages applied to the Al-dot contact on the film surface followed by a voltage reversal toward zero applied bias voltage. The capacitance-voltage (C–V) and conductance-voltage (G–V) measurements were carried out at 1 MHz by a digital LCR meter E7-12. All electrical measurements were performed at room temperature.

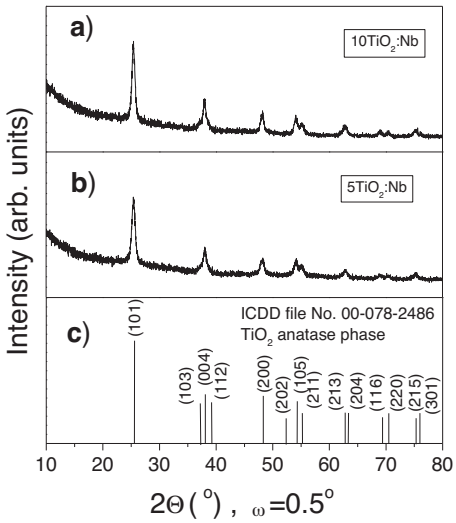

Fig. 1. XRD patterns of the TiO_2:Nb films grown by sol–gel layer-by-layer technology: 10TiO_2:Nb (a) and 5TiO_2:Nb (b). The Bragg peaks for TiO_2 anatase phase are illustrated in (c).

3. Results and discussion

3.1. Structural characterization

The analysis of the recorded XRD spectra in Fig. 1 showed that the films deposited on glass substrate were crystalline, the Bragg peaks corresponded to the anatase phase of TiO_2 (ICDD file no. 00-078-2486 [13]). The most intense peak corresponds to the (1 0 1) crystallographic orientation showing the preferential direction of crystallites growth. No peaks related to rutile phase were detected. Peaks assigned to Nb_2O_5 as a separate oxide could not be found in the XRD patterns. This could have different explanations: low amount of Nb in the films and/or amorphous state of the Nb-based compounds. However, the successful incorporation of Nb ions in the titania matrix was detected by the XPS measurements of these films (Fig. 2). Niobium was present in Nb^{5+} state as illustrated by the perfect match between the XPS spectra of the films and that of an Nb_2O_5 standard sample (Fig. 2) recorded in the same experimental setup.

The crystallites are nano-sized and randomly oriented as evidenced from the multitude of small peaks. The same positions of the Bragg peaks in both XRD patterns clearly indicate an identical film structure. The smaller intensity for 5TiO_2:Nb could be either due to the smaller amount of crystallites and/or the

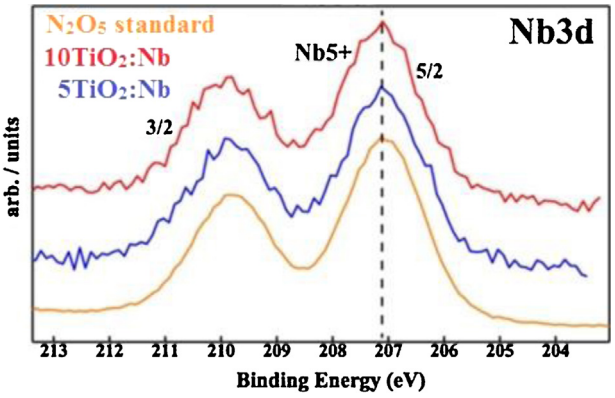

Fig. 2. XPS superimposed spectra of Nb3d for the 10TiO_2:Nb and Nb_2O_5 standard samples.