Journal of Alloys and Compounds 663 (2016) 413–418

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Doping concentration effects upon column-structured Nb:TiO_2 for transparent conductive thin films prepared by a sol–gel method

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ARTICLE INFO

Article history:
Received 6 July 2015
Received in revised form
10 December 2015
Accepted 14 December 2015
Available online 21 December 2015

Keywords:
TiO_2 films
Column-structured
Sol-gel method
Niobium doping

ABSTRACT

The column-structured Nb-doped TiO_2 (TNO) films with various Nb concentrations in the range between 0 and 10 at.% have been prepared by a sol–gel method. The phase compositions, element concentrations, microstructures, and optical-electron properties have been characterized by using X-ray diffraction, X-ray photoelectron spectroscopy, electron microscopy, and UV/Vis/Near-IR spectrophotometer. The experimental results show that all of the samples prepared in the present work exhibit column-structured morphology and Nb doping concentration has a non-monotonic effect upon the microstructure. The relatively low conductivity and high transmittance of the samples demonstrate that column-structured microstructures greatly improve the optical and electronic properties of TNO films. The favorable sample with 10 at.% Nb doping concentration exhibits a resistance of about 2.27 Ω cm and transmittance of approximately 68.78% with 85 nm thickness.

1. Introduction

In recent years, the Nb doped TiO_2 (TNO) films have attracted lots of interests, and were discovered as potential candidate for traditional TCOs [1], such as tin-doped indium oxide (ITO) [2,3], aluminum-doped zinc oxide [4], and fluorine-doped tin oxide [5]. In addition, the TNO thin films have also been investigated in the fields of gas sensors and photo catalysis [6,7]. However, owing to its wide band gap, high carrier mobility, small carrier effective mass, high chemical stability, and a large distribution of Ti element [8–10], these films has been regarded as the next generation TCOs and seized much attention in the past 10 years. The conducting transparent TNO films can be applied in solar cells, blue LEDs [11], window layers to form a junction with the p-CdTe absorber layer [12], and schottky barrier diodes [13,14]. Moreover, since the conductivity of anatase TiO_2 corresponds to *d-orbit* electrons [1] rather than *s-orbit* electrons, its electron conductive mechanism is quite different from other traditional TCOs [15,16].

Transparent conducting TNO ($Ti_{1-x}Nb_xO_2$, x = 0.002–0.2) films were firstly prepared by pulsed laser deposition (PLD) method, which was epitaxially deposited on $SrTiO_3$ (001) substrate, exhibiting a low resistivity of about 2.3×10^{-4} Ω cm. Then polycrystalline TNO films growing on glass substrates were prepared by PLD and sputtering methods, respectively [17,18]. The lowest resistivity of these polycrystalline films were demonstrated to be in the range from 6.0×10^{-4} Ω cm to 7.8×10^{-4} Ω cm. The excellent conductivity of TNO films has been explained by theoretical calculations, indicating that *4d* orbit of Nb doped in Ti sublattices produces an extra doping level at the bottom of conduction bands above the Fermi level, and hence supplying free electrons for the conduction [19–21]. In general, both experimental and theoretical results show that Nb doping concentration is an essential factor influencing the conducting performance of TNO. Using the PLD method Hitosugi et al. [17] reported that nominal doping concentration, for the optimal conductivity, is 6 at.%. Furthermore, the post-annealing process in reducing or vacuum atmosphere is another essential factor effecting conductive properties of TNO films, corresponding to the optimized crystallization and the generation of oxygen vacancy [22–24].

For large area films preparation, the sol–gel method is apparently superior to vapor deposition methods. This scheme not only provides simplicity, low cost, and feasibility, but also proving as a

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http://dx.doi.org/10.1016/j.jallcom.2015.12.102
0925-8388/

precise approach to control doping concentrations. However, it seems that TNO films fabricated by sol–gel method do not show comparable conductivities as observed by other methods [25–28]. Even post annealed in high-vacuum or reducing atmosphere after sintering, the reported lowest resistivity of TNO films prepared by sol–gel method is reported to be about 0.5 Ω cm [28]. It can be attributed to the porosity and the tensile stresses retained in sol–gel coatings during the pyrolysis and densification [29–31]. When compared with granular microstructures, it has been demonstrated that the columnar micromorphology – due to reason of fewer grain boundaries and more compact microstructures – can improve conductivity [32]. To the best knowledge of the authors, however, no column-structured TNO films have been reported.

In the present work, the column-structured TNO films with various Nb doping concentrations have been prepared on quartz substrates by using the acid-catalyzed sol–gel technique along with the spin-coating procedure. After post-annealing process in the reducing atmosphere, the phase compositions, element concentrations, microstructures, and optical-electron properties have been characterized by X-ray diffraction technique, high-resolution transmission electron microscopy, X-rays energy dispersive analysis, X-ray photoelectron spectroscopy, scanning electron microscope, four-probe method and UV/Vis/Near-IR spectrophotometer. The effects of the column-structured morphology and Nb doping concentration upon the optical and electronic properties of TNO films have been discussed in detail.

2. Experiments details

2.1. Films preparation process

TNO films with various Nb doping concentrations were prepared on quartz substrates (4 × 4 cm^2). The substrates were ultrasonically cleaned by detergent, hydrochloric acid solution ($HCl:H_2O$ = 1:10 mass ratio), ethanol, and deionized water, each for 30 min in sequence. The preparation of Nb-doped titania sol was adopted from the previous work [27]. The precursor of titania solution was prepared by using tetrabutyl titanate [$Ti(C_4H_9O)_4$] as Ti source and niobium (V) ethoxide ($C_{10}H_{25}NbO_5$) as Nb source. The nitric acid (HNO_3, 65–68%) and the acetic acid (CH_3COOH, 99.5%) were used as catalysts, and the ethanol (EtOH) as solvent. Briefly, the mixtures with [Ti + Nb]:[CH_3COOH + HNO_3]:[H_2O]:[EtOH] composition of 1: [1.5 + 0.7]: 3.8: 170 (molar ratio) were used as the precursor solution. The mol amount of [Ti + Nb] in the solution was 0.05 M. The nominal doping concentrations of Nb/(Nb + Ti) were in a range of 0–10 at. %.

The sol was vigorously stirring under the room temperature for 60 min. After 24 h ageing, the sol was used to prepare films with fixed spin speed of 2000 rpm on the cleaned substrates. Then the coatings were dried at 70 °C in air for 10 min to evaporate the solvent. Afterward, the dried samples were annealed in muffle furnace for 30 min at 700 °C. After repeating the procedure for 10 times, the as-prepared films were annealed in H_2+N_2 mixed gas ($H_2:N_2$ = 1:9, volume ratio) for 2 h at 750 °C. All chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd., except for $C_{10}H_{25}NbO_5$ purchased from Aladdin Co. LLC., and all the chemicals were used without further purification.

2.2. Analysis methods

The crystal structures of TNO films were characterized by X-ray diffraction (XRD, Rigaku D/max 2550pe) with Cu K_α radiation. The high-resolution transmission electron microscopy (HRTEM, Tecnai F20 from FEI) was carried out to analyze the surface morphology with an acceleration voltage of 200 kV. The point resolution of HRTEM is about 0.24 nm and the fringe resolution is about 0.14 nm. The energy dispersive analysis of X-rays (EDS, INCAx-sight) was used to analyze the distribution of Nb, Ti, and O elements. The X-ray photoelectron spectroscopy measurement (XPS, KRATOS, AXIS ULTRA DLD) was used to characterize the valence of Nb, Ti, and O elements. All the binding energies were referenced to the C_{1s} peak at 284.6 eV of the surface adventitious carbon. A monochromatic Al K_α X-ray radiation (hν = 1486.7 eV) was used as excitation source and a spot size is about 650 μm. Survey scans were carried out over 0–1350 eV binding energy range with 1.0 eV steps. Narrow high-resolution scans were run with 0.1 eV steps. Atomic concentrations were calculated using the CasaXPS software and a Shirley baseline with Kratos library Relative Sensitivity Factors (RSFs). Peak fitting of the high-resolution data was also evaluated using the CasaXPS software. The cross-sectional morphology and thickness of TNO films were observed by a scanning electron microscopy (SEM, S-4800 Hitachi). The square resistance of samples was measured by a four-point probe measurement at room temperature (ST-2258A Suzhou Jingge). The optical measurements in the UV/Vis/Near-IR range were carried out at the room temperature by a spectrophotometer (UV-3600 Shimadzu).

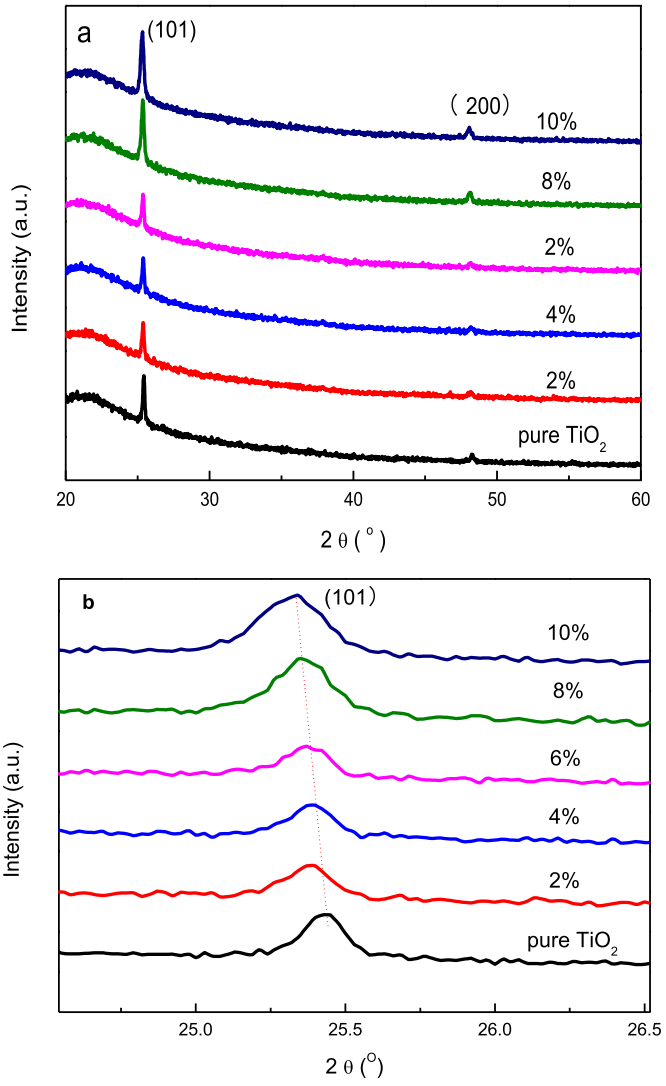

Fig. 1. XRD patterns of TNO films with various Nb concentrations (a) and the magnified patterns in vicinity of (101) peak position (b).