Materials Science in Semiconductor Processing 72 (2017) 99–105

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Structural phase-dependent resistivity of intrinsic-extrinsic co-doped transparent titanium dioxide films

Kashif Safeen[a,b,c,*], V. Micheli[b], R. Bartali[b,c], G. Gottardi[b], Akif Safeen[a,d], Hafeez Ullah[b,c], E. Iacob[b], M. Fidrizzi[b], N. Laidani[b]

[a] Abdul Wali Khan University, Department of Physics, 23200 Mardan, Pakistan
[b] Center for Materials and Microsystems, Fondazione Bruno Kessler, Via Sommarive 18, 38123 Povo, Trento, Italy
[c] University of Trento, Department of Physics, Via Sommarive 15, 38123 Povo, Trento, Italy
[d] Department of Physics, Balochistan University of Information Technology, Engineering & Management Science (BUITEMS), Quetta, Pakistan

ARTICLE INFO

Keywords:
Transparent conducting oxides
TiO_2 thin films
RF sputtering
Structure properties
Electrical properties
Optical properties

ABSTRACT

The authors report a method of enhancing the conductivity of TiO_2 films by controlling their structural phases. Thin films of Nb:TiO_2 (TNO) were prepared on glass and silicon substrates by RF sputtering with varying Nb content at 200 °C. It is shown that fine control over the structural phases of TiO_2 is critical for achieving low resistivity. The resistivity values of the films doped with oxygen vacancies and Nb^{+5} decreased from 3.8×10^{-1} to $4.1 \times 10^{-3}\ \Omega$ cm when the weight percent of rutile in anatase-rutile phase mixture decreases from 52.8% to 32%. Furthermore, the lowest resistivity value of $2.37 \times 10^{-3}\ \Omega$ cm was obtained for the doped TiO_2 films having single phase anatase structure. The physical processes responsible for the diverse electrical properties are discussed and are associated with the growth conditions. Our result indicates that highly conductive doped-TiO_2 film can be obtained by controlling the anatase phase formation via the growth temperature. The obtained results can significantly contribute to the development of transparent electrodes by RF sputtering, a suitable technique for coating large area substrates.

1. Introduction

Transparent conducting oxides (TCOs) have wide-ranging applications in devices such as liquid crystal displays, photovoltaics, architectural and window glass technologies [1]. The performance of such devices is strongly correlated with the desired key properties such as structural phases, electrical resistivity, transparency and optical band gap. Currently, much effort is devoted to explore alternative oxide-based transparent conductors to fulfill the fast growing demand in many optoelectronic devices (flat panel display, photovoltaics etc). Among the TCOs, doped titanium dioxide is a promising material for such applications due its low-cost, excellent chemical stability especially in a reducing atmosphere and high transmittance in the infrared region, beside its excellent conductivity and transparency [2,3]. Therefore, in the recent years, interest in doped TiO_2 films has increased considerably due to the above mentioned useful properties and the potential applications as transparent electrodes.

The conductivity of TiO_2 films is strongly correlated with their crystalline structure particularly with the amount of anatase phase with respect to rutile and with the oxygen vacancies present in the film [4,5]. To grow anatase phase of TiO_2, thin films are usually grown in Ar-O_2 discharges because oxygen rich film inhibit anatase to rutile transformation and enhance the transparency of the films [5,6]. However, for low energetic conditions such as low power density (1 W/cm^2), high sputtering pressure (> 1.3 Pa) etc., growth in Ar-O_2 discharges is not favorable for oxygen vacancies creation owing to the spontaneous formation of oxygen interstitials in oxygen-rich deposition conditions [7]. Oxygen interstitials are predicted to be detrimental defects for the electrical properties of the film as they removes not only the oxygen vacancies but also form localized shallow acceptor states which compensates the electrons-doping by Nb^{+5} ions thus depressing the conductivity [8,9]. On the other hand, in the defective samples (oxygen deficient films), oxygen vacancies accelerate the atomic diffusion by providing a low energy mass transport route and promote the crystallization of thermodynamically stable rutile phase, which is undesirable for electrical properties of TiO_2 [6]. An attempt to stabilize the oxygen-deficient anatase phase in thin film of TiO_2 was made by growing them on single crystalline $SrTiO_3$ (STO) and $LiAlO_3$ (LAO) substrates because their lattice constant (a ~ 3.79 Å) is comparable to the in-plane lattice constant of anatase TiO_2 (3.78 Å) [2,10]. The low lattice mismatch

* Corresponding author at: Abdul Wali Khan University, Department of Physics, 23200 Mardan, Pakistan.
E-mail address: kashifsafeen@awkum.edu.pk (K. Safeen).

http://dx.doi.org/10.1016/j.mssp.2017.09.037
Received 3 May 2017; Received in revised form 5 September 2017; Accepted 28 September 2017
Available online 05 October 2017
1369-8001/

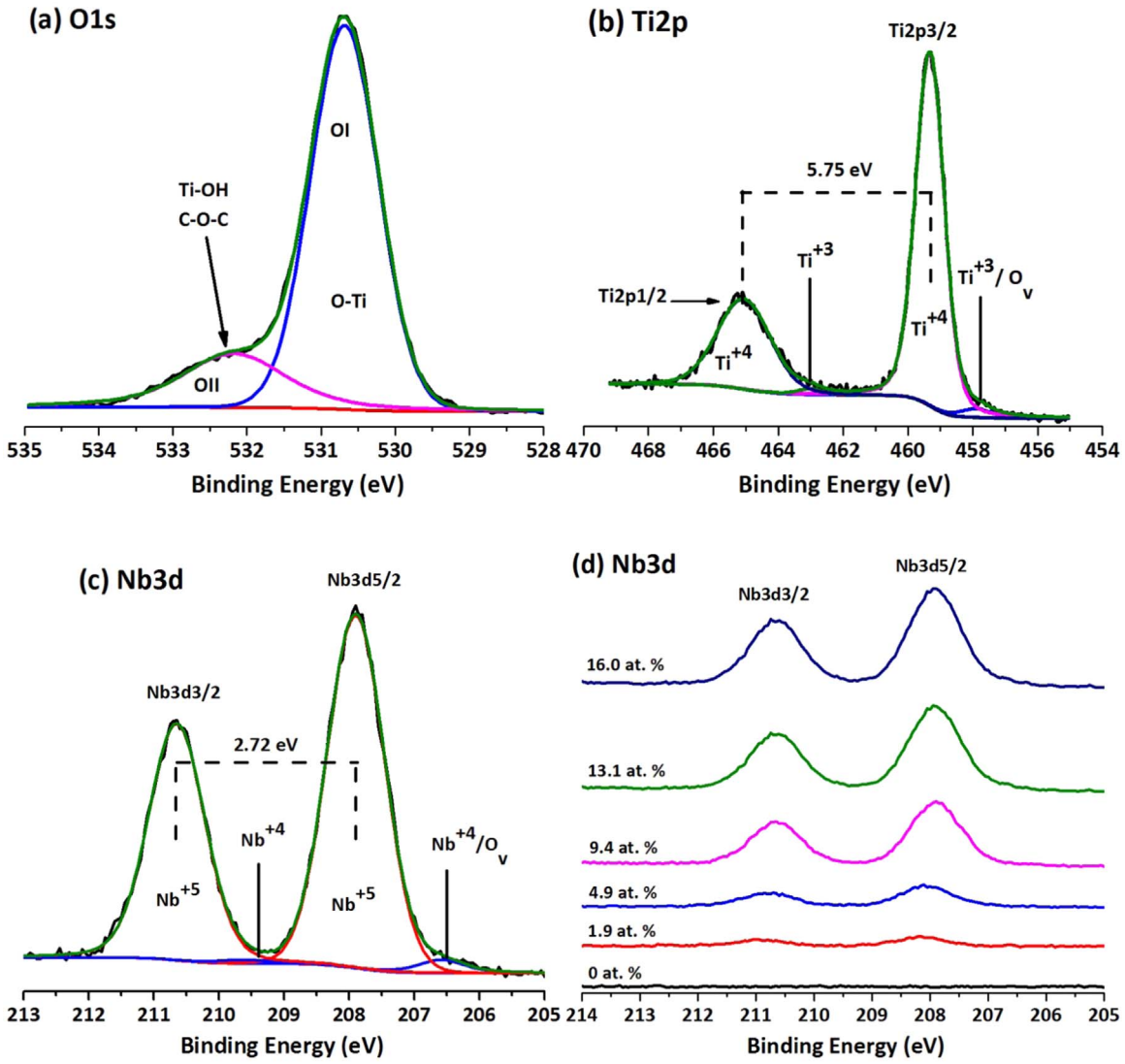

Fig. 1. (a) XPS O1s spectrum of the Nb:TiO_2 films (b) XPS Ti2p core-level spectrum (c) XPS Nb3d core-level spectrum of the as-grown TNO film deposited at 200 °C (d) Nb core-level with increasing Nb concentrations.

between anatase TiO_2 and STO/LAO substrates assisted the preferential growth of highly-oriented anatase TiO_2 film, which is the most suitable phase for transparent conducting properties [10]. Unfortunately, STO and LAO substrates are expensive, hence not really viable for industrial application. In fact under a practical point of view, TCOs film should be preferably deposited over glass or plastic substrates to minimize the cost of the final product. It is therefore crucial finding a feasible way to grow thermodynamically metastable anatase phase TiO_2 film on an economical substrates (glass and polyimide) with high conductivity.

In this work, we present a method to control the various structural phases of TiO_2 that critically influences its electrical properties. The deposition temperature was the experimental parameter whose optimization was used to stabilize the defective anatase phase instead of growing anatase structure in oxygen-rich condition or of using high-cost LAO/STO substrates. We obtained a lowest resistivity of the order of 10^{-3} Ω cm for single anatase structure whereas mixed anatase-rutile phase leads to highly resistive films. Based on the X-ray diffraction results, the electrical properties of the doped TiO_2 films were correlated with the growth temperature parameter.

2. Materials and methods

Nb:TiO_2 films were grown by radio frequency co-sputtering (13.56 MHz) in Ar plasma. An optimized ceramic TiO_2 (99.9% purity), 10 cm of diameter, produced by Materion and Nb_2O_5 (99.95% purity) 5 cm diameter, produced by ACI Alloys was used as sputtering targets. The films were grown on p-type silicon (100) and corning glass substrates at room temperature and at 200 °C. The total pressure of the growth chamber was fixed at an optimal value of 1.33 Pa [5,11]. The power applied to the Nb_2O_5 target was varied from 4 to 12 W (bias voltage: 59–110 V) while the power applied to the TiO_2 target was kept fixed at 78 W (RF self-bias voltage ~ −850 V). Different Nb concentrations in the films (1.9–16.0 at%) were obtained by changing the power applied to the target. The thicknesses of the films were in the range 125–170 nm. The as-deposited films were subsequently annealed in pure argon gas (pressure = 1.33 Pa) at 400 °C for 1 h. The detailed experimental procedure can be found in [6,11,12]. It is important to note here that in this article, primarily the results obtained from the films deposited at 200 °C and annealed at 400 °C is presented while the results of the films grown at room temperature and annealed at 350 °C is mentioned for reference.

The discharge properties were studied using Optical Emission Spectroscopy (OES) where the plasma light (in the wavelength range 200–850 nm with a spectral resolution of 0.2 nm) was collected with an optical fiber through a quartz window of the sputtering chamber. Subsequently, the light was analyzed by means of a Spectrapro 2300i