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Synthesis of conductive and transparent Nb-doped TiO_2 films: Role of the target material and sputtering gas composition

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ABSTRACT

The authors report a comparative study of the electrical and optical properties of $Nb:TiO_2$ thin films (TNO) in relation with their chemical properties. Two types of niobium containing targets, Nb metal and Nb_2O_5 oxide were employed simultaneously with ceramic TiO_2 target for the films growth, in Ar and Ar-O_2 discharge. Niobium is found to incorporate easily and substitutionally into titanium lattice site when deposited from oxide targets in oxygen-deficient discharge (Ar plasma). Consequently, the TNO film exhibits lowest resistivity of $1.4 \times 10^{-3}\ \Omega$ cm with optical transparency of more than 80% in the visible region. On the contrary, doping was not effective in case the TNO films were grown from Nb metal and TiO_2 targets in Ar and Ar-O_2 plasma, probably due to the growth of niobium sub-oxide phases and lack of oxygen vacancies. The possible reasons of diverse electrical properties are discussed and are link with the growth conditions. Our result indicates that highly conductive and transparent doped-TiO_2 film can be obtained by choosing appropriate target material and sputtering gas. The obtained results can significantly contribute to the development of transparent electrodes by RF sputtering, a suitable technique for coating on large area substrates.

1. Introduction

Transparent conducting oxides (TCOs) are electrical conductive materials with high transparency in the visible range (~400–750 nm). They are usually prepared with thin film technologies and used in opto-electrical devices such as solar cells, displays, opto-electrical interfaces and circuitries [1]. Recently, Niobium doped titanium oxide (Nb-doped TiO_2) emerged as a potential indium-free transparent conducting oxide material due to its low resistivity of the order $10^{-4}\ \Omega$ cm, high visible transparency of 90%, with source materials being inexpensive and non-toxic [2]. This discovery is substantial because ITO (tin doped indium oxide), with the indium shortage issue, is not able to fulfill the future demands for the rapid development of photovoltaics, organic light emitting displays and flat panel displays, etc. [3].

Given the growing significance of TNO ($Nb:TiO_2$) as an electronic material, it is of interest to understand the effective doping in TiO_2 by transition metal elements (Nb in this case) by exploring the growth parameter-properties relationship. The effective doping in TiO_2 is critical because this can lead to the multifunctional properties of the oxide [3,4]. In the widely used sputtering technique, the target material and oxygen content in Ar plasma are the crucial parameters in the context of optimization because they can modify the chemistry of intrinsic defects, doping and hence the physical properties of TCOs [5,6]. However, contradictory works specifically to these conditions can be found in the literature. For example, Soto et al. study showed that the films conductivity is high when it is grown from the reduced oxide target [6]. On the other hand, few researchers reported the preparation of transparent-conductive films from the oxidized targets [7,8]. Further, titanium and niobium metal targets have been widely used for the synthesis of conductive films in Ar-O_2 discharge [9,10]. On the contrary, Lee et al. reported that growth in oxygen-rich condition is not suitable for the synthesis of transparent-conductive films due to the spontaneous formation of oxygen interstitials, which is deleterious for the electrical properties of TCOs [4]. Therefore a comprehensive study is needed that explains the role of the target materials and sputtering gas composition to improve our understanding about the development of TCOs.

In this work, we report the factors dominating the doping process and hence the conductivity and transparency of TiO_2 films. We investigated the effect of different niobium targets and sputtered gas

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composition on the surface, electrical and optical properties of TNO films. The optimized electrical and optical properties were obtained for the films grown from oxide targets in Ar discharge. Based on the X-ray photoelectron spectroscopy (XPS) results, the electrical and optical properties were correlated with the growth parameters and chemical properties of the annealed TNO films.

2. Material and methods

The detailed experimental condition is reported elsewhere [11,12]. In this work, we have chosen two types of niobium containing targets, Nb metal and Nb_2O_5 disc (5 cm diameter, ACI Alloys) along with ceramic TiO_2 target with 10 cm of diameter (Materion). TNO films ($Nb:TiO_2$) were grown on un-heated p-type silicon (100) and corning glass substrates using RF (13.56 MHz) sputtering in pure Ar and Ar-O_2 discharge (1.6% O_2 in Ar-O_2 gas mixture otherwise stated). Prior to deposition, a base pressure of approximately 7×10^{-6} Pa (Pascal) was established before fixing the total working pressure during the films growth process (1.3 Pa). During the sputtering process, a dc self-bias on the TiO_2 cathode was kept at −850 V (load power of 75 W) while power applied to Nb_2O_5 target was fixed at 8 W (self-bias voltage ~78 V). Further, power applied to Nb metal target in Ar and Ar-O_2 discharge were set at 6 and 15 W respectively (self-bias voltage ~62 and 95 V). The as-deposited films were annealed in Ar atmosphere (pressure 1.3 Pa) at 400 °C for 1 h. The following are the nomenclature and specifications of the three samples. Generally, symbol of the films can be imagine as TNO (Niobium target_sputtering gas), where TNO represents $Nb:TiO_2$ films and the term in parentheses indicates the type of niobium target (metallic or oxide) and the sputtering gas used.

1. $Nb:TiO_2$ films prepared from TiO_2 and Nb metal targets in Ar plasma is represented by TNO (Nb_Ar) film/sample (thickness of 250 ± 10 nm)
2. $Nb:TiO_2$ films deposited from TiO_2 and Nb metal targets in Ar-O_2 plasma is denoted by TNO (Nb_Ar-O_2) film (thickness of 65 ± 5 nm)
3. $Nb:TiO_2$ films grown from TiO_2 and Nb_2O_5 oxide targets in Ar plasma is symbolized by TNO (Nb_2O_5_Ar) (thickness of 90 ± 8 nm)

The discharge properties were characterized using Optical Emission Spectroscopy (OES). The light signal was acquired from 200 nm to 850 nm (spectral resolution of 0.2 nm) with an optical fiber through a quartz window. The plasma light was subsequently analyzed by means of a Spectrapro 2300i (Acton Research Corporation) instrument, equipped with an ICCD camera. The phase of the prepared films was identified by X-ray diffractometer. The measurements were carried out using CuKα (λ=1.5406 A°) radiation on an Italstructures APD2000 system working at 40 kV and 30 mA. The average thicknesses of the films were measured using a surface profiler (Tencor Instruments). The chemical composition of the films was analyzed with a Scienta ESCA 200 spectrometer with a monochromatic Al Kα x-ray source (1486.6 eV). The spectra of C1s, O1s, Ti2p and Nb3d core lines were acquired at 150 eV pass energy (resolution of 0.4 eV). Raw data were fitted with Voigt functions after Shirley background substation using a homemade software based on R platform [13]. A double beam spectrophotometer (Model–JASCO V-670), single monochromator design covering a wavelength range of 200–2800 nm was used to record the optical transmittance of the grown films at normal light incidence. The transport properties including resistivities, carrier density and their mobility were measured by van der Pauw method and Hall Effect measurements using RH 2030 PhysTech instrument.

The well-known Tauc model was used to estimate the optical band gap of the films.

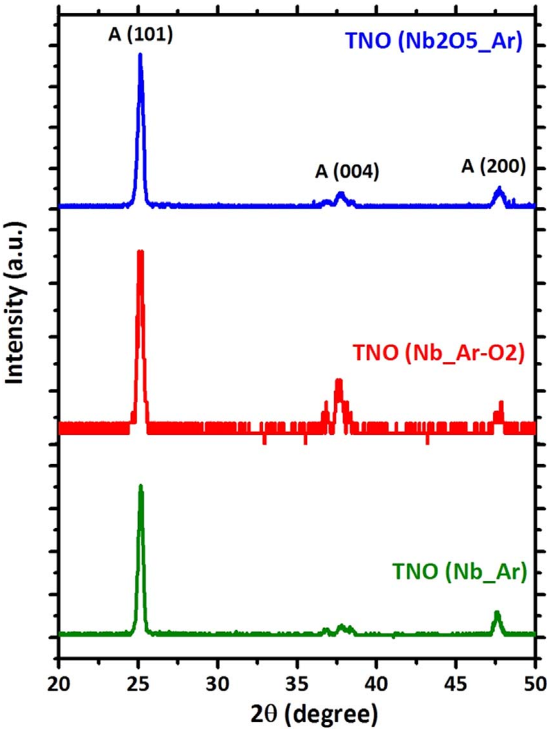

Fig. 1. XRD pattern of the annealed TNO (Nb_Ar), TNO (Nb_Ar-O_2) and TNO (Nb_2O_5_Ar) films.

3. Results and discussions

3.1. Structural properties of $Nb:TiO_2$ films

All the as-deposited TNO films were amorphous which were transformed into crystalline phase after thermal annealing at 400 °C. Fig. 1 shows the X-ray diffraction (XRD) profile of the annealed TNO films on p-type silicon (100) substrate for all the three samples. The strongest intensity of the (101) diffraction peak around 25.18° indicates a preferred oriented anatase polycrystalline structure for all the samples. No other extra peak corresponding to rutile or niobium oxide phase was evident from the XRD profile. The crystallites size of anatase estimated using Scherer's equation [14] was in the range 19–23 nm for all the prepared films. More importantly, the anatase peak position corresponding to (101) plane is shifted towards lower angle by 0.10° with respect to the bulk value (25.28°) indicating lattice expansion. The lattice expansion is due to the incorporation of Nb^{+5} into TiO_2 matrix which has slightly higher ionic radii ($Nb^{+5}\sim0.70$ Å) compared to the host cations (Ti^{+4} ~0.68 Å) [15].

3.2. Plasma Properties

The optical emission spectrum was acquired from 200 to 850 nm where many emission peaks related to Ar, Ar^+, Ti, and Ti^+ were observed. For this particular work, we focused primarily on the 777 nm line because it has significant effect on the films electrical properties. Fig. 2 illustrates an optical emission spectrum of the excited atomic oxygen line at 777 nm. As evident from the Figure, the atomic oxygen emission line at 777 nm was not present when Nb and Nb_2O_5 were sputtered separately with TiO_2 targets in pure Ar discharge. In contrast, when Nb metal and TiO_2 were used as a sputtering targets in Ar-O_2 discharge (1.6% O_2), the atomic oxygen characteristic emission line at 777 nm was appeared as shown in Fig. 2. The origin of the atomic oxygen emission line emission line is reported elsewhere [11]. The electrical and optical properties of the prepared films are discussed based on these observations. Briefly as indicated in the Fig. 2, the TNO