Solar Energy Materials & Solar Cells 94 (2010) 75–79

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Transparent and conducting TiO_2:Nb films made by sputter deposition: Application to spectrally selective solar reflectors

C.M. Maghanga [a,*], J. Jensen [a], G.A. Niklasson [a], C.G. Granqvist [a], M. Mwamburi [b]

[a] Department of Engineering Sciences, The Ångström Laboratory, P.O. Box 534, SE-75121 Uppsala, Sweden
[b] Moi University, Physics Department, P.O. Box 1125, Eldoret, Kenya

ARTICLE INFO

Article history:
Received 15 August 2008
Received in revised form
8 February 2009
Accepted 21 February 2009
Available online 25 March 2009

Keywords:
Transparent conducting oxide
Spectral selectivity

ABSTRACT

Transparent and conducting thin films of TiO_2:Nb were prepared on glass and aluminum substrates by dual-target reactive DC magnetron sputtering in an Ar+O_2 plasma. The Nb content lay between 0 and 4.9 at% as determined by ion beam analyses. X-ray diffraction showed that vacuum annealing at 450 °C led to crystallinity and prevalence of the anatase phase. The influence of Nb doping was studied with regard to structural, optical, and electrical data. Optical constants were determined from spectrophotometric recordings for films on glass, and the onset of free-electron behavior was documented for annealed films. The latter films, deposited onto Al_2O_3-coated Al, were found to display optically selective reflectance and to be useful for solar energy applications.

1. Introduction

Titanium oxide films are widely studied and employed in numerous applications as a consequence of their manifold useful properties, including thermal and chemical stability and environmentally benign character. TiO_2 can exhibit three different crystal structures, viz., rutile, anatase, and brookite. The anatase phase, with a band gap of ~3.2 eV, is a transparent dielectric with well-known photo-catalytic properties [1,2].

Recently it has been shown that Nb doping of TiO_2 can lead to electrical resistivity as low as $2–3\times10^{-4}\,\Omega$ cm while optical transparency is preserved, i.e., TiO_2:Nb is a transparent conducting oxide (TCO). These films have been produced by pulsed laser deposition onto $SrTiO_3$ [3–6] and glass [7–9] as well as by sputtering onto $SrTiO_3$ [10] and glass [11]. Films of TiO_2:Ta, made by pulsed laser deposition onto $SrTiO_3$, exhibit similar properties [12]. These TiO_2-based films are newcomers to the class of well-established TCOs embracing members such as In_2O_3:Sn (known as ITO), ZnO:Al, ZnO:Ga, and SnO_2:F [13]. TCOs attract very widespread attention today owing to their applications to solar energy utilization and energy savings, transparent electronics, light-emitting devices, etc. [14]. The new TiO_2-based TCOs are of particular interest since they are based on readily available constituents and may combine favorable optical and electrical property with photo-catalytic self-cleaning [1].

The present work investigates TiO_2:Nb films with particular regard to the possibility of using them in spectrally selective reflectors (SSRs) for solar cell applications [15–17]. The efficiency of a solar cell operating at high temperatures is significantly decreased. This is particularly the case with solar cells employing reflectors to concentrate the incoming solar radiation onto the cell. If the reflecting concentrator is replaced with a spectrally selective reflector that reflects only the useful radiation onto the solar cell, the heat buildup on the cell can be minimized. The reflectance should depend on wavelength λ and, ideally, be unity below the wavelength corresponding to the band gap of the absorber (λ_c) and zero for $\lambda>\lambda_c$ so that they can direct solar radiation that is effective for photoelectric conversion towards the solar cells and simultaneously suppress radiation that would only heat up the solar cell and thereby diminish its efficiency. In this work, the spectrally selective reflector has been modeled and fabricated for use with a conventional silicon solar cell, which has a band gap corresponding to $\lambda_c\approx1100$ nm.

2. Film deposition

Thin films of TiO_2 with varying amounts of Nb were prepared by reactive DC magnetron sputtering from 5-cm-diameter targets of Ti (99.99% pure) and Nb (99.99% pure). After an initial pump-down to $\sim4.0\times10^{-4}$ mTorr, Ar (purity 99.997%) and O_2 (purity 99.997%) were introduced into the deposition chamber so that the pressure becomes 8.5 mTorr. The O_2/Ar ratio was kept at 0.058 by the use of mass-flow-regulated gas inlets. In order to sputter films with different Nb content, the Ti target was maintained at a power of 220 W while the power to the Nb target was between 0 and 45 W. A small amount of H_2 was added to avoid target poisoning and allow stable sputtering conditions. Sputtering was performed

* Corresponding author. Permanent address: Kabarak University, P.O. Private Bag 20157, Kabarak, Kenya. Tel.: +254 722986967; fax: +254 51 343529.
E-mail address: christopher.maghanga@yahoo.com (C.M. Maghanga).

0927-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2009.02.023

onto glass (microscope slides) and Si plates positioned ~13 cm below the targets on a rotatable holder. The substrates were maintained at 330 °C during sputtering as measured by thermocouples. After the deposition, the films were allowed to cool within the sputter unit. They were later vacuum-annealed at 450 °C for 30 min in the deposition chamber at a pressure of $\sim 4.0 \times 10^{-4}$ mTorr. Film thicknesses were measured using a Tencor Alpha-Step 200 profilometer. The films were between 210 and 293 nm in thickness and were deposited at a rate ranging from 7 to 10 nm/min.

Samples for testing spectrally selective reflectance used a TiO_2:Nb/Al_2O_3 bi-layer on Al. The substrate was prepared from 0.5-mm-thick commercial anodized electroplated rolled aluminum, which was etched in a solution containing CrO_3 and H_3PO_4 to remove the anodic layer [16,17] and subsequently coated with Al_2O_3 by sputter deposition under the same conditions as those for making our TiO_2 films. The sputter rate for Al_2O_3 deposition was 23 nm/min.

3. Film characterization

3.1. Composition

The compositions of the TiO_2:Nb films deposited on Si were determined by ion beam techniques [18] in the range of atomic weights from 1 (H) to 41 (Nb). Specifically we employed Rutherford backscattering spectrometry (RBS) and time-of-flight energy elastic recoil detection analysis (ERDA) using facilities of the Uppsala University Tandem Laboratory. Recent work [19] has documented the usefulness of the latter technique to study thin films for solar-energy-related applications.

RBS was performed with 2.0 MeV $^4He^+$ ions backscattered into a detector at 167° relative to the incident beam direction. Fig. 1 shows characteristic data with clear features due to O, Ti, and Nb. Analyzing the spectrum, it was found that the Ti/O ratio was 0.42 and that the Nb doping was 3.7 at%.

ERDA analysis used $^{127}I^{9+}$ ions and techniques that have been reported recently [20]. In contrast to RBS, this method is capable of detecting light atoms. The data in Fig. 2 show evidence for H, O, Si, Ti, and Nb. The results are consistent with those from RBS and also indicate the presence of ~2 at% H. Importantly, Nb appears to be evenly distributed over the cross-section of the film. The Si signal originates from the substrate.

3.2. Structure

Thin film structures were investigated by X-ray diffraction (XRD) using a Siemens D5000 instrument operating with CuK_α radiation. Fig. 3 shows data for TiO_2 films with different Nb contents in the as-prepared state (i.e., after *in situ* heat treatment at 330 °C) (Fig. 3(a)) and after a subsequent annealing at 450 °C (Fig. 3(b)). The various diffraction peaks could be unambiguously assigned to reflections corresponding to the anatase and rutile phases of TiO_2 (JCPDS data cards 00-021-1272 and 00-21-1276, respectively). The prominence of the diffraction peak at $2\theta = 25.2°$ points at preferential orientation along the (0 0 4) direction.

The XRD data show, expectedly [21], that the crystallinity was improved when the films were annealed at a higher temperature and the presence of a diffraction peak at $2\theta \approx 27°$ shows that the undoped film contains some rutile phase. The presence of Nb seems to impede the formation of this phase, and nothing but the anatase phase is evident when the Nb content is as small as 1.3 at%.

Crystallite sizes were estimated from the XRD data by using the well-known Debye–Scherrer formula, i.e.,

$$D = (0.9\lambda_x)/(\beta \cos \theta), \quad (1)$$

where D is the diameter of the crystallites forming the film, λ_x is the wavelength of the X-ray line, and β is the full-width at half maximum of the XRD peak. As shown in Fig. 4, for samples annealed in vacuum at 450 °C the estimated crystallite size increases with increasing Nb content as long as it remains below 2 at%.

3.3. Optical and electrical properties

Spectral transmittance $T(\lambda)$ and reflectance $R(\lambda)$ at normal and near-normal angle of incidence, respectively, were measured in

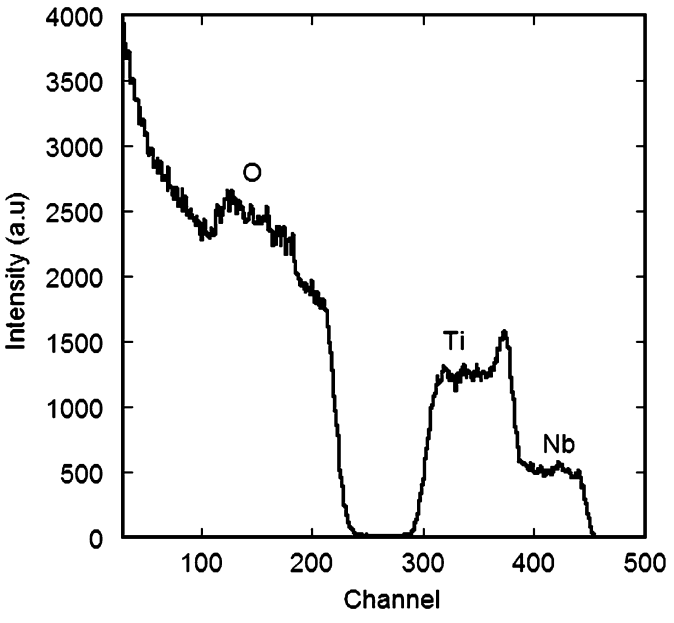

Fig. 1. RBS spectrum for a TiO_2:Nb thin film with 3.7 at% Nb.

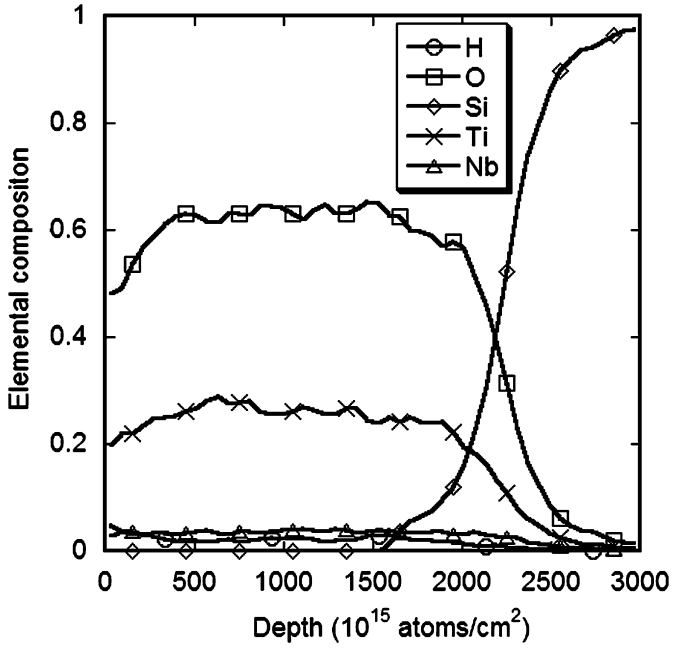

Fig. 2. ERDA data for a TiO_2:Nb film with 3.7 at% Nb.