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Transparent and Conducting TiO₂:Nb Films Made by Sputter Deposition: Application to Spectrally Selective Solar Reflectors

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Abstract

Transparent and conducting thin films of TiO₂:Nb were prepared on glass and aluminum substrates by dual-target reactive DC magnetron sputtering in an Ar + O₂ plasma. The Nb content lay between zero 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 structure. 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 Al₂O₃-coated Al, were found to display optically selective reflectance and to be useful for solar energy applications.

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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 $2\text{--}3 \times 10^{-4} \text{ } \Omega\text{cm}$ while optical transparency is preserved, *i.e.*, $\text{TiO}_2\text{:Nb}$ is a transparent conducting oxide (TCO). These films have been produced by pulsed laser deposition onto SrTiO_3 [3,4,5,6] and glass [7,8,9] as well as by sputtering onto SrTiO_3 [10] and glass [11]. Films of $\text{TiO}_2\text{:Ta}$, made by pulsed laser deposition onto SrTiO_3 , exhibit similar properties [12]. These TiO_2 -based films are newcomers to the class of well known TCOs embracing members such as $\text{In}_2\text{O}_3\text{:Sn}$ (known as ITO), ZnO:Al , ZnO:Ga , and $\text{SnO}_2\text{:F}$ [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 their favorable optical and electrical property with photo-catalytic self-cleaning [1].

The present work investigates $\text{TiO}_2\text{:Nb}$ films with particular regard to the possibility of using them in spectrally selective reflectors for solar cell applications [15-17]. The reflectance should depend on the wavelength λ and, ideally, be unity for $\lambda < \lambda_c$ 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 only would heat up the solar cell and thereby diminish its efficiency. A conventional silicon solar cell has a band gap corresponding to $\lambda_c \approx 1100$ 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 $\sim 4.0 \times 10^{-4}$ mTorr, Ar (purity 99.997 %) and O₂ (purity 99.997 %) were introduced into the deposition chamber so that the pressure became 8.5 mTorr. The O₂/Ar ratio was kept at 0.058 by use of mass-flow-regulated gas inlets. Sputtering was conducted with the power to the Ti target being 220 W and the power to the Nb target lying between zero and 45 W in order to make films with different Nb content. A small amount of H₂ was added in order to avoid target poisoning and allow stable sputtering conditions. Sputtering was performed 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 minutes in the deposition chamber. Film thicknesses were measured using a Tencor Alpha-Step profilometer. The films were between 210 and 293 nm in thickness and were deposited at a rate ranging from 7 to 10 nm/s.

Some films of Al₂O₃ were used to make samples for solar applications. Films of TiO₂:Nb/Al₂O₃/Al were fabricated in situ by first depositing Al₂O₃ on Al substrate at a rate of ~ 22.5 nm/s followed by Nb:TiO₂. Deposition conditions of the Nb:TiO₂ films were as described above.

3. Film characterization

A. Composition

The compositions of the TiO₂:Nb films backed by 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. Figure 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. %.

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

Fig. 1. RBS spectrum for a $\text{TiO}_2\text{:Nb}$ thin film with 3.7 at. % Nb.

Fig. 2. ERDA data for a $\text{TiO}_2\text{:Nb}$ film with 3.7 at. % Nb.

B. Structure

The film structure was investigated by X-ray diffraction (XRD) using a Siemens D5000 instrument operating with $\text{CuK}\alpha$ radiation. Figure 3 shows data for TiO_2 films with different Nb contents in as-prepared state (*i.e.*, after *in situ* heat treatment at 330 °C) (upper panel) and after a subsequent annealing at 450 °C (lower panel). 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 $2\theta = 25.2^\circ$ points at preferential orientation along the (004) direction.

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

Fig. 3. XRD data for as-deposited TiO_2 and $\text{TiO}_2\text{:Nb}$ films in as-deposited state involving annealing at 330 °C (upper panel) and after a subsequent annealing at 450 °C in vacuum (lower panel). The diffraction peaks are assigned to the anatase (A) and rutile (R) structures.

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, recorded for samples annealed in vacuum at 450 °C, the crystallite size increases with increasing Nb content as long as it remains below 2 at. %.

Fig. 4. Crystallite size for TiO₂:Nb films annealed at 450 °C in vacuum. Lines were drawn between data points solely for convenience.

C. Optical and electrical properties

Spectral normal transmittance $T(\lambda)$ and near-normal reflectance $R(\lambda)$ were measured in the $300 < \lambda < 2500$ nm range by use of a Perkin-Elmer Lambda 900 double-beam spectrophotometer. A barium sulphate film served as reflectance standard. As found from Fig. 5, the doping changes the optical properties of the films to a major degree only after annealing at 450 °C. In particular the infrared transmittance is suppressed in the TiO₂ film with 3.7 at. % Nb.

Fig. 5. Spectral transmittance and reflectance for TiO_2 and $\text{TiO}_2\text{:Nb}$ films in as-deposited state involving annealing at 330 °C (upper panel) and after a subsequent annealing at 450 °C in vacuum (lower panel).

The resistivity of the films was determined by the van der Pauw method [22] applied to $4 \times 4 \text{ mm}^2$ samples with sputter deposited Au contacts. Undoped TiO_2 films had a resistivity of $\sim 300 \text{ } \Omega\text{cm}$. Nb doping made the resistivity drop monotonically for increasing doping from $\sim 1.2 \times 10^{-2} \text{ } \Omega\text{cm}$ for 1.3 at. % Nb to $1.9 \times 10^{-3} \text{ } \Omega\text{cm}$ for 4.9 at. % Nb. Correspondingly the carrier density is increased from 2.5×10^{20} to $2.4 \times 10^{21} \text{ cm}^{-3}$.

These results are in good agreement with literature data for $\text{TiO}_2\text{:Nb}$ films made by sputtering [10,11], whereas films on SrTiO_3 have yielded lower resistivities as mentioned in the Introduction.

4. Analysis of optical properties

A. Optical constants and band gap

Dispersion analysis using a model for the dielectric susceptibility of the film consisting of Drude [23] and Brendel terms [24,25] was used to model the measured reflectance and transmittance. Model parameters were determined from the best fit between computed and experimental data, using commercial software (Scout) [26]. The best fit gives us directly the optical constants of the film under study. Figure 6 shows spectral refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ for TiO_2 and $\text{TiO}_2\text{:Nb}$ with two doping levels. The films had been annealed to 330 °C (upper panel) and 450 °C (lower panel) as earlier described. Annealing at the lower temperature leads to films with clear-cut dielectric properties, as apparent from k being close to zero. The refractive index was slightly enhanced for increased Nb content, which may be associated with the fact that Nb promoted crystallinity (*cf.* Fig. 3). After annealing at 450 °C, the optical properties are qualitatively different, and $k(\lambda)$ goes up steeply for $\lambda > 500$ nm, which signals a metallic-like behavior. For the undoped TiO_2 , n is slightly larger after annealing at the higher temperature, as expected from some densification.

Fig. 6. Spectral refractive index n and extinction coefficient k for TiO_2 and $\text{TiO}_2\text{:Nb}$ films in as-deposited state involving annealing at 330 °C (upper panel) and after a subsequent annealing at 450 °C in vacuum (lower panel). Arrows indicate the appropriate vertical scale.

The optical band gap E_g was evaluated from the standard expression [21]

$$\alpha h\nu \propto (h\nu - E_g)^m, \quad (2)$$

where $\alpha = 2\pi k/\lambda$ is absorption coefficient, $h\nu$ is photon energy, and $m = 2$ accounts for the fact that the indirect allowed transitions across the band gap are expected to dominate. Figure 7 shows data on $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for a TiO_2 film; a band gap of 3.36 eV is obtained from the intersection of the fitted straight line and the abscissa. Band gaps for films annealed at different temperatures and containing different amounts of Nb lay in the range 3.35 to 3.51 eV.

Fig. 7. $(\alpha h\nu)^{1/2}$ vs. photon energy $h\nu$, where α is absorption coefficient, for a TiO_2 film annealed at 450 °C. The fitted straight line is used to derive the band gap.

B. Spectrally selective reflectance: Modeling and experiment

The optical constants of the $\text{TiO}_2\text{:Nb}$ films, reported in Fig. 6, were used to evaluate the spectral selectivity for solar cell applications, as introduced above. We considered, as in earlier work of ours [16,17], a structure with a transparent conductor on top of an aluminum substrate coated with an oxide layer and used literature data for the optical

constants of Al [27] and Al₂O₃ [28]. The reason for the intermediate oxide layer is to suppress the strong optical interference effects—ensuing from the high refractive index of TiO₂-based films—that would otherwise compromise the spectral selectivity.

The spectral selectivity is conveniently characterized by two parameters pertaining to radiation with energy higher and lower than that leading to energy generation in a solar cell. For a Si solar cell the parameters are

$$R_{\text{cell}} = \frac{\int_{300}^{1100} G(\lambda)R(\lambda)d\lambda}{\int_{300}^{1100} G(\lambda)d\lambda} \quad (3)$$

and

$$R_{\text{therm}} = \frac{\int_{1100}^{2500} G(\lambda)R(\lambda)d\lambda}{\int_{1100}^{2500} G(\lambda)d\lambda} \quad , \quad (4)$$

where $G(\lambda)$ is the AM 1.5 solar spectrum [29].

Calculations of R_{cell} and R_{therm} were carried out for a large range of parameters, and it was found that a structure with Al covered with 90 nm of Al₂O₃ and 90 nm of TiO₂:Nb having 3.7 at. % of Nb gave good selectivity with $R_{\text{cell}} = 0.787$ and $R_{\text{therm}} = 0.314$. The corresponding spectral reflectance is shown in Fig. 8.

The accuracy of the calculated spectral reflectance was verified in experiments on a tandem structure incorporating a 90-nm-thick film of TiO₂:Nb, on a substrate of Al₂O₃-coated Al. This substrate was prepared from 0.5-mm-thick commercial anodized electroplated rolled aluminum which was etched in a solution containing CrO₃ and H₃PO₄ [16,17] and subsequently coated with 90 nm of Al₂O₃ by sputtering. As seen from Fig.8, the experimental and theoretical data are in very good agreement. Specifically, the experimental sample yielded $R_{\text{cell}} = 0.77$ and $R_{\text{therm}} = 0.28$.

Fig. 8. Computed and measured spectral reflectance for a $\text{TiO}_2\text{:Nb}/\text{Al}_2\text{O}_3/\text{Al}$ structure as described in the main text.

5. Conclusion

Thin films of $\text{TiO}_2\text{:Nb}$ were made by reactive DC magnetron sputtering. Annealing at 450°C led to electrical conduction while optical transparency was preserved, thus verifying recent work from a few laboratories showing that $\text{TiO}_2\text{:Nb}$ can serve as a transparent conductor. We determined the optical constants of this material and demonstrated, computationally as well as experimentally, that a tandem structure of $\text{TiO}_2\text{:Nb}$ and Al_2O_3 on top of Al has spectrally selective reflectance of interest for solar cell applications.

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