



High performance TiO₂ nanotubes antireflection coating



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ABSTRACT

The present study analyzes the use of TiO₂ layer as antireflection coating. TiO₂ thin films were prepared on silicon substrate by electrochemical anodization process with thicknesses of 130 and 170 nm. The films exhibit a uniform nanotubular structure. The ellipsometry measurement data were analyzed using a multi-layer model, the bottom layer is a dense layer of TiO₂ and the top layers are porous; they are formed by a mixture of TiO₂ and void. The values of refractive index are obtained by the Bruggeman effective medium approximation. The refractive indexes of the bottom and top TiO₂ sublayers were about 2.3 and 1.6, respectively. The lower values of reflectance are obtained with the thinnest film. For these samples the reflectance decreases about 90% compared to silicon and in some cases the reflectivity is less than 5%. The thickness influences of TiO₂ thin films and their synthesis parameters on the optical constants are discussed.

1. Introduction

TiO₂ nanostructured has been found to possess a variety of highly useful applications, including their use in gas sensors [1–3], solar cells [4,5], photocatalysis [6,7], UV photodetectors [8,9], supercapacitors [10,11] and so on. It has been widely used in optoelectronic devices due to its excellent electrical and optical properties. Particularly, one way to increase the efficiency of solar cells is to implement antireflective coatings (ARC). Considering silicon solar cells, this material reflects from 30% in the infrared light to more than 60% in the ultraviolet light. For this reason is necessary to minimize the reflected light at the front surface and thus increase the absorbed energy. Suitable materials as antireflective coatings are TiO₂, SiO₂, Al₂O₃ and ZnS [12–14].

Antireflection coatings can be based on homogeneous layers or on inhomogeneous coatings [15]. An example of the homogeneous case is thin dielectric multilayers, which consists in stack the layers so that the index of refraction is decreasing from the substrate to the air to reduce the apparent abruptness of the interface. An example of the inhomogeneous case could be ARC focusing on the material and its topography, such as porous or textured surface of the substrate or the coating [16]. The work of Xi et al. [17] presents nanorods grown by oblique-angle deposition using electron beam evaporation. Other research group works in ZnO nanotubes, fabricated by hydrothermal growth on triple junction solar cell devices [18]. In the homogenous case, as in the inhomogeneous case, graduated effective index coatings are obtained.

On the other hand, the manufacturing of solar cells with ARC requires compatibility between the manufacturing stages of the ARC and the manufacturing process of the device.

This work is focused on the study of antireflective films of TiO₂ nanotubes compatible with silicon solar cells. The films were prepared by anodic oxidation method, which offer good optical performance, excellent adherence and are compatible with the process of manufacturing solar cells at laboratory scale.

2. Materials and methods

2.1. Deposition of a Ti thin film on a Si substrate

Titanium (Ti) films were deposited by magnetron sputtering on p-type silicon (Si) (100) wafer at room temperature. Target of 99.9% Ti with 50 and 6 mm in diameter and thickness, respectively, was used as the material source. The chamber pressure was maintained at 0.4 Pa during the deposition process.

Sputtering was carried by pure argon with 8 cm³/min volume flow rate. The distance between the target and the substrate was 14 cm and the sputtering power was 160 W using a DC power supply. Under these conditions, the deposition rate was 4.4 nm/min and 80 and 120 nm thick Ti films were obtained after 18 and 27 nm, respectively.

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Table 1
Parameters for the anodization process of Ti thin films.

Sample	Voltage	Time	Sample	Voltage	Time
T-1	20 V	700 s	M-1	20 V	1200 s
T-2	30 V	600 s	M-2	30 V	800 s
T-3	30 V	500 s	M-3	30 V	900 s
T-4	30 V	400 s	M-4	30 V	1000 s
T-5	40 V	300 s	M-5	30 V	1200 s

2.2. Preparation of TiO₂ nanotubes

Highly ordered, vertically oriented TiO₂ nanotube-arrays were fabricated by potentiostatic anodization of titanium. The anodization was conducted in a two electrode electrochemical cell with a platinum foil as cathode and Si substrate with Ti as anode at a constant potential. The growth of the nanotube arrays has been obtained in a glycerol solution with 0.6 wt% NH₄F at room temperature. Anodization was performed applying a potential ramp of 1 V/s until it reached the desired voltage using a Keithley 2612A system sourceter. The detailed procedure for the preparation of TiO₂ nanotubes is described in our previous works [19,20].

The samples are grouped into two series according to the thickness of the Ti film prior to electrochemical anodization. The set corresponding to 80 and 120 nm of thickness is indicated with the letter T and M, respectively. The parameters for the anodization of Ti films are shown in Table 1.

After the electrochemical treatment, the samples were immediately washed with deionized water and dried in nitrogen stream. Finally, in order to convert the amorphous TiO₂ structure into a crystalline one, samples were annealed at 350 °C for 2 h in air [21].

2.3. Film characterization

The structural analysis of the films was carried out using Grazing Incidence X-Ray Diffraction (GIXRD), with a PANalytical model Empryan diffractometer equipped Cu K α radiation ($\lambda = 0,15418$ nm) using a generator voltage of 40 kV and current of 40 mA, operating at $\theta = 2^\circ$.

Scanning electron microscope (SEM) Zeiss model Supra40 Gemini was employed for the morphological characterization of the TiO₂ samples.

Spectroscopic ellipsometer (SE) Horiba model AUTO-SE was used to examine the optical property in the wavelength range between 400 and 800 nm and at a constant angle of incidence of 69.95°.

The spectral hemispherical reflectivity was measured with a GMC UV-Vis 920 spectrophotometer with an integrating sphere at almost normal incidence.

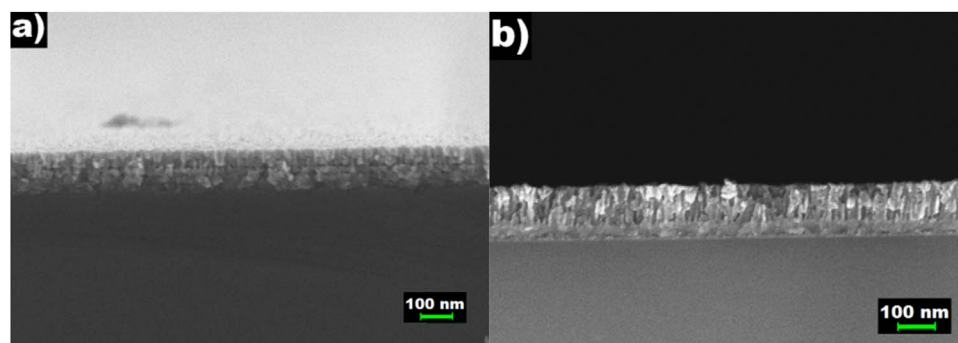


Fig. 1. Cross-sectional SEM images of the TiO₂ samples with different thickness (a) T-1 (b) M-1.

3. Results and discussion

3.1. Structural and morphology of the films

Fig. 1 shows SEM images cross-sectional of TiO₂ films prepared by electrochemical anodization after annealing.

The films have (Fig. 1a–b) thicknesses about 130 and 170 corresponding to the sample of 80 and 120 of Ti film thickness respectively. In Image 1b it can be seen clearly two zones: a compact lower and a higher columnar. Fig. 2 shows the top-view images of the TiO₂ sample M-1 at two magnifications,

The length expansion when the Ti is converted to TiO₂ is about 50%. The length expansion can be explained by the Pilling-Bedworth ratio (PBR). This factor represents the ratio of the volume per metal ion in the oxide to the volume per metal atom in the titanium. The PBR strongly depends on the applied anodization potential and the electrolyte used [22,23].

From the top view, the SEM image of all samples exhibits a uniform nanotubular structure. All the nanotubes have an inner diameter of ~20–40 nm. These results are consistent with the literature [24,25].

Fig. 3 shows the XRD patterns of the sample M-1 after annealed. The peaks are indexed as the anatase phase (01-086-1157) and rutile (00-034-0180). The ratio of the phases depends strongly on the heat treatment but also depends on the anodizing voltage. The samples crystallized into two phases with anatase dominant at lower temperature and then the more stable rutile appeared when the temperature was raised [21].

3.2. Reflectivity measurements

The reflectance of the TiO₂ films and silicon are shown in Fig. 4a–b. The lower values of reflectance are obtained with the thinnest film (T). For these samples the reflectance decreases about 90% compared to silicon. It can also be noted that in some cases the reflectivity is less than 5% (Fig. 4a). In contrast, for thicker films, the reflectivity values do not decrease considerably for the analyzed spectral range.

The reflectance spectra depend considerably on the fabrication-process parameters. In particular, the lowest reflectance values are obtained for sample T-1 and a minimum reflectance of 0.6% at 633 nm. Table 2 shows a comparison of reflection average of present work with similar type in bibliography; a good performance is evident.

The performance of an antireflective coating is measured for solar cells by [35]:

$$Rw = \frac{\int_{\lambda_{\min}}^{\lambda_{\max}} R(\lambda) N_{ph}(\lambda) d(\lambda)}{\int_{\lambda_{\min}}^{\lambda_{\max}} N_{ph}(\lambda) d(\lambda)} \quad (1)$$

where $R(\lambda)$ is the wavelength dependent reflection and N_{ph} is the photon flux, AM1.5 spectrum, of the solar spectrum. Rw was calculated for two wavelength ranges for the sample T-1.

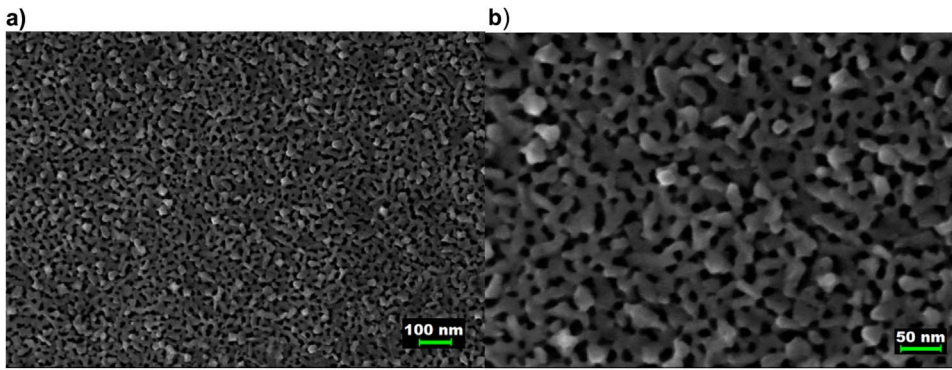


Fig. 2. Top-view SEM images of the TiO₂ sample M-1 (a) low and (b) high magnification.

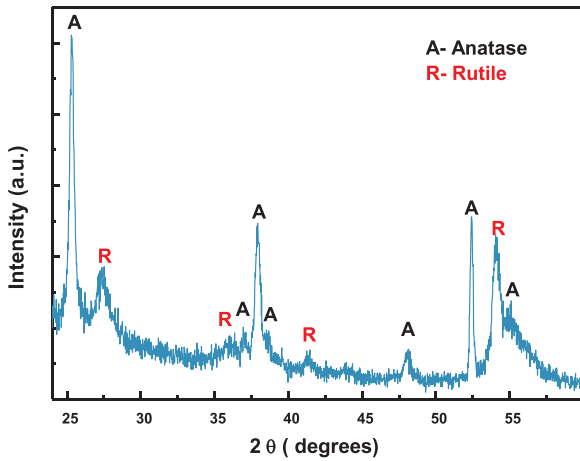


Fig. 3. X-ray diffraction pattern of the TiO₂ after annealing.

R_w (400–800 nm) = 0.02453 (o 2.4%)
 R_w (200–900 nm) = 0.04244 (o 4.2%)

3.3. Ellipsometric models

The ellipsometric parameters $\psi(\lambda)$ and $\Delta(\lambda)$ were used to obtain the optical properties of the film using two model involving: Model 1: two layers and silicon substrate. The bottom and the top layers are dense and porous layers of TiO₂, respectively (Fig. 5).

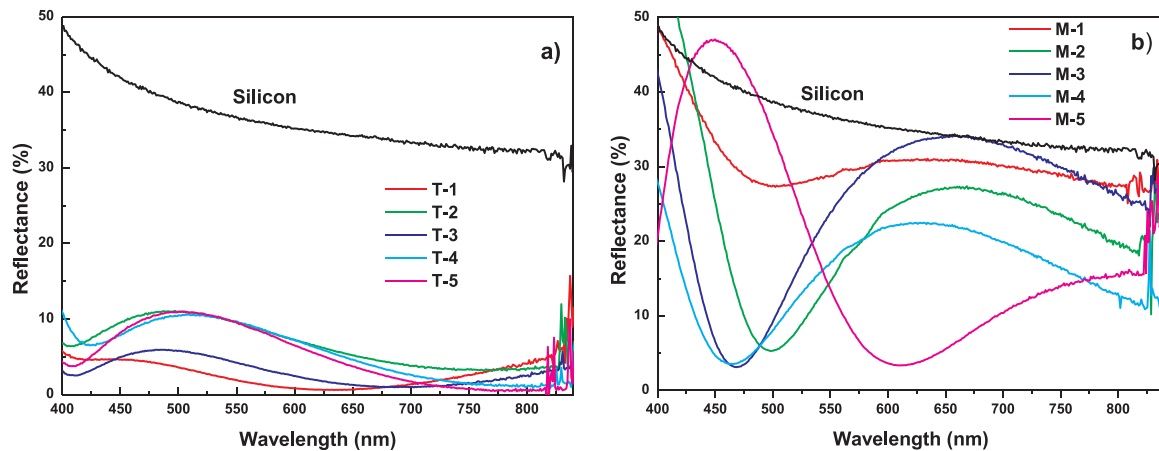


Fig. 4. Reflectance spectra of TiO₂ films on Si substrate as a function of wavelength with different thickness (a) T and (b) M.

The values of refractive index are obtained by Cauchy transparent model [36] described in Eq. (2).

$$n(\lambda) = A + \frac{10^4 B}{\lambda^2} + \frac{10^9 C}{\lambda^4} \quad (2)$$

where A , B and C are the model parameters.

The top layer is porous; it is formed by a mixture TiO₂ and void. The values of effective refractive index are obtained by the Bruggeman effective medium approximation [36].

Model 2: Several layers and the silicon substrate. A dense bottom layer of TiO₂ and the upper layers are porous; each one is formed by TiO₂ and vacuum in a composition gradient. Fig. 6 shows a schematic representation of the proposed physical model 2.

Model 1 was applied to adjust the optical data of the films. Fig. 7 shows the experimental and adjusted data of the spectroscopic ellipsometer for T-1 and M-1 as an example of each of the thicknesses.

Table 3 shows the adjusted results for these samples, the value of χ^2 was also included as an indicator of the quality of fit. The fit was very suitable for the thinner samples and acceptable for the thicker ones. The values for thickness are directly compared with obtained from cross sectional SEM. It can be seen that the values are similar for both film thickness. Using the values of fitting parameters A , B , C and Eq. (1) were obtained the refractive indices of the dense layer. The refractive index of T-1 sample was similar with the values of the literature [37,38]. In contrast, the value of the M-1 sample was lower. This value is probably inadequate because the model 1 is very simple and it is necessary to consider a more complex model.

Model 2 was applied to adjust the optical data of the films using two layers as porous layer. Fig. 8 shows the experimental and adjusted data

Table 2
Comparison of antireflective coating of different materials on silicon substrate.

No.	Reflection average (%)	Range (nm)	Materials	Layers	Ref.
1	3.3	400–800	Al ₂ O ₃ /TiO ₂	2	[26]
2	6.2	400–1000	SiO ₂ /SiO ₂ -TiO ₂ /TiO ₂	3	[27]
3	14	400–1000	NiO	2	[28]
4	3.8	700	Hydrogenated diamond like carbon	1	[29]
5	6	300–1100	Si random nanostructures and nanoparticles	1	[30]
6	3	300–1100	InO ₃ nanocones	1	[31]
7	4	300–1100	SiN _x /SiO ₂ N _y	> 3	[32]
8	7.8	400–1000	ZnO/Al ₂ O ₃ core-shell nanorods	> 3	[33]
9	< 5	300–1100	Si nanorod	1	[34]
10	10.4	400–800	TiO ₂	1	[35]
11	15	350–1150		2	
	2.5	400–800	TiO ₂	1	This work

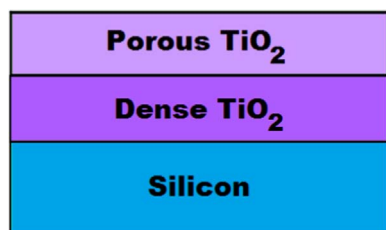


Fig. 5. Schematic representation of the proposed physical model 1.



Fig. 6. Schematic representation of the proposed physical model 2.

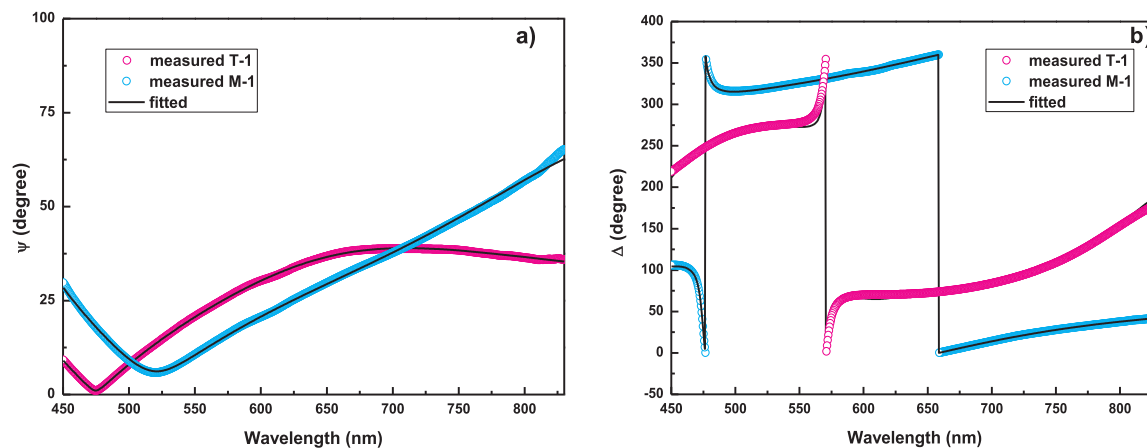


Fig. 7. Experimental data and fitted for T-1, M-1, using model 1 (a) ψ , (b) Δ .

of the spectroscopic ellipsometer for the samples T-1 and M-1 to allow a comparison with model 1. Table 4 shows the adjusted results for these samples. The fit was very suitable for the thinner samples and acceptable for the thicker ones. The thicknesses are compared directly with the obtained values from cross sectional SEM.

The refractive indices of the films were calculated as a function of the wavelength using the adjustment values obtained with model 2. The refractive index of dense layer was about 2.3 for all samples. The calculated values of the refractive index of the top and bottom porous layer were approximately 1.6. The fact that the refractive index gradually decreases from the substrate to the air reduces the abrupt change in the silicon-air interface. Taking into account a specific multilayer model and the optical properties of each of the layers it is possible to optimize the optimum thicknesses to achieve the minimum reflectivity. This allows the layers of TiO₂ (dense) and TiO₂ (porous) to function as an antireflective coating.

It should be noted that by varying the anodizing parameters it is possible to adjust the optical properties within a certain range to achieve very low reflectivity values. At higher anodizing voltage, the greater inner diameter and the lower the percentage of TiO₂ in the porous layer achieving decrease the refractive index. Increasing anodization time it is possible to obtain greater thickness of the porous layer.

In summary, by modifying the fabrication parameters of the films (e.g. deposited titanium thickness, anodizing voltage and annealing temperature) it is possible to modify the optical properties to achieve a very low reflectivity. In the present work it was possible to obtain an average reflectivity of 2.5% (400–800 nm).

4. Conclusions

In this paper, TiO₂ nanotube layer coating on silicon was prepared by a simple electrochemical anodization method. The results obtained by fitting ellipsometry spectra in the 400–800 nm range, using a multilayer model consisting of a dense bottom of TiO₂ and the top layers are porous; they are formed by a mixture TiO₂ and void. The refractive indices of the top and bottom TiO₂ layers were approximately 2.3 and 1.6, respectively.

The thicknesses and optical properties were adjusted by controlling the manufacturing parameters to achieve a coating with very low reflectivity. The average reflectance of the coated sample was 2.5%. This manufacturing process can be used for different optoelectronic applications such as solar cells.

Table 3
Fitted results with proposed model 1.

Sample	Thickness (nm)				% TiO ₂	Refractive index (at 600 nm)		χ^2
	Dense layer	Porous layer	Total	Cross sectional SEM		Porous layer	Dense layer	
T-1	63	61	124	130	47	2.29	1.56	0.22
M-1	74	116	190	170	61	1.84	1.46	1.36

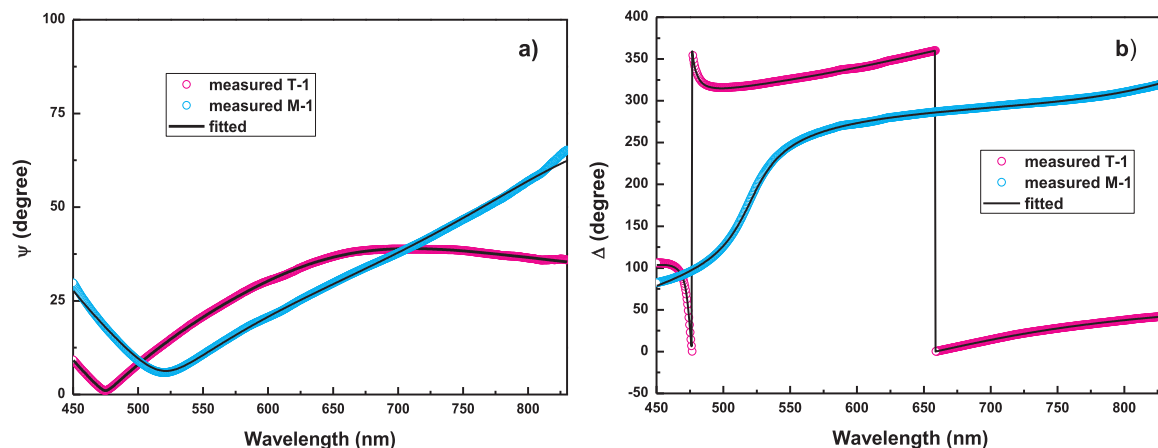


Fig. 8. Experimental data and fitted for T-1, M-1, using model 2 (a) ψ , (b) Δ .

Table 4
Fitted results with proposed model 2.

Sample	Thickness (nm)				% TiO ₂		Refractive index (at 600 nm)				χ^2
	Dense layer	Porous layer	Total	Cross sectional SEM	Porous layer		Dense layer	Porous layer			
					Bottom	Top		Bottom	Top		
T-1	60	64	124	130	50	44	2.31	1.57	1.55	0.23	
M-1	23	170	193	170	50	40	2.31	1.57	1.54	1.91	

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