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Structural and optical study of titanium dioxide thin films elaborated by APCVD for application in silicon solar cells

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Abstract. In this work, titanium dioxide (TiO_2) thin films have been deposited on glass and monocrystalline silicon by Atmospheric Pressure Chemical Vapor Deposition (APCVD) technique using titanium tetrachloride $TiCl_4$ as precursor. The structural, electrical and optical properties of the prepared TiO_2 thin films were evaluated by Atomic Force Microscopy (AFM), Four Point Probe (FPP) and Spectroscopic Ellipsometry (SE), respectively. These properties were exploited for application of the TiO_2 layers as antireflection coatings on monocrystalline silicon solar cells. Our experimental results show that the deposited TiO_2 thin films were polycrystalline, homogenous, compact and relatively smooth. The measured average optical transmittance of the TiO_2 films was about 85-90%. From the ellipsometry analysis, the refractive index of our TiO_2 thin films was found to be n=2,25 at the wavelength λ= 550 nm, with a thickness of 56,2 nm. These experimental results obtained by APCVD are in excellent agreement with the computed results of the TiO_2 refractive index and thickness required for a high quality antireflection coating in industrial conditions. The obtained results demonstrate the real opportunity of the APCVD technique to prepare high quality antireflection coatings for crystalline solar cells. This indicates that the APCVD antireflection coatings may have a high potential industrial application.

Keywords: Titanium dioxide, APCVD, structural properties, optical properties, AFM, Ellipsometry, Four-Point Probe.

1. Introduction

Titanium dioxide (TiO_2) in thin films form has several properties that make it a material of interest for lots of applications. Indeed, TiO_2 films can be used as coating in anticorrosive protection, as catalysts in chemical industry and environmental purification phenomena.TiO_2 thin films have excellent electrical and optical properties, such as a high refractive index [1], [2] and excellent transmittance in the visible and near IR region of the solar spectrum [3], [4]. Since TiO_2 is highly transparent, it acts like a window for the transmission of solar radiations. Due to its interesting optical properties, these films have been widely used as antireflection coatings (ARC).

High quality antireflection coatings are required for the realization of high performance solar cells. One of the optical requirements for antireflection coating is high refractive index. This characteristic can be achieved by optimization of the film preparation technique. Several techniques have been developed for elaborating the TiO_2 thin films [5], [6], [7], [8]. Among them, atmospheric pressure chemical vapor deposition or APCVD is one of the most attractive, as it is known to be a low cost process giving high density stoichiometric and uniform films [9]. Moreover, it is especially applicable to large area, continuous deposition, as required for growth on glass or crystalline silicon [9]. Due to its several advantages, CVD has become one of the main processing methods for the deposition of amorphous, monocrystalline and polycrystalline thin films and coatings for a wide range of applications.

In this work, TiO_2 thin films were fabricated on glass and monocrystalline silicon substrates by APCVD from the reaction of titanium tetrachloride $TiCl_4$ with oxygen. The structural, electrical and optical properties of the prepared TiO_2 thin films were evaluated by Atomic Force Microscopy (AFM), Four-point probe (FPP) and Spectroscopic ellipsometry (SE), respectively. In the light of these results, these properties were exploited for application of the TiO_2 layers as single-layer antireflection coatings (SLARC) on monocrystalline silicon solar cells.

According to [10], achieving low reflectance for monocrystalline silicon solar cells having TiO_2 as antireflection coating, is possible when the refractive index of the TiO_2 layer is equal to n=2,2 at λ=550 nm with an estimated thickness of 56,8 nm as illustrated in figure 1. These values can be achieved experimentally by optimization of the film preparation conditions.

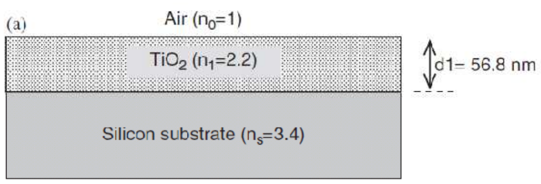


Figure1. Design diagram of a TiO_2 single-layer antireflection coating [10].

2. Experimental details

A. Preparation of TiO_2 thin films

In this work, we have deposited the titanium dioxide thin films on glass and monocrystalline silicon using the APCVD technique. The titanium tetrachloride $TiCl_4$ (liquid) was used as the main precursor to form the titanium dioxide films.

The APCVD equipments consists of a Pyrex glass reactor with three inlets (for $TiCl_4$, O_2 and N_2), and a chemical vapor precursor supply system. The CVD reactor consists of a reaction chamber equipped with a substrate holder, and a heating system with temperature control.

The glass and silicon substrates were washed successively in acetone, alcohol and distilled water to obtain clean surfaces which were dried before being placed in the reactor.

The $TiCl_4$ liquid precursor was heated in a tube connected to the reactor. The $TiCl_4$ vapor was transported into the reactor by oxygen as a carrier gas. The formation of the TiO_2 films is due to the reaction of $TiCl_4$ vapor with oxygen at the surface of the sample as follows:

$$TiCl_4(g) + O_2\,(g) \rightarrow TiO_2(S) + 2\,Cl_2\,(g)$$

A nitrogen gas (N_2) was injected into the chamber during the reaction in order to avoid undesirable oxidation of silicon at high temperature and to obtain a good uniformity of the films.

The CVD system being an “open” reactor, the resulting gases after deposition (Cl_2 in this case) were removed from the reactor.

A range of films were then grown at the deposition temperature of 450°C during 15 min and the oxygen pressure of 1 bar. Film thickness was controlled directly by deposition time. The deposited TiO_2 films on silicon and glass substrates at 450°C were then annealed at 450°C for a period of 1 hour.

B. Characterization methods

The surface morphology of the films was studied by Atomic Force Microscopy using the AFM apparatus of NT-MDT Solver (France) operating in the air at ambient conditions. Samples topography was imaged by scanning in the non-contact (NC-AFM) mode at resonant frequency of 310,75 kHz and a scan rate of 1 Hz. For comparison, the AFM measurements were also performed on bare silicon served as substrate and its RMS surface roughness was given. Roughness analysis and grain size measurements were performed using the Nanoscope software: “Nova”.

The optical properties of the deposited TiO_2 thin films were studied on the basis of the spectrophotometric measurements of the transmittance using the UV-VIS-IR "spectrophotometer 0306029S1" in the wavelength range of 300-800 nm.

The refractive index of the prepared TiO_2 films was evaluated by ellipsometry measurements using the "WINELLI_II 2.2.0.6" ellipsometer ("SOPRA" software). The thickness of the TiO_2 layers was measured by AFM and ellipsometry for comparison.

The four-point probe (FPP) "KEITHLEY 236/237 TUTORIAL" in the linear probes configuration was used to measure the electrical resistivity of the prepared TiO_2 films. Once the probes were in contact with the surface, a constant current was passed through the outer pins while the corresponding voltage drop was measured across the inside pins. In this work, currents of 1-2 mA were employed.

3. Results and discussion

A. Morphological studies

Figure 2, illustrates the two-dimensional (2D) AFM topographic images of a Si substrate and annealed thin film of TiO_2 on Si. The AFM images reveal the polycrystalline structure and the homogenous surface of the prepared TiO_2 films. These films are dense, uniform and compact. They showed an excellent adhesion and passed the scotch Tape test with no visible degradation.

As estimated by AFM, the thickness of the TiO_2 film on silicon substrate was found to be 56,2 nm which is confirmed by ellipsometry measurements.

The surface roughness can be quantitatively identified by the root-mean-squared roughness (rms. Roughness: R_{rms}). R_{rms} is given by the standard deviation (S.D) of the data from AFM images, and determined using the standard definition as follows [11]:

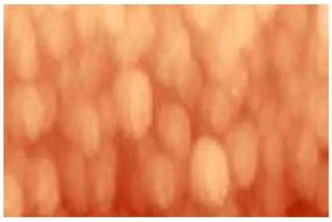
$$R_{rms} = \sqrt{\frac{\sum_{n=1}^{N}(Z_n - \bar{Z})^2}{N-1}} \qquad (1)$$

Where Z_n represents the height of the n th data, $\bar{Z}$ is equal to the mean height of Z_n in AFM topography, and N is the number of data.
From our analysis, we observed a regular roughness and uniform grain sizes which varied from 30 nm to 34 nm for the as-deposited TiO_2 films and after annealing at 450°C for 1 hr, respectively. These values are in good agreement with the mean crystallite size determined as a function of deposition temperature in TiO_2 films, in other studies [12], [13].

In our work, the RMS surface roughness is determined from the area of 1,5 µm × 1,5 µm for all samples.

As it can be seen in figure 2, the bare silicon is relatively smooth and its characteristic RMS roughness is 2,5 nm. An RMS roughness of 5,1 was estimated for the as-deposited TiO_2 films at 450°C.
After annealing (at 450°C for 1 hr), we observed that the surface roughness increases to R_{rms}= 7,97 nm due to an increase in grain sizes. According to [11], our TiO_2 films exhibit values of RMS roughness similar to those obtained by B.S. Richards.

a) Si substrate R_{rms}= 2,5 nm



b) TiO_2 on Si R_{rms}= 7,97 nm

Figure 2: 2D-AFM images of:
a) Silicon substrate
b) TiO_2 thin films deposited by APCVD at 450°C after annealing at 450°C for 1 hr.

B. Optical studies

B.1. Optical transmittance

Information concerning optical transmittance is important for evaluating the optical performance of the TiO_2 thin films. The optical transmittance spectrum of the TiO_2 films deposited on glass at 450°C and annealed at 450°C for 1 hr is shown in figure 3.
As it can be seen, the TiO_2 films are optically transparent.

At the wavelength 350 nm, the transmittance of the deposited film was found to be 32%. A similar value was obtained by [14] for TiO_2 films using the APCVD technique.

The maximum transmittance obtained in this work for the TiO_2 films was estimated to 90% (at λ= 800 nm) which is in good agreement with the calculated transmittance into the TiO_2 films given by [15] as shown in table 1. The presence of the interference peaks in the transmission spectrum of TiO_2 films was also observed and clearly explained by [5].

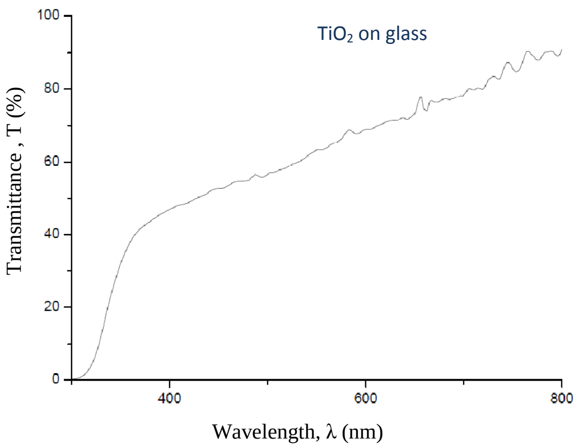


Figure 3. Optical transmittance spectrum of TiO_2 thin film on glass.

TABLE 1: Transmittance results comparison on TiO_2 thin films.

Wavelength λ	Transmittance T Experimental results obtained in this work	Transmittance T Simulation results given by [15]
800 nm	90,2 %	90%

B.2. Ellipsometry

The estimated variation of the refractive index versus wavelength for the deposited TiO_2 thin film on silicon substrate, and the corresponding best fit 2D graph are shown in figures 4 and 5 respectively. As mentioned above, the TiO_2 film thickness was 56,2 nm.

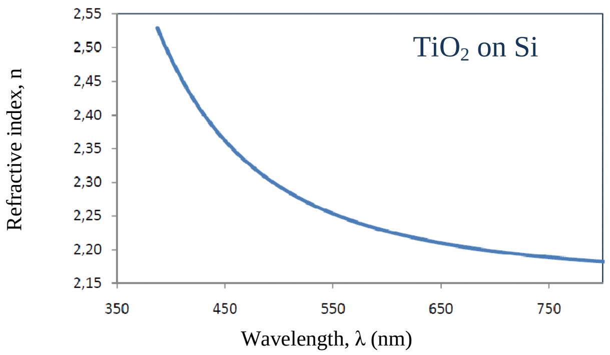


Figure 4. The variation of refractive index n versus the wavelength λ for TiO_2 Thin film deposited on Si at 450°C after annealing at 450°C for 1 hr.

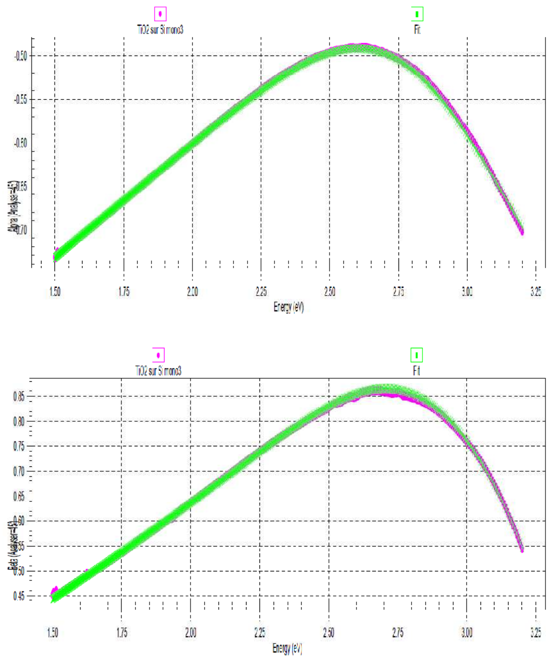


Figure 5. The corresponding best fit 2D graph

In this work, the refractive index of our TiO_2 film was found to be n = 2,25 at the wavelength λ = 550 nm which is in excellent agreement with the literature values for CVD TiO_2 films illustrated (by the dotted horizontal line) in figure 6.

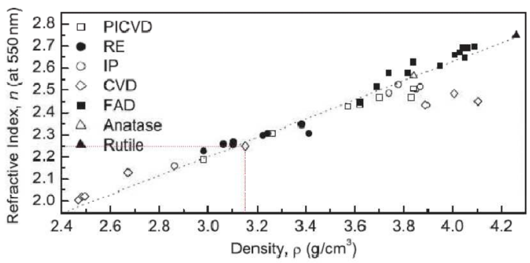


Figure 6. A linear relationship between values of TiO_2 film density and refractive index is observed for many films reported in the literature. (The dotted horizontal line shows the refractive index at 550 nm for the TiO_2 films elaborated by CVD [16]).

A decrease of the refractive index from n = 2,52 to n = 2,18 with increased wavelengths between 390 and 800 nm, was observed (figure 4).

To estimate the TiO_2 film density $\acute{\rho}$ in (g/cm^3), the expression used is given below [16]:

$$\acute{\rho} = \frac{n_f - 0{,}91933}{0{,}42751} \qquad (2)$$

Additionally, the porosity φ (the volume of pores per volume of film) of the TiO_2 film depends on the refractivity of the film layer. It can be estimated by the equation (3) [16], [17], [18]:

$$\varphi = \left(1 - \frac{n_f^2 - 1}{n_d^2 - 1}\right) \times 100\ (\%) \qquad (3)$$

Where n_f is the refractive index of the TiO_2 film, and n_d is the refractive index of pore free anatase TiO_2 which is found in the literature equal to 2,52 at 550 nm [17].

In this study, the density of the deposited TiO_2 film is calculated using equation (2) at 550 nm and is found to be $\acute{\rho}$ = 3,11 g/cm^3.

The porosity of the prepared TiO_2 film which is assumed to be homogenous, is determined using equation (3) and found to be φ = 24 %.

TABLE 2: Ellipsometric results comparison.

Deposition technique	Deposition temperature	Refractive index obtained in this work[a] at 600 nm.	Refractive index given by [16][b] at 600 nm.
APCVD	450°C	2,2	2,19

[a]The TiO_2 thin films are deposited from $TiCl_4$ at 450°C and then annealed at 450°C for 1 hour.

[b]The TiO_2 thin films are deposited from TPT $Ti(OC_3H_7)_4$ at 450°C and annealed at 1000°C for 1 hour.

As shown in table 2, the good agreement reached between our experimental values of refractive index and those obtained by B.S. Richards [16] in spite of the difference in the annealing temperature can be explained in terms of the growth rate of the films, which was faster in the case of TPT than the $TiCl_4$, as it was observed by Philip Evants [12].

C. Electrical properties

As mentioned above, the electrical resistivity of the deposited TiO_2 films was estimated with the Four-point probe, using the relation (5):

$$\rho = \frac{\pi}{Ln2}\left(\frac{\Delta V}{I}\right) e \qquad (4)$$

Or

$$\rho = 4{,}53\left(\frac{\Delta V}{I}\right) e \qquad (5)$$

Where *ΔV* is the measured voltage, *I* the applied current and *e* is the thickness of the TiO_2 film which is equal to 56,2 nm.

The sheet resistance of the layer is then given by:

$$R_{\square} = 4{,}53\ \frac{\Delta V}{I} \qquad (6)$$

In this work, the electrical resistivity of the deposited TiO_2 films at 450°C annealed at 450°C for 1 hr, was found to be $\rho = 1{,}7\times10^{-3}\Omega.cm$, which is in good agreement with the TiO_2 resistivity estimated by Ginley [19].

The sheet resistance of our TiO_2 films was equal to $R_{\square} = 303\ \Omega/\square$.

It is interesting to note that the good conductivity of our TiO_2 films is very compatible with the conductivity requirements of TCO (Transparent Conducting Oxide) for application as ARC in silicon solar cells.

4. Application to antireflection coating

The above results show the possibility to fabricate TiO_2 layers with the optimal optical qualities required for antireflection coating, using the APCVD technique.

TABLE 3: Comparison between the experimental and calculated results of two parameters: refractive index and thickness of TiO_2 layers for application as ARC.

ARC parameters	Experimental results obtained in this work	Calculated results obtained by [10]
Refractive index n at λ = 550 nm.	**2,25**	**2,2**
Thickness d	**56,2 nm**	**56,8 nm**

As shown in table 3, an excellent agreement is reached between our experimental results and calculated results given by Shui-Yang Lien [10] for TiO_2 single-layer antireflection coating (SLARC) on monocrystalline silicon solar cells.

5. Conclusion

In this work, we demonstrated by AFM studies that the TiO_2 thin films produced by APCVD technique from $TiCl_4$ as precursor at 450°C were polycrystalline, homogenous, compact and relatively smooth. The surface roughness of these films was observed to increase after annealing.

From the spectrophotometric measurements, the deposited TiO_2 thin films were optically transparent having an average optical transmittance of about 85-90%.

The ellipsometry analysis shows the good optical properties of our TiO_2 thin films having a refractive index of 2,25 at λ = 550 nm with corresponding thickness of 56,2 nm. These experimental results obtained by APCVD are in excellent agreement with the calculated results of the TiO_2 refractive index and thickness required for a high quality antireflection coating in industrial conditions.

Combining the high quality films deposition, lower cost processing, we believe that the APCVD elaborated TiO_2 antireflection coatings have good promise and potential to meet the goal of large-scale industrial applications.

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