Optica Applicata, Vol. L, No. 4, 2020
DOI: 10.37190/oa200412

The optical parameters of TiO_2 antireflection coating prepared by atomic layer deposition method for photovoltaic application

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Titanium dioxide thin films have been deposited on silicon wafers substrates by an atomic layer deposition (ALD) method. There optical parameters were investigated by spectroscopic ellipsometry and UV/VIS spectroscopy. A material with a refractive index of 2.41 was obtained. Additionally, in a wide spectral range it was possible to reduce the reflection from the silicon surface below 5%. The Raman spectroscopy method was used for structural characterization of anatase TiO_2 thin films. Their uniformity and chemical composition are confirmed by a scanning electron microscope (SEM) energy dispersive spectrometer (EDS).

Keywords: thin film, atomic layer deposition, titanium dioxide.

1. Introduction

Nowadays, the optical elements used with the antireflection coatings become the standard. Antireflective (AR) coatings are a type of coating applied to surfaces of optical elements to reduce reflection. They improve system performance by maximizing the use of light energy. In complex systems, *e.g.* telescopes, the reduction of reflections also improves the contrast and sharpness of the image. In other applications, such as correction lens, coatings increase visual comfort [1–4]. The AR coverage can also reduce the reflex of binocular lenses or optical sights. In photovoltaic, antireflection coatings are used both on solar cells and on the surface of the glass covering the solar module. In both cases, it is crucial to choose the parameters of the reflection reduction layer [5, 6]. The thickness and refractive index are mainly influenced by antireflection properties of the layer. Optical methods allow verification of the calculated optimal thicknesses and refractive indices for a given spectral range. The light beam is reflected from the border by an external medium (*e.g.* air) – a layer and a substrate (*e.g.* glass or silicon) [7, 8]. The thickness of the antireflection coating results from the following relationship assuming very poor absorption: $nd = \lambda/4$, where: n is the real part of the refractive index light in the layer, λ is the wavelength of light from the area of the maximum photosensitivity of the solar cell, and d is the thickness of the layer. The relationship $n_2 = n_1^2/n_0$ is also important, where n_0 is the refractive index of the air, n_1 is the refractive index of the layer and n_2 is the refractive index for the appropriate type of a substrate [9, 10]. The reflectance of a bare silicon wafer surface is greater than 30%, and can be reduced below 5% by using an antireflection coating on its surface. At present, one of the most common antireflection layers used in the crystalline silicon solar cell industry is SiO_2/TiO_2, Si_3N_4 or SiN_x:H [11, 12]. Considering the coatings used also on PV panels, they are often required to protect against weather conditions, have self-cleaning surfaces (catalytic) and to protect against the deposition of water and fats (hydrophobic and oleophobic coatings [13–16]. The choice of a layer deposition method is also important. Within the framework of this article, the application of the atomic layer deposition (ALD) method was proposed. The ALD method is a variation of the CVD method, which is distinguished by the fact that the precursor and reagent are introduced separately into the chamber. They react with each other only on the surface of the substrate. The advantage of ALD is to control the thickness at the nanometer level, and uniformly coat the developed surface [1–4].

2. Material descriptions and research methodology

The TiO_2 thin films have been deposited by an atomic layer deposition (ALD) using an R-200 Standard reactor of Picosun company. It is a system in which the process is heat activated. It is equipped with two liquid, one solid and one gas sources precursors. Titanium chloride ($TiCl_4$) was used as a precursor material, water as a reactant, and nitride as a carrier gas. Schematic of ALD growth mechanism using titanium chloride and water was shown in Fig. 1. Each of the periodically repeated growth cycles in-

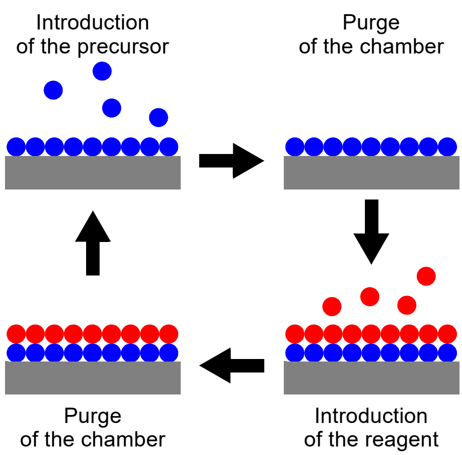

Fig. 1. Schematic of ALD growth mechanism using titanium chloride and water.

T a b l e 1. Technological parameters of the ALD processes.

$TiCl_4$	Carrier gas flow rate (N_2) [sccm]	150
	Loading time of the precursor [s]	0.2
	Flushing time of the chamber [s]	4.0
H_2O	Carrier gas flow rate (N_2) [sccm]	200
	Loading time of the reagent	0.2
	Flushing time of the chamber [s]	5.0
Chamber temperature [°C]		300
Number of cycles		600–1000

cluded a $TiCl_4$ pulse, purge of the chamber, H_2O pulse and another purge of the chamber. The vapours of $TiCl_4$ and H_2O were carried into the reaction zone in the flow of pure (99.999%) nitrogen gas. During the purge times, only the carrier gas was led through the reactor. The process was carried out at the pressure of 5 Pa. The technological parameters of the ALD processes are presented in Table 1. Temperature is the most important technological condition for the ALD method that allows controlling the layer growth mechanism. The effect of temperature on the course of layer deposition can be described by introducing the concept of the so-called "temperature window". Incorrect temperature selection can cause a significant slowdown in layer growth and its low stability. The temperature in the chamber must be high enough to prevent condensation of the reagents. If the temperature is too low, the activation energy will not be reached, which may result in incomplete bonds in the monolayer. Based on a series of experiments, a temperature of 300°C was determined. Optimized parameters are such as: carrier gas flow rate, loading time of the precursor and reagent and flushing time of the chamber to achieve uniform growth of the layer on the substrate. The number of cycles was changed to obtain layers with different thickness.

Optical constants were tested using ellipsometry. In this method, the linearly polarized light reflects from the sample surface, becomes elliptically polarized, and travels through a continuously rotating polarizer (referred to as the analyzer). The amount of light allowed to pass will depend on the polarizer orientation relative to the electric field "ellipse" coming from the sample. The detector converts light to electronic signal to determine the reflected polarization. This piece of information is compared to the known input polarization to determine the polarization change caused by the sample reflection. This is the ellipsometry measurement of Ψ (the ratio of the amplitude diminutions) and Δ (the phase difference induced by the reflection). After measuring them, the dispersions of the refractive index were determined with J.A. Woolam Software basing on a constructed model. Thin films of TiO_2 deposited onto silicon wafers were fitted with a simple sandwich model $Si/SiO_2/TiO_2/air$. In the case of TiO_2 thin films, the Cauchy model was used. This model is most often used for transparent oxide materials. The model includes layers of native SiO_2 having a thickness of 2.51 nm found on the surface of silicon. The thickness of the oxide layer was determined based on the analysis of the uncovered silicon substrates.

The TiO_2 thin films have been examined by using an evolution 220 UV-VIS spectrometer Thermo scientific company equipped with Xenon flash lamp. Measurements were made in the 300–1000 nm wavelength range. The ISA-220 Integrating Sphere Accessory was used to for measuring total reflection.

Further testing of structure of deposited thin films is made by using an inVia Reflex Raman spectrometer equipped with an Ar ion laser with a 514.5 nm length. Spectral range is 150–3200 cm^{-1}. Using confocal microscope images, the data point on the sample was presented.

Observations of topography and surface morphology of the ZnO thin films were carried out in a scanning electron microscope Supra-35 from Zeiss.

3. Results and discussion

The best match between the model and the experiment was achieved through regression (Fig. 2). An estimator, like the mean squared error (MSE), is used to quantify the difference between curves. The minimum MSE = 1.52 was reached. By fitting the experimental data from our spectroscopic ellipsometry measurements with a single Gauss oscillator, we obtained thickness values in the range of 41–62 nm with a roughness of 1.89–2.66 nm for all the TiO_2 samples (Table 2). The n and k spectra quantitatively are in a very good agreement with literature data for polycrystalline anatase (Fig. 3) [14].

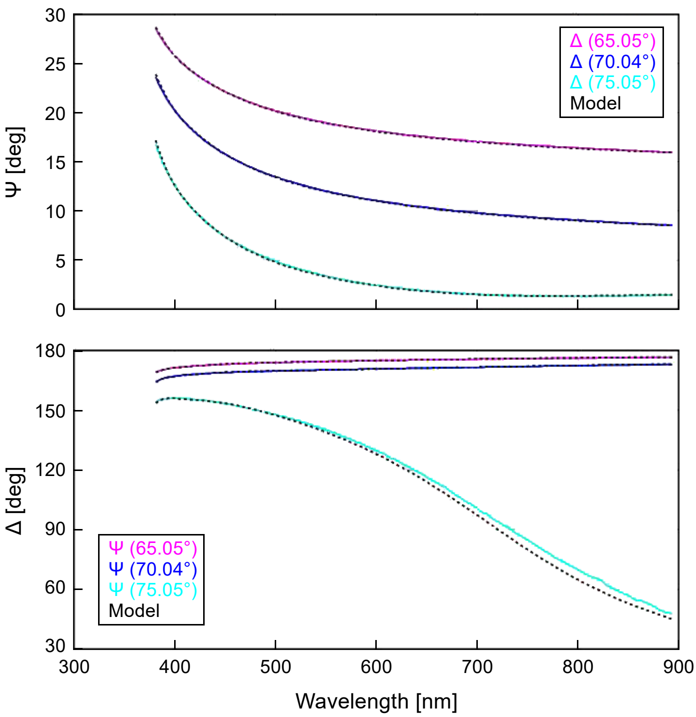

Fig. 2. Experimental and model generated data fits.

T a b l e 2. Ellipsometric measurements of thickness and refractive index for deposited TiO_2 films.

Sample	MSE	Roughness [nm]	Thickness [nm]	*n* (for 632.8 nm)
600 cycles	1.449	1.89	41.60	2.415
800 cycles	1.426	2.34	57.42	2.417
1000 cycles	1.538	2.66	61.82	2.413

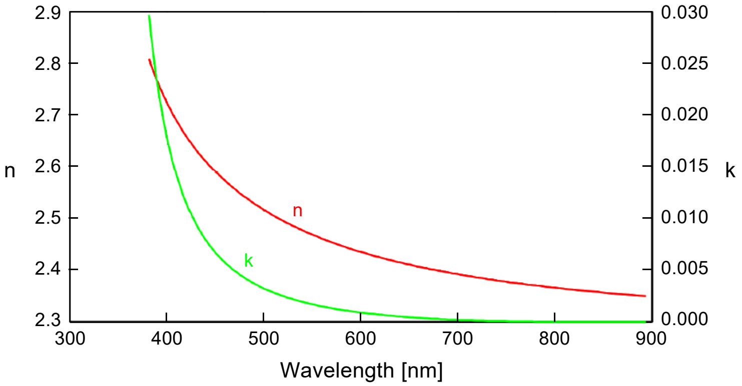

Fig. 3. The refractive index *n* and the extinction coefficient *k* of the studied TiO_2 thin films.

For a wavelength of 632.8, the refractive index is around 2.41 regardless of recorded thicknesses (Table 2). The refractive index varies between different TiO_2 thin films just from the third decimal on.

The reflections of different cycles of TiO_2 are shown in Fig. 4. The best results were obtained for silicon with 800 (240–410 nm) and 1000 (320–520 nm) cycles of TiO_2. The light reflection was minimized below 5%. The structural studies were implemented by using a Raman spectrometer and the recorded spectrum is shown in Fig. 5. The results were processed by using the WiRE 3.1 program determining the structure of the deposited thin films as an anatase, which confirmed our assumptions based on

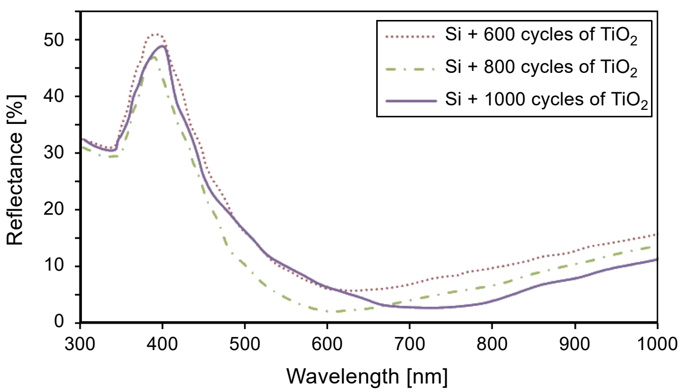

Fig. 4. The spectrum of reflection for different numbers of TiO_2 ALD cycles.

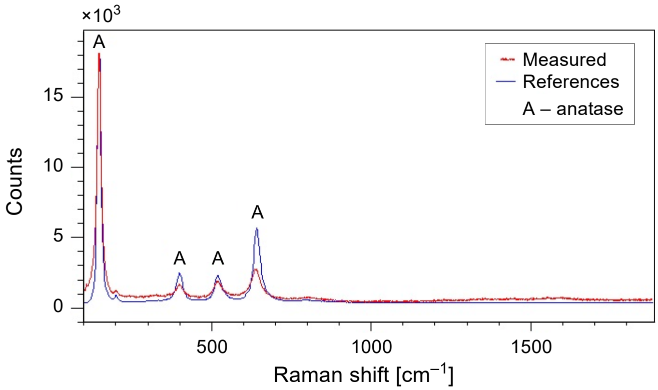

Fig. 5. Raman spectra of ALD titanium oxide thin film.

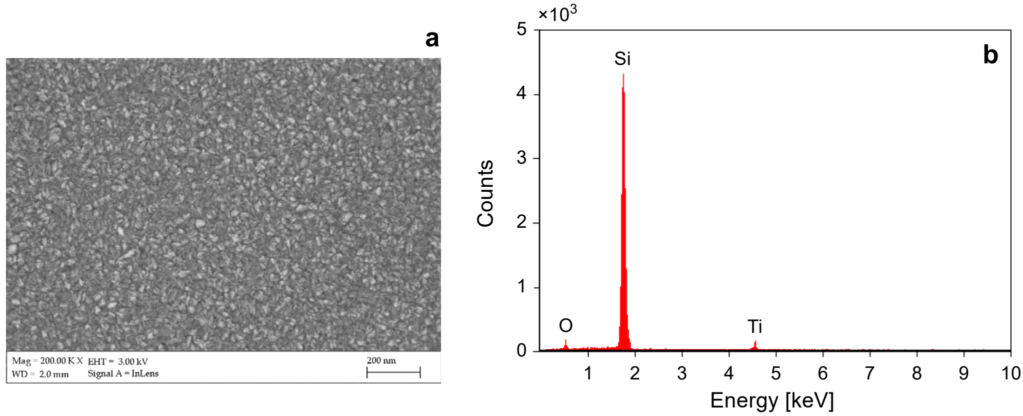

Fig. 6. SEM images of the surface topography of TiO_2 thin film deposited on silicon substrate at 300°C after 1000 cycles (**a**) and EDS spectrum (**b**).

the measured refractive index with spectroscopic ellipsometry. All the as-deposited thin films in the ALD system showed the anatase phase. The morphology of TiO_2 layers deposited by ALD is homogeneous and uniform (Fig. 6**a**). The surface does not show any discontinuities, cracks, pores and defects. In Figure 6**b** the EDS spectra of the thin film of ALD TiO_2 are shown. There are peaks observed at about 0.5 and 4.5 keV in these EDS spectra, which are assigned to oxygen and titanium, respectively. Such an analysis can be additionally confirmed by the presence of titanium dioxide.

4. Conclusions

The TiO_2 thin films in pure anatase form were obtained using the atomic layer deposition technique. Raman spectroscopy has proven to be a useful technique for the rapid identification of the phases present in the samples. From spectroscopic ellipsometry measurements were obtained thickness values of ALD TiO_2 thin film in the range of 41–62 nm with constant refractive index equal to 2.41 (for 632.8 nm). Additionally, in a wide spectral range, it was possible to reduce the reflection from the silicon surface below 5%. The obtained results indicate that it is possible to obtain a titanium oxide layer by the ALD method with the desired refractive index (which is related to the crystal structure) of the appropriate thickness, thus minimizing the reflection of light from the silicon surface. Basing on obtained results, we can conclude that TiO_2 thin films obtained with the ALD deposition method have good antireflection properties and could be applied in photovoltaic industry as an antireflection coating of silicon solar cells.

Acknowledgements – Publication supported under the own scholarship fund of the Silesian University of Technology in the field of scientific research and development works, Year 2020.

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Received February 17, 2020
in revised form June 1, 2020