Sol-gel Synthesis and Optical Characterisation of TiO$_2$ Thin Films for Photovoltaic Application

N. H. Arabi, Aicha Iratni, Talaighil Razika, Bruno Capoen, Mohamed Bouazaoui

Abstract—TiO$_2$ thin films have been prepared by the sol-gel dip-coating technique in order to elaborate antireflective thin films for monocrystalline silicon (mono-Si). The titanium isopropoxyde was chosen as a precursor with hydrochloric acid as a catalyser for preparing a stable solution. The optical properties have been tailored with varying the solution concentration, the withdrawn speed, and the heat-treatment. We showed that using a TiO$_2$ single layer with 64.5 nm in thickness, heat-treated at 450°C or 300°C reduces the mono-Si reflection at a level lower than 3% over the broadband spectral domains [669-834] nm and [786-1006] nm respectively. Those latter performances are similar to the ones obtained with double layers of low and high refractive index glasses respectively.

Keywords—Dip coating, mono-Si, titanium oxide, thin film.

I. INTRODUCTION

IN order to enhance the solar cell efficiency by decreasing the reflectivity, the antireflection coatings (ARC) are necessary to the solar cells manufacturing. According to the Fresnel equations [1], the conditions to achieve a minimal reflection at a normal incidence are:

- Thin film refractive index must be equal to the geometric mean of the refractive indices of the environment medium and of the silicon substrate ($n_{ARC} = \sqrt{n_s n_0}$)

- Optical thickness must be equal to a quarter of the wavelength ($n_{ARC} d_{ARC} = \lambda / 4$).

In the case of the solar spectrum standard AM1.5 conditions (solar zenith angle 48.19°), the refractive index and the thickness of the antireflective layer are selected so as to minimize the reflection light at a wavelength 600 nm. This one is indeed close to the maximum emission of the spectrum standard and authorizes a significant penetration of the photons within silicon. Thus, by considering the air as the environment medium, the optimal values of the antireflective thin film refractive index and thickness are equal to n$_{ARC}$ = 2 and d$_{ARC}$ = 75 nm.

Titanium dioxide (TiO$_2$) shows suitable characteristics to carry out antireflection thin films for photovoltaic applications. Its optical properties are adjustable according to

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the deposition conditions and to the annealing treatment: its refraction index varies between 1.8 and 2.6 at 600 nm [2], [3]. Its absorption coefficient is low in the visible and the infrared regions.

TiO$_2$ thin films can be deposited by several methods, such as chemical vapour deposition [4], pulsed laser deposition [5], and the sol-gel technique [6], [7]. Nevertheless, the interest in sol-gel technology to produce ARC has increased for these last years, because the process is simple, fast and low-cost. The sol-gel depositions are performed at ambient temperature, under atmospheric pressure, and allow covering large surface areas. The obtained coating is of great purity and good homogeneity. In addition, the sol-gel process allows an accurate control of thin film porosity and thickness.

In this paper, we present the experimental optimization of a sol-gel TiO$_2$ ARC for mono-Si. The film depositions have been carried out by dip-coating on the following substrates: glass, mono-Si. We have focussed our attention on the physicochemical parameters that influence the optical properties of the TiO$_2$ thin film. This has made it possible to optimise the thin film preparation conditions, giving the adequate refractive index and thickness, thus resulting in a minimal reflectivity in the visible spectra for mono-Si.

II. EXPERIENCE

In this study the TiO$_2$ thin film was prepared by sol-gel process. The precursor was the titanium isopropoxyde (Ti (^{i}OPr)$_4$) (Aldrich 97%), which has a high reactivity with water. Indeed, it has been noted that the direct addition of deionised water (rank III) alone to this precursor leads to a strong precipitation. By introducing hydrochloric acid (Aldrich 37%) into the titanium isopropoxyde/water mixture under stirring, the appearance of the precipitate could be avoided, making it possible to obtain perfectly transparent sols, stable for several months. The ethanol (Aldrich 98%) was chosen as a solvent due to its capacities to wet silicon substrates, and due to its great volatility, thus authorizing its fast elimination during the drying phase.

After several attempts, the adopted molar proportions [Ti]/ [H$_2$O]/ [HCl] were 1/0.8/0.5. Once mixing, the titanium oxide sol was aged for one day at room temperature and under atmospheric pressure. The viscosity and pH of the prepared TiO$_2$ sol were 2.4 cP and 2 respectively. The particle sizes in the sol were smaller than 10 nm, as observed by the dynamic light scattering technique. Before sol deposition, polished mono-crystalline silicon wafers with resistivity 0.01 Ω cm and with thickness 300 μm, were cleaned with ethanol in an

ultrasounds bath for a quarter hour, and then they were dried under N_2 gas.

TiO$_2$ thin film deposition was carried out by the dip-coating process. It consisted in immersing the substrate in the sol, then withdrawing it at a constant speed, which has been varied from 0.02 cm/s to 0.2 cm/s. Subsequently, the coated sample was heated at 400°C for 600 s, to remove solvent and residual organics. In addition, a second longer heat-treatment was performed between 200°C and 1000°C for one hour in air to increase the film density.

The thin film transmission spectra were obtained at ambient temperature in the wavelength range 300-1200 nm, using a spectrophotometer Perkin-Elmer Lambda 19. The film thickness and refractive index were measured at room temperature by using a phase-modulated spectroscopic ellipsometer (UVISEL - Jobin Yvon) at an incident angle of 70° in the photon energy range 0.75-4.55 eV. Finally, the total reflectivity was measured using a Hitachi UV-VIS-NIR 4001 spectrophotometer equipped with an integrating sphere, in the 350–1200 nm wavelength range at room temperature.
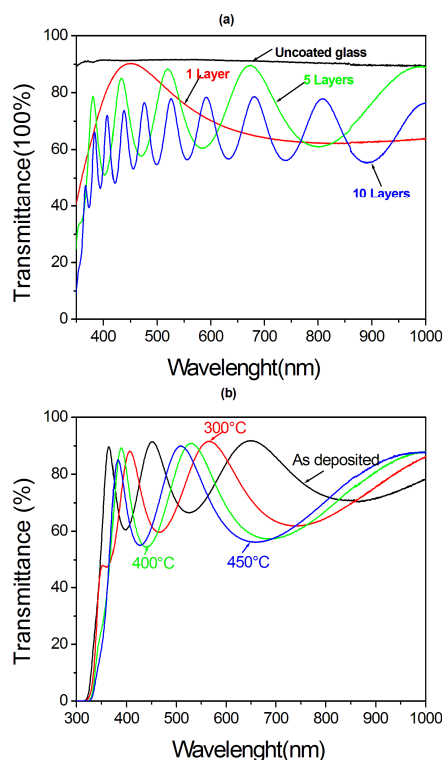

Fig. 1 Transmittance spectra of TiO$_2$ thin film in function of (a) layers number, (b) annealing temperature

III. RESULTS AND DISCUSSION

A. Transmittance Spectra

Fig. 1 exhibits the transmission spectra of a TiO$_2$/glass substrate/TiO$_2$ system at a normal incidence for different numbers of dipping and different annealing temperatures, in the wavelength range 350-1200 nm. The transmittance of the uncoated glass substrate remains almost constant and equal to 91% over the entire spectrum region. By using a 0.6 M solution to cover the glass with one TiO$_2$ single layer on each side, at a withdrawn speed of 1 mm/s, the transmittance drops to less than 90%, depending on the wavelength (Fig. 1 (a)). The enhanced reflection phenomenon is explained by the large difference in the refractive index between TiO$_2$ layers and the glass substrate. However, for one TiO$_2$ layer heat-treated at 400°C, the interference yields a maximal transmittance at 450 nm.

In addition, the transmittance has an abrupt decrease for wavelengths lower than 350 nm, due to the TiO$_2$ absorption (band gap of 3.2 eV). When increasing the number of layers, transmittance globally decreases and multiple interference extrema appear in the wavelength range 400-1200 nm. The number of maxima and minima increases, but the amplitude of the interference pattern decreases. On the other hand, the amplitude of interference spectra increases with increasing annealing temperature and their extrema shift to lower wavelengths (see Fig. 1 (b)). Such variations are obviously caused by changes in film thickness and refractive index under annealing. This system of N layers of high refractive index deposited on a glass substrate represents a reflective filter.

B. Spectroscopic Ellipsometry Measurements

Ellipsometry is an accurate method in order to determine the film thickness and its complex refractive index *via* a simulation of the material by means of a structural model. This model takes into account different parameters: the material density, thickness of the film, dispersion law of the material, etc. The measured amplitude ratio Ψ (λ) and the phase difference Δ (λ) between perpendicular and parallel reflected polarizations have to be fitted using this theoretical model [8].

In our case, the model consists of a semi-infinite Si substrate, covered by an interfacial layer of SiO$_2$ of assumed thickness 2 nm (this hydrophilic native oxide layer is essential for a homogeneous dip-coating of the aqueous sol onto the Si substrates), and a homogenous dense TiO$_2$ layer. The refractive indices of the Si substrate and of the SiO$_2$ layer have been kept constant. Since the TiO$_2$ layer is a polycrystalline dielectric, it is described by the Tauc–Lorenz dispersion law which is based on the Lorenz oscillator and on the Tauc joint density of states [9].

$$\varepsilon_2(E) = \left[\frac{AE_0C(E - E_g)^2}{(E^2 - E_0^2)^2 + C^2E^2} \cdot \frac{1}{E} \right], E > E_g \quad (1)$$

$$\varepsilon_2(E) = 0, \qquad E \leq E_g \quad (2)$$

where ε_2 is the imaginary part of the film dielectric function, A is its amplitude, E_0 is the peak transition energy; C is a broadening constant and E_g is the band gap. The real part $\varepsilon_1(E)$ of the dielectric function is derived from the expression of $\varepsilon_2(E)$ using a Kramers–Kronig integration [10]. Hence, the fitting parameters are A, C, E_0, E_g, ε^∞ and the film thickness (d_f). The parameter ε^∞ appears in the expression of the real part and represents the high frequency dielectric constant.

The experimental spectra of the ellipsometric variables $I_s = \sin(2\psi)\sin(2\Delta)$ and $I_c = \sin(2\psi)\cos(2\Delta)$, acquired at the incident angle 70° are shown in Fig. 2 for the TiO_2 single layer after a 600 s heat-treatment at 400°C (solution concentration 0.8 M and withdrawn speed 0.1 cm/s). These are in good agreement with the fitting results, confirming the validity of the optical constants chosen in the model. We have also tried to use other dispersion relations proposed by Fourouhi-Bloomer for amorphous materials [11]. However, the experimental data are found to be better fitted with the Tauc- Lorenz dispersion model.
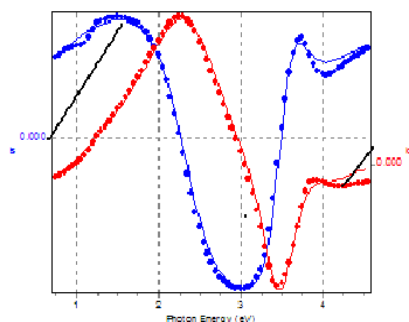

Fig. 2 Experimental (symbols) and theoretical (lines) spectra of the ellipsometric variables I_s and I_c for the TiO_2 single layer heat-treated at 400°C for 600 s.

Fig. 3 shows the ellipsometry fitting result of the optical constants of the 0.8 M TiO_2 film deposited on monocystalline Si substrate. These results are given within the spectral region 300-1200 nm, as a function of the heat-treatment. The measured refractive index of the consolidated film (heat-treated at 400°C for 600 s) evolves between 3.1 at 300 nm and 2.1 at 1200 nm (Fig. 3 (a)). It verifies the Cauchy law [12] in the wavelength range [400-1200] nm. On the other hand, the extinction coefficient is very close to zero for wavelengths down to λ = 350 nm (Fig. 3 (b)), confirming the transparency of TiO_2 in the visible spectral region.

Even when increasing the annealing temperature up to 600°C for one hour, a small decrease of the refractive index is observed. This result means that such heat-treatments do not change significantly the film porosity. On the contrary, the re-arrangement of a disordered medium into a crystallized system sometimes leaves voids between the crystallites. Further increase in the annealing temperature over 600°C causes a real decrease in the porosity and a considerable structural transformation to crystalline anatase, which leads to an increase in the refractive index.

In our dip-coated TiO_2 layer obtained from an acid catalyzed sol, the important transformation from amorphous phase to crystalline anatase phase is observed only for heat-treatment at temperatures above 600°C, as indicated by the XRD study in our previously work [13]. Consequently, the refractive index value is strongly connected to the layer cristallinity and to the porosity of the material. In the low wavelength region, the extinction coefficient (k) does not change when increasing the temperature up to 600°C and then

slightly increases for annealing temperatures higher than 600°C, as indicated in Fig. 3 (b). This increase in the extinction coefficient is due to the decrease in the band gap energy when the structure is transformed from amorphous to anatase [14], [15]. Also, we note that the extinction coefficient does not change in the visible region within the investigated temperature range.
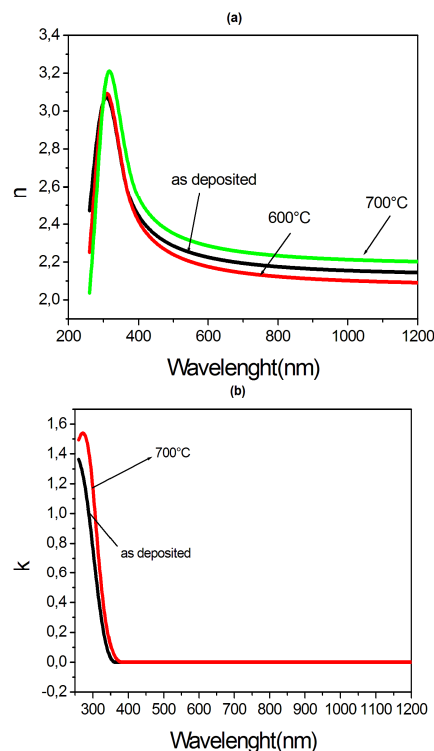

Fig. 3 Spectra of (a) the refractive index and (b).the extinction coefficient of TiO_2 single layer as deposited and after annealing: Ti concentration is 0. 8 M and the withdrawn speed is 0.1cm/s

Ellipsometry also gives information about film thickness. In Fig. 4 are reported the thickness values of the TiO_2 single layer for different withdrawn speeds,, and different heat-treatment temperatures. These measurements are in good agreement with those measured by SEM technique. As expected, the thickness continuously increases from 62.5 nm to 94.5 nm when increasing the withdrawn speed from 0.06 cm/s to 0.14 cm/s (see Fig. 4 (a)), although it does not follow the Landau-Levich [16] behavior $h \propto v^{2/3}$.

At last, Fig. 4 (b) shows the TiO_2 single layer thickness decreasing with increasing the temperature of one hour heat-treatment from 400°C to 700°C. This shrinkage is associated with the film densification.

C. Antireflective Properties for Photovoltaic Applications

In this section our goal is the elaboration of an antireflection TiO_2 thin film for mono-crystalline silicon, whose the thickness is a quarter of wave and the index is close to 2 (Minimal reflection conditions). The experimental study of refraction index and thickness according to the solution

concentration, the withdrawn speed, and the annealing temperature, allow us to find the appropriate deposition conditions, which will make it possible to obtain the anti-reflection TiO$_2$ thin film.

400°C for 600 s to a second heat-treatment at 300°C and then at 450°C for a half hour.
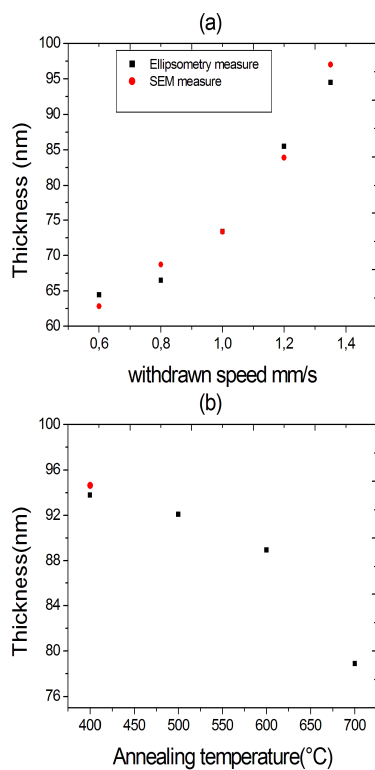

Fig. 4 Thickness versus (a) withdrawn speed (b) annealing temperature (the red square represents the layer thickness as deposited)

By using a concentration solution of 0.8 M and a withdrawn speed of 0.6 mm/s, with temperature annealing is 400°C for 600 s, the thickness and the refractive index of the TiO$_2$ single layer deposited on polished mono-Si of type (100) are respectively 64.5 nm, and 2.22 at 600 nm. These optical parameters theoretically check the minimal reflection conditions at 600 nm. What was also proved in experience, by measuring the silicon reflectance (R) before and after TiO$_2$ layer deposition as shown in Fig. 5.

It is observed that before deposition silicon wafer has a reflectance of more than 37% in the majority of the solar spectral range. When the TiO$_2$ single layer with 66.50 nm in thickness is deposited, the reflectance is minimized. By increasing the TiO$_2$ layer thickness when the withdrawn speed is increased, the reflectance minimum shifts toward longer wavelengths, as shown in Fig. 5 (a). However, a slight difference (smaller than 0.3%) exists in the minimal values of reflectance between a thicker and a thinner layer because of the small difference between their refractive indices.

In order to get a broader low reflectance effect, we submitted the as-deposited TiO$_2$ single layer prepared from 0,8M and withdrawn with 0.135 mm/s and heat treated at
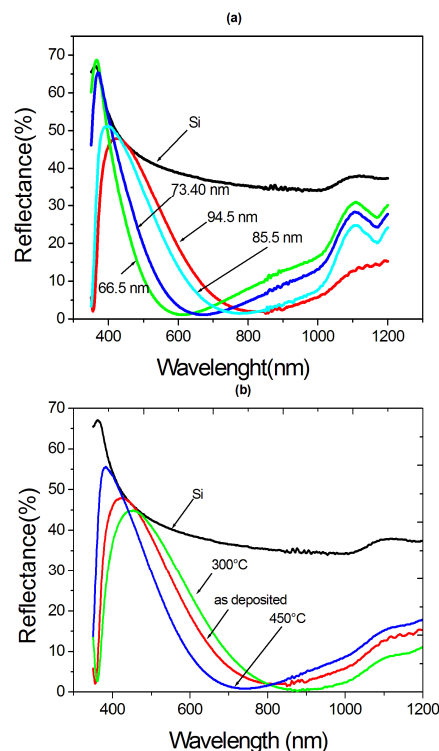

Fig. 5 Reflectance spectra of polished Si (100) wafer with and without TiO$_2$ single layer: (a) for different thicknesses, and (b) for different annealing temperature

As illustrated in Fig. 5 (b), the reflectance minimum dropped from 1.5% to 0.2% at 300°C and rose again to 0.9% at 450°C. Meanwhile, the wavelength of this minimum shifts from 820 nm in the as-deposited layer to 876 nm at 300°C and then to 729 nm at 450°C. In addition, the wavelength range where the reflectance is lower than 5% is 638-900 nm at 450°C, and between 747-1048 nm at 300°C, as compared to 720-970 nm for the as-deposited film.

This result indicates that the heat-treated layers are characterised by a broader low reflectance domain. Comparing our results with those obtained by other research groups on polished silicon [17]-[20], we find that using a TiO$_2$ single layer heat-treated at 450°C or 300°C, it is possible to get similar characteristics as double layers with low and high refractive indices.

IV. CONCLUSION

In this work sol- gel TiO$_2$ thin films have been prepared and the effect of annealing temperature, also the withdrawn speed on their optical properties were examined in order to optimise the optimal coating parameters which allow the best antireflective properties for mono-crystalline. The UV-Vis transmission spectra show that TiO$_2$ thin films are transparent in the visible range and opaque in the UV region, irrespective of the heat treatment temperature and the number of dipping.

The fitting results according to the ellipsometric spectroscopy indicate that the refractive index and extinction coefficient are noticeably increased with an increase of the heat temperature above 600°C due to densification at higher temperature. The film thickness varied linearly with concentration solution and withdrawn speed, and it decrease with increasing the heat treatment temperature.

The study of antireflective properties of polished mono-crystalline silicon covered with 0,8M TiO_2 single layer with 64.5 nm in thickness, heat-treated at 450°C or 300°C, reveals that this layer can reduces the silicon reflection at a level lower than 3% over a broadband spectral domain [669-834] nm and [786-1006] nm respectively, which are the similar characteristics as double layers with low and high refractive indices. And when increasing the layer thickness the minimum reflection shift toward longer wavelength.

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