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TITANIUM DIOXIDE AS ANTI-REFLECTIVE COATING FOR CRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT: We investigate the optimum thickness combination of an anti-reflection titanium dioxide film and a surface passivation silicon dioxide layer. Titanium dioxide is deposited in an Atmospheric Pressure Chemical Vapour Deposition at 260°C and silicon dioxide is grown by a dry oxidation on a mono-crystalline silicon substrate. Measurements of unencapsulated samples show optimum results of around 10.5 % weighted reflectance (corresponding to the AM1.5G spectrum) for polished and 3.5 % for textured samples. When encapsulated, reflectance increases to 11 % for polished respectively 5.5 % for textured samples. These optima occur for titanium dioxide thicknesses between 60 nm and 85 nm, and silicon dioxide thicknesses between 0 nm and 15 nm. Sufficient surface passivation (emitter saturation current density ≤ 50 fA/cm^2) is achieved for silicon dioxide thicknesses greater than 10 nm for <100> and 20 nm for <111> oriented surfaces. Relying on a simple solar cell model, the optimum thickness combinations (silicon dioxide, titanium dioxide), regarding cell efficiency, are (15 nm, 50 nm) for <100> and (20 nm, 50 nm) for <111> oriented surfaces.
Based on the experimental results a model has been developed, that allows to reliably predict reflectance for further experiments. For 15 nm silicon dioxide, the calculated optimum titanium dioxide thickness shifts to 55-60 nm.
Keywords: TiO_2, Antireflection Coating, c-Si

1 INTRODUCTION

If photovoltaics, the direct conversion of sunlight into electricity via solar cells, is to compete with fossil energy sources, every component of a solar cell has to be optimised to contribute to a higher cell efficiency and has to be cheap at the same time.

An important part of a solar cell is its surface coating; it has to provide both anti-reflective characteristics and surface passivation. For multi-crystalline silicon solar cells, Plasma Enhanced Chemical Vapour Deposition (PECVD) silicon nitride is superior to Atmospheric Pressure Chemical Vapour Deposition (APCVD) TiO_2, because the included hydrogen saturates not only dangling bonds at the surface but also grain boundaries in the bulk. For high efficiency single-crystalline silicon solar cells however, the advantages of APCVD TiO_2 emerge; these are its excellent optical properties (refractive index $n \approx 2.1$, extinction coefficient $k \leq 0.01$ over a large spectral range) and its low costs (estimated by *McIntosh* [1] at approximately one third that of PECVD SiN_x).

In the first part of this work, the competitiveness of APCVD TiO_2 with an additional passivation layer (thermally grown SiO_2) is experimentally evaluated. For this purpose several samples are prepared. Their parameters reflectance, emitter saturation current density and their optical constants are measured.

Based on these experimental results a model is developed that reliably predicts reflectance for further experiments.

2 SAMPLES

2.1 APCVD

The machine for the TiO_2 depositions is a *SierraTherm 5K6 APCVD*. Its essential setup is a twelve feet long belt furnace with a CVD injector head in the middle. The wafers are placed on the belt and run continuously through the whole processing. Hence the furnace is easily integrated into an in-line fabrication process.

During the deposition process in the reaction chamber, the titanium source TPT (tetraisopropyl titanate) and its reaction partner H_2O are separated by a N_2 flow until they reach the surface of the sample; there the TPT is hydrolysed leaving TiO_2 behind.

All depositions take place at 260°C because previous research at *CSES* has indicated suitable optical constants for this temperature.

2.2 Sample Assembly

Figure 1 shows the assembly of the prepared samples. In figure 1 a) the unencapsulated samples for the reflectance measurements are depicted; figure 1 b) shows them encapsulated with a low-iron glass. They are passivated from both sides via a dry oxidation and at the top surface the anti-reflective TiO_2 is deposited. The samples for the measurements of the surface passivation quality have the assembly of figure 1 c). Additionally they have the TiO_2 layer also deposited on the backside to ensure a symmetric behaviour and a light emitter (sheet resistance $R_{\square} \approx 250\ \Omega/\square$) diffused under the top passivation layer. Some reflectance samples are also random pyramid textured with a TMAH solution.

2.3 Choice of the layer thickness combinations

The choices of the double layer thickness combinations for the measurements are made relying on a reflectance model based on the matrix method, that is discussed for example by *Heavens* [2]. Assumptions are: $n_{TiO2} = 2.1$, $n_{SiO2} = 1.46$, $k_{TiO2} = k_{SiO2} = 0$. For silicon, standard values are chosen. Additionally the substrate is considered to be "infinitely thick", that is reflection at the back surface is neglected. Figure 2 depicts the results of

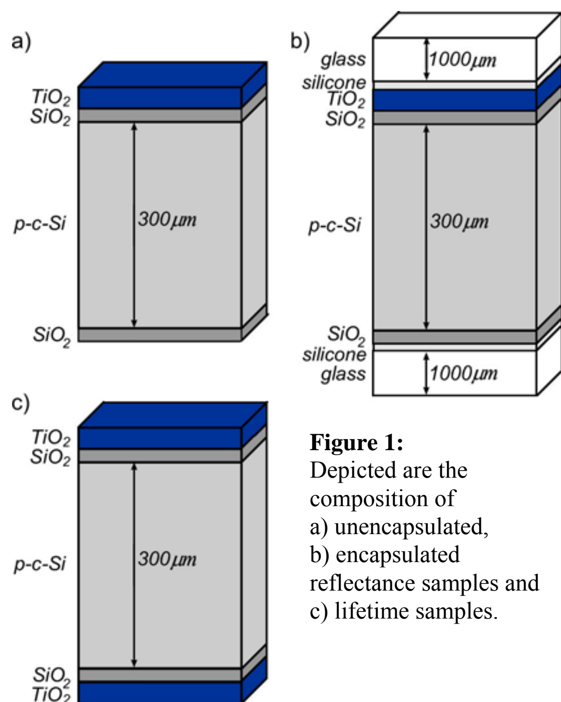

Figure 1: Depicted are the composition of a) unencapsulated, b) encapsulated reflectance samples and c) lifetime samples.

the calculations for the reflectance samples. The contours show the weighted reflectance (AM1.5G) dependent on the layer thicknesses. Upon these contours, the target thicknesses are chosen. The dots represent the reflectance and the crosses the lifetime samples. Additionally the surface configuration of the reflectance samples is given.

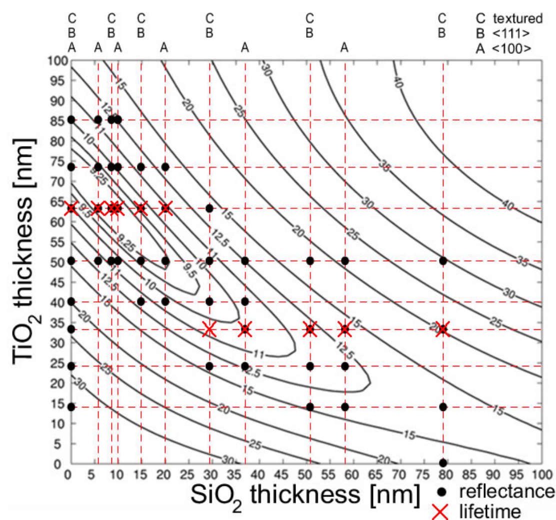

Figure 2: The contours show the results of the weighted (AM1.5G) reflectance calculations. Upon these, the layer thickness combinations for the reflectance and lifetime samples are chosen.

3 EXPERIMENTAL RESULTS

3.1 Optical constants of the TiO_2 film

The optical constants of the TiO_2 film are determined via ellipsometry. The used ellipsometer is a J.A. Woolum variable angle spectroscopic ellipsometer (WVASE 32), which is a rotating analyser ellipsometer. The measurements are made on the reflectance samples without SiO_2 to eliminate unnecessary parameters. Figure 3 shows the results after applying a Cauchy model on the experimental data for the optical constants.

The values for the thinnest films are not trustworthy, which may be caused by the growing importance of surface roughness with decreasing thickness. Roughness has been neglected in the modelling. The values seem to converge for thicker films for both refractive index n and extinction coefficient k. For the reflectance model, introduced later, the values for 50 nm TiO_2 are chosen. The coincidence of the measured and calculated reflectance curves with the values for 50 nm TiO_2 indicate, that these values are trustworthy.

The layer dependence, that is indicated by these measurements, is yet to be proven by further experiments.

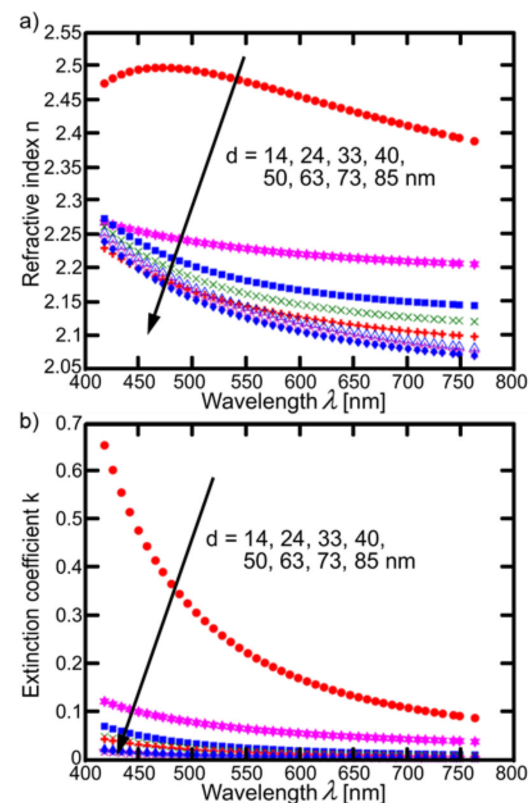

Figure 3: Results of the optical constant measurements. Both refractive index n, figure 3 a), and extinction coefficient k, figure 3 b), seem to saturate for thicker TiO_2 films. The values for the thinnest film are not trustworthy.

3.2 Reflectance

The reflectance measurements are made with a *VARIAN Cary 5000 spectrophotometer* with its *Internal Diffuse Reflectance Accessory*; this is an integrating sphere that measures reflectance at discrete wavelengths. The reflectance curves are taken for the wavelength range from 300 - 1100 nm, which is relevant for the weighted reflectance. These curves are then weighted with the AM1.5G spectrum.

The minimum weighted reflectance for each SiO_2 thickness is depicted in figure 4. The general trend is that reflectance increases with increasing SiO_2 thickness.

For thicker SiO_2 layers, the minimum weighted

reflectance shifts to smaller TiO_2 thicknesses, which is explainable by interference effects. The range of the absolute reflectance minima with their corresponding layer thickness combinations is shown in table I.

As expected by the calculations, an as thin as possible SiO_2 layer is preferable regarding reflectance.

Table I: Absolute minima of measured weighted reflectance with the corresponding layer thickness ranges.

sample	R_w [%]	d_{TiO2} [nm]	d_{SiO2} [nm]
unenc. polished	10.5-11	65-75	0-10
unenc. textured	3.5	75-85	0-15
enc. polished	11	50-75	5-8
enc. textured	5.5	75-85	0-8

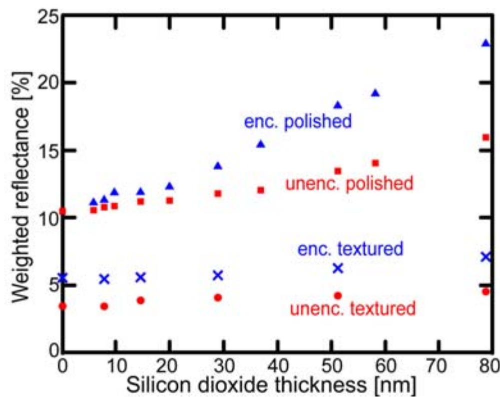

Figure 4: Minimum measured weighted reflectance at each silicon dioxide thickness for all kinds of prepared reflectance samples.

3.3 Lifetime

To determine recombination lifetime and afterwards derive emitter saturation current density, J_{oe}, the generalised model, introduced by *Nagel et al.* [3], with the quasi-steady-state photoconductance method (QSSPC) is applied. The excess carrier density is determined with the setup developed by *Sinton and Cuevas* [4].

The samples are measured, forming gas annealed at 400°C for 30 min and measured again.

The calculations of J_{oe} are made at an excess carrier density of $\Delta n = 10^{15}$ cm^{-3}. Figure 5 shows the results of the measurements after annealing. For every SiO_2 thickness two samples are prepared. Because previous research at *CSES* has shown no evidence of a dependence on the TiO_2 thickness, only the SiO_2 thickness is regarded.

The anneal reduces J_{oe} by approximately one order of magnitude. The results of the measurements are, that J_{oe} reduces with increasing SiO_2 thickness and <100> oriented surfaces are easier to passivate than <111> oriented ones. For thin SiO_2 thicknesses, J_{oe} reduces drastically with growing thickness, whereas the values seem to converge for thicknesses greater than about 10 nm for <100> and 20 nm for <111> oriented samples.

Hence, regarding surface passivation, an as thick as possible SiO_2 layer is preferable.

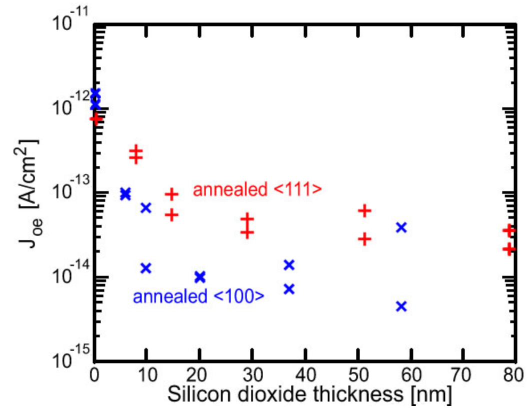

Figure 5: Measured J_{oe} after a 30 min forming gas anneal. Sufficient surface passivation is achieved for SiO_2 thicknesses greater than 10 nm for <100> and 20 nm for <111> oriented samples.

4 DISCUSSION

Because optimising reflectance and surface passivation conflict, a trade-off has to be made. This is done via a model of the efficiency of a solar cell. Efficiency is expressed dependent on weighted reflectance R_w and J_{oe} via the parameters short circuit current density $J_{sc} = J_{sco}(1 - R_w)$ and dark current saturation density $J_o = J_{o,cell} + J_{oe}$. Assumptions are ideality factor $n_{id} = 1$, shunt $R_{\parallel} \rightarrow \infty$, temperature $T = 300$ K, an optimum short circuit current density value $J_{sco} = 40$ mA/cm^2, series resistance $R_s = 0.7$ Ωcm^2 and input power $P_{in} = 100$ mW/cm^2.

Figure 6 shows the results of the calculations for each minimal reflectance at a certain SiO_2 thickness for both measured J_{oe} and their average. A good industrial cell with $J_{o,cell} = 10^{-13}$ A/cm^2 is assumed. The efficiency maxima are at $d_{SiO2} \approx 15$ nm and therefore $d_{TiO2} \approx 50$ nm for <100> and $d_{SiO2} \approx 20$ nm, $d_{TiO2} \approx 50$ nm for <111> oriented samples. For worse cells with a higher $J_{o,cell}$, d_{SiO2} shifts to slightly thinner SiO_2 films and for better cells to slightly thicker SiO_2 films.

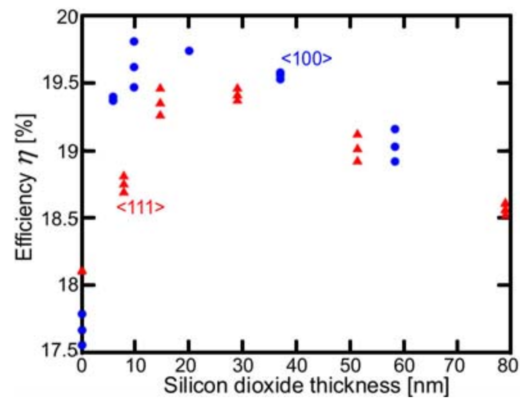

Figure 6: Calculated efficiency for each silicon dioxide thickness resulting from a simple solar cell model for a good industrial cell with $J_{o,cell} = 10^{-13}$ A/cm^2. The optimal thickness combinations are 15 nm SiO_2 / 50 nm TiO_2 for <100> and 20 nm SiO_2 / 50 nm TiO_2 for <111> oriented samples.

5 MODEL

The simplified calculations that led to figure 2 were useful to predict certain trends, that the choices of the layer thicknesses were based on. Nonetheless, the measured weighted reflectance values differ significantly from predicted, and especially the actual reflectance curves show a different shape in a part of the spectrum. That is why a new model is developed.

The first improvement is to incorporate the measured optical constants for the TiO_2 layer. For this purpose the measured values, that are due to restrictions of the ellipsometer in the wavelength range from 417 – 763 nm, have to be extrapolated. As a guideline the findings of *Kamataki et al.* [5] and *Saitoh et al.* [6], who deposited TiO_2 at 300°C, are used. This leads to a better fit in the short wavelength range and a coincidence of the minimum at the point of destructive interference as illustrated in figure 7.

The second improvement is to consider the finite thickness of the substrate. This leads to an increase of reflectance for long wavelengths due to backside reflection. Because of the roughness of the inner backside of the samples, the finiteness is taken care of by an average of many substrate thicknesses.

The fitting is done for no SiO_2 and 50 nm TiO_2. Figure 7 illustrates the curve gained from the original calculations, the measured curve and the curve derived from the new model. For any other arbitrary double layer thickness combination, the fit is satisfying, too. The model is also extended to the encapsulated samples and shows good fits there as well. With the new model, all measured weighted reflectance values lie within one percent from the calculated values, also for the encapsulated samples.

The minimum measured weighted reflectance for 10 nm and 20 nm SiO_2 coincide with the TiO_2 predictions by this model, that is 65 nm respectively 50 nm. For 15 nm SiO_2, the optimal TiO_2 value for a good industrial cell and <100> orientation, is expected at in the range of 55 nm to 60 nm.

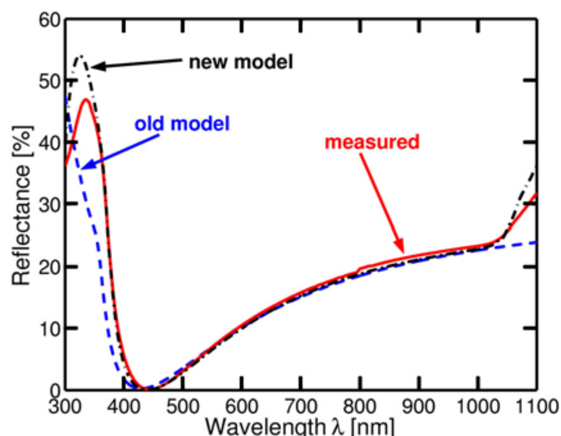

Figure 7: Reflectance curve for no SiO_2 and 50 nm TiO_2. Depicted are the results of the old model, the new model and the measured curve.

6 CONCLUSION

The low measured weighted reflectance values for all types of prepared samples and the low measured emitter saturation current densities indicate a competitiveness of the TiO_2/SiO_2 double layer solution.

Continuative research include the investigation of the effects of surface charge on the passivation characteristics and the impact of outside influences as moisture on the crystal structure of TiO_2. Also, the longterm stability is yet to be proven.

If the suspicion of a layer thickness dependence of the optical constants of TiO_2 proves to be true, the model is improvable by incorporating two-dimensional functions n (λ, d_{TiO2}), k (λ, d_{TiO2}).

This work has supplied the evidence, that APCVD TiO_2 has, in principle, the possibility to again become a serious alternative to more expensive techniques, currently favoured by PV industry.

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