SOL-GEL DOUBLE-LAYER ANTIREFLECTION COATINGS FOR SILICON SOLAR CELLS

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Summary

Double-layer thin films of SiO₂ and TiO₂, applied using the sol-gel process, were utilized as antireflection coatings on silicon solar cells. When coated with these films, the efficiency of a solar cell was increased by 44%, which agrees well with the measured increase in cell solar absorbance of 47%. Modeling of the reflectance properties of the coated cells, using thickness and index of refraction values determined from ellipsometric measurements, was in excellent agreement with the spectral reflectance properties measured from 300 to 1100 nm. Transmission electron microscopy on sectioned samples revealed sharp interfaces between the sol-gel films and thicknesses in good agreement with the ellipsometric values.

1. Introduction

Silicon solar cells have a high, real index of refraction across most of the solar spectrum, from approximately 350 to 1100 nm [1], resulting in a large solar averaged reflectance loss of about 36% for this material. This large reflectance loss can be appreciably reduced by coating the silicon with a thin, transparent dielectric layer with an appropriate dielectric constant and thickness. Single-layer, antireflection (AR) coatings used to date have included SiO, SiO₂, TiO₂, Si₃N₄, Ta₂O₅, and Al₂O₃ [2-4]. The coating thickness in each case is adjusted so that a minimum in reflectance occurs at approximately 600 nm. In this case, the reflectance losses are reduced to 10 - 12%. Further reductions in the reflectance losses have been obtained by Johnson et al. [5] through the deposition of SiNₓ films with a graded composition so that the index of refraction varies from 1.5 at the outer surface to 2.6 at the silicon substrate. With these films, the reflectance losses are reduced to below 7%. By applying double-layer antireflection coatings on silicon, the reflectance losses can be reduced even further. In this paper, double layers of SiO₂ and TiO₂, produced using sol-gel glass technology, were used as AR coatings on silicon solar cells (see Fig. 1). Coatings were obtained with reflectance values as low as 5%, with the optimum value predicted as being only 3%.
Fig. 1. Schematic diagram of a double-layer SiO$_2$/TiO$_2$ coating on silicon.

2. Experimental details

2.1. Sol-gel processing

Chemical preparation of glasses by the sol-gel method was achieved by the use of metal alkoxides M(OR)$_x$ as oxide glass precursors (M = Si, B, Ti, Al etc.; R = CH$_3$, C$_2$H$_5$, C$_3$H$_7$ etc.). The alkoxides were mixed with water and catalyst at low temperatures in an alcohol solution and underwent hydrolysis and condensation reactions to form a polymeric network. The properties of these solutions could be tailored for a specific application by controlling the H$_2$O content, pH, temperature, dilution and aging [6, 7]. Sol-gel-derived solutions could then be deposited onto a substrate by dipping, spinning or spraying, whereupon the solvent evaporated and gelation occurred. After drying, the porous gel coating was fired at a relatively low temperature (<800°C) to form a dense, transparent glass film which could function as a protective [8], dielectric [9] or optical coating [2, 10] depending on the preparation conditions.

SiO$_2$ and TiO$_2$ sol-gel solutions were prepared using titanium tetraethoxide Ti(OC$_2$H$_5$)$_4$ and silicon tetraethoxide Si(OC$_2$H$_5$)$_4$ as oxide precursors. The SiO$_2$ solution was prepared by partially hydrolyzing the silicon tetraethoxide in ethanol (1 mole water/1 mole ethoxide) at 60°C with a small amount of 1 M HCl to promote hydrolysis. The final water content was adjusted to 10 moles water/1 mole ethoxide and the solution diluted with ethanol to an oxide concentration of 2.5 wt.%. TiO$_2$ solutions were prepared as previously discussed [2] using titanium tetraethoxide, concentrated HNO$_3$ and ethanol. The requisite amount of water was added to achieve a water/ethoxide molar ratio of 1.5.

Solutions were applied to 5 cm diameter, polished, n-type, phosphorous-doped silicon wafers using a photoresist spinner. The thickness of the coating could be adjusted, within limits, by varying the rotational speed (rev min$^{-1}$) of the spinner. Typically, 0.25 ml of solution was added dropwise to the center of a wafer spinning at the required speed. Samples were spun for 30 s after the solution addition and dried under a heat lamp for 5 min. The thickness of TiO$_2$ required for optimum optical properties was achieved by the application of a single coating at 3200 rev min$^{-1}$, while two coats at 5000 rev min$^{-1}$ were necessary to obtain the optimum thickness of SiO$_2$ film. Multiple coats were applied with only a heat-lamp treatment between coatings. After coating, the wafers were rapidly heated to 450°C. Heat treatment for 5 min was sufficient to densify the individual layers.
2.2. Ellipsometry

The real index of refraction $n$ and the thickness $t$ of SiO$_2$ and TiO$_2$ sol-gel coatings were measured using a Gaertner Model L119X ellipsometer operating with a He–Ne laser source (632.8 nm). The resulting ellipsometric values were analyzed to determine the thickness and index of refraction of the sol-gel film, using a value of 3.86 for the real and 0.08 for the imaginary index of refraction of the silicon substrate. The resulting $n$ and $t$ values of the sol-gel films, when checked against standards supplied with the instrument, appeared to be accurate to ±0.003 for $n$ and ±2.0 nm for $t$.

2.3. Reflectance measurements

The spectral hemispherical reflectance properties $R_{2\pi}(\lambda)$ of both coated and uncoated cells were measured from 300 to 2400 nm using an integrating sphere reflectometer attached to a Beckman Model 5270 spectrophotometer. All data were referenced to packed halon diffuse reflectance standards, using the reflectance values published by the National Bureau of Standards [11]. Reflectance values should be accurate to within ±0.010 reflectance units. In order to determine the effectiveness of an AR coating, the solar averaged reflectance $R_s$ was calculated by averaging the reflectance data over an AM 1.5 solar photon spectral distribution $S_p(\lambda)$ of Thekaekara as reported [12], according to the equation

$$R_s = \frac{\int S_p(\lambda) R_{2\pi}(\lambda) \, d\lambda}{\int S_p(\lambda) \, d\lambda} \quad (1)$$

A plot of $S_p(\lambda)$ is shown in Fig. 2(a). The limits of integration were set equal to the active range of silicon which extends from 320 to 1120 nm. The average reflectance values calculated in this way represent the fractional amount of solar photons within the active range for silicon that are reflected by the cell. Since silicon is opaque over this wavelength range, one minus the average reflectance gives the fraction of photons that are absorbed by the cell.

![Fig. 2. (a) Plot of the AM 1.5 solar photon spectrum as a function of wavelength; (b) graph of the quantum efficiency of an ASEC solar cell as a function of wavelength.](image-url)
For a specific cell, the average reflectance calculation should also include the quantum efficiency characteristics of the cell. For example, the quantum efficiency determined for an Applied Solar Energy, Corp. (ASEC) solar cell (provided by B. H. Rose, Sandia National Labs., Photovoltaic Concentrator Research Division) is shown in Fig. 2(b). Note that the quantum efficiency in this case is roughly equivalent to a uniform response from 320 to 1120 nm. Average reflectance values calculated with the quantum efficiency response (Fig. 2(b)) included in the integration were consistently lower than the values calculated using eqn. (1), with the maximum difference being 0.020 reflectance units for AR coatings of interest. Since the difference is approximately equal to the measurement error, these variations in the averaging procedure can be ignored.

3. Optical modeling

A computer program was used to calculate the reflectance properties of various thin film layers on silicon. The modeling results were used for two purposes. First, calculated reflectance properties of single-layer SiO₂ and TiO₂ coatings on silicon were compared with measured reflectance properties over the solar spectral range. Agreement between the calculated and measured reflectance spectra would indicate that the appropriate index of refraction and thickness had been obtained for the sol-gel films from the ellipsometric measurements and that the model could be used to predict accurately the reflectance properties of this system. Second, results from the modeling program were used to determine the optimum configuration of the double-layer coatings, i.e. those values of n and t which result in a minimum solar averaged reflectance value and thereby lead to a maximum solar averaged absorbance. Finally, the sensitivity of the solar average reflectance properties to variations in the film thicknesses around the optimum values could be determined.

The optical modeling program can accommodate a multilayer stack made up of both thick and thin films. Thick films are defined as films whose thickness is much greater than the wavelength of the incident radiation. For these films, phase information between beams reflected from the top and bottom of the film is lost [13]. In the case of thin films, the phase information, and thus interference effects, is included. Details of the optical model are discussed in a separate report [14]. Input parameters for the model include the number of films in the stack, the complex index of refraction \( n = n - iK \), where \( i = \sqrt{-1} \) and thickness of each film, whether a film is considered to be thick or thin, and the incident angle for the calculation. The output consists of the reflectance and transmittance properties of the entire stack for each polarization over the wavelength range of interest. In the case of a double-layer coating on silicon, as shown in Fig. 1, the two outer films were considered “thin” films while the silicon was considered a “thick” film. Complex index of refraction data were obtained from ref. 1 for silicon, from...
ref. 15 for TiO₂ and from ref. 16 for SiO₂. Since the hemispherical reflectance properties were measured at an incident angle of ~10°, the calculations were all performed at normal incidence where the values for both polarizations were equal.

For some of the sol-gel coatings, the real index of refraction measured at 632.8 nm was higher or lower than the value found in the literature. This difference probably resulted from a coating with a density that was slightly higher or lower than that used for the literature sample or which had a slightly different composition [2, 6]. In these cases, the literature index of refraction values at all wavelengths were shifted by an amount equal to the shift measured at 632.8 nm. The use of this procedure is justified since for TiO₂ films Schroeder [15] has shown that the dispersion of the index of refraction, when appropriately normalized, describes a universal curve independent of either the composition or the structure of the film. By following this procedure, slightly better agreement between measured and calculated curves was obtained in this study.

4. Results and discussion

4.1. Uncoated silicon

Calculated and measured reflectance properties of a bare silicon wafer are shown in Fig. 3. The silicon wafer used for these measurements was 0.3 mm thick and polished on the top side only. Below ~1000 nm, the calculated and measured results agree to within the measurement uncertainty. Above 1000 nm, the silicon becomes partially transparent so that some radiation reaches the back surface and is reflected. This leads to an increase in both the measured and calculated reflectance values in this wavelength range. However, above 1100 nm, where the reflectance levels off, the two curves do not agree in magnitude. The lower reflectance values of the measured curve probably result from scattering of the incident beam by the
rough, unpolished second surface of the sample. In the model, the second surface was assumed to be smooth and polished. Because the region of interest for solar applications is below \( \sim 1000 \) nm, this discrepancy is not important. The solar averaged reflectance values for both curves were in good agreement, with the measured value being 0.358 and the calculated value being 0.357.

4.2. \( \text{SiO}_2 \)-coated silicon

To achieve the optimum thickness for the \( \text{SiO}_2 \) film, two successive applications of the silica solution were employed as described above. By varying the sample rotation speed during the coating operation from 2000 to 6000 rev min\(^{-1} \) the thickness of the double-layer \( \text{SiO}_2 \) film after densification at 450 °C could be varied from 90 to 45 nm. For modeling purposes, two samples of \( \text{SiO}_2 \) coatings were prepared which consisted of first one and then two coatings of \( \text{SiO}_2 \).

The measured and calculated reflectance properties of both a single \( \text{SiO}_2 \) coating with a measured thickness of 50.4 nm and a double \( \text{SiO}_2 \) coating with a measured thickness of 98.9 nm on silicon are shown in Fig. 4. For the calculated curves, the measured index of refraction at 632.8 nm (1.414) was used. This value, which is slightly lower than the published value of 1.457 for fused silica, probably indicates that the silica film is slightly porous. Below 1000 nm, the agreement between the measured and calculated reflectance curves is within measurement uncertainty. Also note that the thickness of the double coating is almost twice the value of the single-layer coating (50.4 nm \textit{versus} 98.9 nm). If an initial silica layer of \( \sim 2 \) nm thickness is assumed to be present on the silicon before application of the first sol-gel coating, the sol-gel coating thickness would exactly equal 48.5 nm for each application.

![Fig. 4. Spectral hemispherical reflectance properties of single (50.4 nm) and double (98.9 nm) coatings of \( \text{SiO}_2 \) on silicon: 1A, measured, single; 1B, calculated, single; 2A, measured, double; 2B, calculated, double. Calculated curves use the listed thickness values determined from ellipsometric measurements.](image-url)
4.3. TiO$_2$-coated silicon

By appropriately varying the rotational speed used in the coating process, the optimum thickness of the TiO$_2$ layer could be achieved from a single coating operation. Therefore, a single coating of TiO$_2$ on silicon was prepared for testing. Measured and calculated reflectance properties of TiO$_2$ on silicon are shown in Fig. 5. For this sample, the thickness was measured as 47.8 nm and the index of refraction at 632.8 nm was 2.243, compared to the literature value of 2.104 obtained for a similar sol-gel prepared sample. The higher index value indicates that the film is partially crystalline (as observed microscopically in Section 4.5). Using the measured \( n \) and \( t \) values, the agreement between the calculated and measured reflectance curves below 1000 nm is excellent, except for a slight discrepancy in matching the sharp peak in reflectance near 350 nm. By decreasing either the thickness or real index of refraction slightly, the fit near 300 nm could be improved slightly. However, because there are very few solar photons in this low wavelength region, the discrepancy between the two curves is not considered important. The solar averaged reflectance values for the measured and calculated curves are 0.161 and 0.157 respectively.

![Spectral hemispherical reflectance properties of a single 47.8 nm coating of TiO$_2$ on silicon: 1, measured; 2, calculated. The calculated curve uses the listed thickness value determined from ellipsometric measurements.](image)

4.4. SiO$_2$/TiO$_2$-coated silicon

Multiple layers of SiO$_2$ and TiO$_2$ were applied to silicon substrates using the same sol-gel solutions and coating procedures as discussed above. Thus, the final film thickness and index of refraction values should correspond to the values measured for the individual films: for SiO$_2$, \( t = 98.9 \) nm and \( n = 1.414 \) while for TiO$_2$, \( t = 47.8 \) nm and \( n = 2.243 \). The resulting measured and calculated reflectance curves for the double-layer coating on silicon are shown in Fig. 6. Over the entire wavelength range from 300 to 1000 nm, the agreement between the two curves is well within experimental error, except for a slight difference near 500 nm. The solar averaged reflectance values for the measured and calculated curves were 0.058 and 0.050 respectively.
Several changes in the model calculations were investigated in order to improve the agreement near 500 nm. The calculated reflectance near 500 nm can be increased to match better the measured curve by simultaneously increasing the SiO$_2$ film thickness and decreasing the TiO$_2$ film thickness by approximately 3 nm each. However, this change also shifts the steep rise in reflectance at wavelengths below 400 nm to shorter wavelengths. This results in large errors of about 0.05 reflectance units in this region. Adding a thin (2 - 4 nm) SiO$_2$ film between the TiO$_2$ and the silicon substrate in order to simulate the natural oxide film that forms on silicon only increases the difference between the calculated and measured curves near 500 nm.

As a final modification it was assumed that the TiO$_2$/SiO$_2$ interface was not a sharp boundary but consisted of a thin region with an index of refraction intermediate between those of TiO$_2$ and SiO$_2$. Thus, a 2 nm thick film with an index of refraction of 1.8 was assumed to be interposed between the TiO$_2$ and SiO$_2$ layers. Adding this layer also decreased the calculated reflectance near 500 nm, leading to further disagreement with the measured reflectance in this region. Therefore, several otherwise plausible changes to the modeling calculations were not successful in improving the agreement between the calculated and measured results.

### 4.5. Characterization of SiO$_2$/TiO$_2$ coatings

To verify our hypothesis, a double-layer SiO$_2$-TiO$_2$ coating on silicon was sectioned perpendicular to the plane of the coating, polished and ion thinned for transmission electron microscopy (TEM) examination. The TEM micrograph in Fig. 7 shows that the SiO$_2$/TiO$_2$ interface is indeed very distinct, suggesting little or no interdiffusion. Rutherford back-scattering experiments provided further evidence that the interface was extremely sharp as required by the optical analysis. Thickness values measured from the TEM micrograph agree very well with the ellipsometric values: for SiO$_2$, 90.0 nm versus 98.9 nm and for TiO$_2$, 50.0 nm versus 47.8 nm. In addition, the TiO$_2$
film is seen to be partially crystalline as suggested from the index of refraction value. Preliminary analysis of the diffraction pattern from the film indicates the anatase structure.

5. Optimum coating conditions

Using the optical modeling program, solar average reflectance values were calculated for SiO$_2$/TiO$_2$ films on silicon according to eqn. (1). The real index of refraction values used for each film were set equal to the values obtained for the individual films as measured experimentally and discussed above. For the calculations, the thickness of the SiO$_2$ layer was varied from 65 to 125 nm, while the TiO$_2$ layer was varied from 40 to 80 nm, both in steps of approximately 5 nm. The resulting reflectance properties were solar averaged and these values fit with a contour plot as shown in Fig. 8. Note that the minimum reflectance value is 0.038, which is about 0.07 reflectance units lower than a typical single-layer AR coating and 0.03 reflectance units lower than the graded index SiN$_x$ films reported by Johnson et al. [5]. This optimum sol-gel double-layer coating has an SiO$_2$ thickness of ~98.5 nm and a TiO$_2$ thickness of ~61.5 nm. From the contour plot, the sensitivity of the optical properties to changes in the thicknesses of the two coatings can be determined. This information may be helpful in defining a process specification or in diagnosing a coating problem. The region of minimum reflectance is quite insensitive to small changes in the film thicknesses. Thus, for example, an increase in reflectance of only 0.01 reflectance units above the
Fig. 8. Contours of constant solar averaged reflectance for double-layer coatings on silicon as a function of the thicknesses of the SiO$_2$ and TiO$_2$ layers. The point of minimum reflectance • corresponds to 95 nm of SiO$_2$ and 62 nm of TiO$_2$. X locates the double-layer coating discussed in the text.

The optimum value results from SiO$_2$ variations of ±15 nm or from TiO$_2$ variations of ±10 nm. It can be seen that the minimum point is slightly more sensitive to the TiO$_2$ film thickness than it is to the SiO$_2$ film thickness. The location of the previously discussed double-layer coating is shown in the upper left part of Fig. 8 (X).

6. Cell efficiency measurements

In order to determine whether the decrease in reflectance measured for the coated silicon results in a corresponding increase in cell efficiency, the performance of a solar cell was determined before and after application of the double-layer sol-gel coating. The reflectance properties are shown in Fig. 9. For the AR coated cell, the reflectance minimum is only 0.05 which

Fig. 9. Measured spectral hemispherical reflectance properties of uncoated (as received) and AR coated solar cells.
results from the high reflectance characteristics of the silver metallization on the cell. The AR coating will not appreciably decrease the reflectance of these metallized areas. Solar averaged reflectance values before and after AR coating are 0.374 and 0.079 respectively. The corresponding absorption increased from 0.626 to 0.921, an increase of 47%. The measured cell efficiency increased from 12.1 to 17.4%, an increase of 44%. Because the increase in measured cell efficiency is in excellent agreement with the increase in cell solar absorbance, the 450 °C firing temperature necessary to densify the sol-gel coating apparently has no detrimental effect on cell performance. Based on the measured reflectance of uncoated silicon of 0.36 and the minimum reflectance value possible with the optimum sol-gel coatings of 0.038, it should be possible to increase the efficiency of a solar cell by slightly over 50% by using double-layer SiO₂/TiO₂ films.

7. Conclusions

Thin films of SiO₂ and TiO₂ produced using the sol-gel process have been used to provide AR coatings for silicon solar cells. Through proper control of the film thickness and index of refraction, the reflectance averaged over a solar photon spectrum could be reduced to values approaching 0.04. Coating a solar cell with these films increased the measured cell efficiency by 44%, which was in good agreement with the measured increase in cell solar absorbance of 47%. Therefore the high firing temperature of 450 °C which is required to densify the sol-gel films had no detrimental effect on cell performance.

Optical modeling calculations, which used thickness and index of refraction values determined from ellipsometric measurements, were able to predict accurately the spectral reflectance properties of single-layer films of SiO₂ and TiO₂ on silicon, as well as those of the double-layer films. Based on the optical properties determined for these films, modeling calculations determined that the optimum double-layer coating should have an SiO₂ thickness of 95 nm and a TiO₂ thickness of 62 nm. Variation of the SiO₂ thickness by ±15 nm or the TiO₂ thickness by ±10 nm increased the reflectance by only 0.01 reflectance units relative to the optimum value.

Transmission electron microscopy and Rutherford back-scattering measurements both indicated that the interface between the SiO₂ and TiO₂ films was very sharp and that no interdiffusion had occurred during the high-temperature firing process. In addition, the film thicknesses determined from the TEM micrographs were in excellent agreement with the ellipsometric values.

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