High-rate plasma-deposited SiO₂ films for surface passivation of crystalline silicon

Citation for published version (APA):

Hoex, B., Peeters, F. J. J., Creatore, M., Blauw, M. A., Kessels, W. M. M., & Sanden, van de, M. C. M. (2006). High-rate plasma-deposited SiO₂ films for surface passivation of crystalline silicon. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 24(5), 1823-1830. <https://doi.org/10.1116/1.2232580>

DOI:

[10.1116/1.2232580](https://doi.org/10.1116/1.2232580)

Document status and date:

Published: 01/01/2006

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

High-rate plasma-deposited SiO₂ films for surface passivation of crystalline silicon

B. Hoex^{a)}

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and OTB Solar B.V., P.O. Box 7108, 5605 JC Eindhoven, The Netherlands

F. J. J. Peeters, M. Creatore, M. A. Blauw, W. M. M. Kessels,^{b)} and M. C. M. van de Sanden

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 1 May 2006; accepted 20 June 2006; published 7 August 2006)

SiO₂ films were deposited by means of the expanding thermal plasma technique at rates in the range of 0.4–1.4 $\mu\text{m}/\text{min}$ using an argon/oxygen/octamethylcyclotetrasiloxane (OMCTS) gas mixture. The film composition was studied by means of various optical and nuclear profiling techniques. The films deposited with a low OMCTS to oxygen ratio showed no residual carbon and a low hydrogen content of $\sim 2\%$ with a refractive index close to thermal oxide. For a higher OMCTS to oxygen ratio a carbon content of $\sim 4\%$ was detected in the films and the refractive index increased to 1.67. The surface passivation of the SiO₂ films was tested on high quality crystalline silicon. The films yielded an excellent level of surface passivation for plasma-deposited SiO₂ films with an effective surface recombination velocity of 54 cm/s on 1.3 $\Omega\text{ cm}$ *n*-type float zone crystalline silicon substrates after a 15 min forming gas anneal at 600 °C. © 2006 American Vacuum Society.

[DOI: 10.1116/1.2232580]

I. INTRODUCTION

To further decrease the cost of energy from crystalline silicon (*c*-Si) solar cells, the *c*-Si solar cell wafer thickness is reduced and higher conversion efficiencies schemes are explored. For this purpose, both the optical and electrical quality of the *c*-Si solar cell wafer have to be optimized. SiO₂ is the material of choice to meet these requirements and is already effectively used in the world-record efficiency *c*-Si solar cell produced by the University of New South Wales.¹ Thermally grown SiO₂ has an ideal refractive index to maximize internal reflection at the back of the solar cell. The surface passivation of the as-grown SiO₂ is rather poor due to a relative high interface defect density, but is significantly improved by a postdeposition anneal in a hydrogen containing gas (forming gas anneal). The best level of surface passivation is, however, obtained by evaporating a sacrificial high quality aluminum film (0.1–1 μm) on the SiO₂ and subsequently annealing the Si substrate at 350–400 °C. In this so-called *alneal* step, atomic hydrogen resulting from the aluminum oxidation process passivates defects states at the interface between *c*-Si and SiO₂.² Applicationwise, the main disadvantages in obtaining a passivating thermal SiO₂ are the long and elaborate processing and the high temperatures in the range of 1000–1100 °C that can deteriorate the wafer bulk quality, especially for lower quality substrate material [e.g., Czochralski (Cz) *c*-Si or multi-*c*-Si (mc-Si)]. Recently, these disadvantages were partly solved by using a wet oxidation process at 800 °C that resulted in the world-record mc-Si solar cell.³ However, the processing times were still in

the order of hours due to the requirement of a rather thick SiO₂ film of $\sim 100\text{ nm}$ for optimal optical performance at the back of the solar cell. The application of a plasma-deposited SiO₂ films, obtained in a low temperature process and with a good level of surface passivation, might form a solution to reduce the processing time needed.

SiO₂ films synthesized by plasma enhanced chemical vapor deposition (PECVD) already have numerous technological applications. They are used as a dielectric in complementary metal-oxide semiconductor (CMOS) devices,⁴ as an oxygen and water permeation barrier on polymers,^{5,6} as a scratch resistant coating for, e.g., car glazing, and as protective layer for semiconductor devices.^{7,8} In the field of microelectronics a lot of effort is put in the development of plasma-deposited SiO₂ films with a low interface defect density. This has led to plasma-deposited SiO₂ films with an interface defect density of $\sim 5 \times 10^{10}\text{ cm}^{-2}\text{ eV}^{-1}$ after an anneal at 400 °C.⁹ These SiO₂ films also showed excellent surface passivation on nearly intrinsic ($>500\text{ }\Omega\text{ cm}$) *n*-type *c*-Si.¹⁰ However, for the production of solar cells generally lower resistivity wafers are used and it is well known that the level of surface passivation is strongly dependent on the substrate doping level. The effective surface recombination velocity on the commonly used *p*-type *c*-Si substrates with a resistivity of 1 $\Omega\text{ cm}$ was only in the range of 700 cm/s.¹¹ Leguit *et al.* and Sivoththaman *et al.* were able to reach minimal effective surface recombination velocities of $\sim 100\text{ cm/s}$ on moderately doped *p*- or *n*-type *c*-Si.^{12,13} However, for higher doping levels the effective surface recombination velocity strongly increases.^{12,13} It should be noted that the surface passivation of the as-deposited SiO₂ films in all these studies was rather poor and a 20 min or 15 h anneal at

^{a)}Electronic mail: b.hoex@tue.nl

^{b)}Electronic mail: w.m.m.kessels@tue.nl

TABLE I. Spectroscopic ellipsometry results for SiO₂ films obtained at different OMCTS flow rates. The argon (2000 SCCM) and oxygen (200 SCCM) flows, were set to their maximum value, while the plasma source current was 75 A. The deposition temperature was 400 °C and the deposition time was 12 s for all samples.

OMCTS flow (SCCM)	Reactor pressure (mbar)	Refractive index (at 2 eV)	Extinction coefficient (at 5 eV)	Film thickness (nm)	Deposition rate (μm/min)
6.3	0.41	1.46	...	76	0.38
9.2	0.42	1.47	...	110	0.54
13.5	0.44	1.47	...	158	0.77
16.6	0.45	1.49	...	196	0.98
19.5	0.46	1.52	0.02	224	1.12
28.3	0.49	1.67	0.15	286	1.35

assuming a mixture of 50% bulk layer and 50% voids. More information about the surface roughness was obtained by atomic force microscopy (NT-MDT Solver P49 pro). Infrared absorption spectra were measured by Fourier transform infrared (FTIR) spectroscopy (Bruker Vector 22) in the 370–8000 cm⁻¹ range with a resolution of 4 cm⁻¹. The measurements were taken at normal incidence both prior to and after deposition to obtain a reliable background of the transmission spectrum. At least 20 spectra were averaged to obtain a sufficiently high signal-to-noise ratio. The absorption spectrum of the SiO₂ film was deduced by taking into account interference effects in the films.²⁴ The atomic composition of the films was obtained from RBS and elastic recoil detection (ERD) measurements. For the RBS/ERD measurement a monoenergetic beam of high energy He⁺ ions (2 MeV) was directed at the sample at normal incidence in the case of RBS or at 75° with respect to the normal for ERD.²⁵ The impurity content of the SiO₂ films was further investigated by dynamic secondary ion mass spectrometry (SIMS) using a 3 keV O₂⁺ primary beam with a current of 180 nA on a 180 μm² spot size.²⁶

C. Surface passivation

The surface passivation of the SiO₂ films was tested on double side polished float zone (FZ) 1.3 Ω cm *n*-type *c*-Si substrates with a thickness of 380 μm. The *c*-Si substrates were cleaned using a conventional Radio Corporation America clean and received a final cleaning step in diluted HF (5%) prior to the deposition. A SiO₂ film was deposited on both sides of the *c*-Si wafer and the effective lifetime of the charge carriers in the lifetime sample was determined by means of the photoconductance decay method (Sinton WCT100). These measurements were performed both in transient and quasi-steady-state mode taking the reflectivity of the wafer into account.²⁷ The effective surface recombination velocity was calculated by assuming an infinite bulk lifetime in the float zone *c*-Si substrates.

The impact of a post-thermal anneal on the level of surface passivation of the SiO₂ films was studied by annealing the lifetime samples in a forming gas (10% H₂ in N₂) environment in the temperature range of 400–700 °C using a rapid thermal anneal oven (AST SHS-100). The impact of a

forming gas anneal (FGA) on the SiO₂ film properties was also investigated by means of FTIR and RBS.

III. FILM PROPERTIES

A. Optical analysis

From our previous depositions using HMDSO as the main growth precursor, we know that a high amount of Ar⁺ ions and atomic oxygen is needed to remove the methyl groups from the organosilicon growth precursor.²⁸ For this reason the highest Ar (2000 SCCM), highest plasma current (75 A), and O₂ flow rates (200 SCCM) were chosen in this experiment and the OMCTS flow was varied in the range of 6–30 SCCM at a substrate temperature of 400 °C. The resulting refractive index (at 2 eV), extinction coefficient (at a photon energy of 5 eV), film thickness, and deposition rates obtained at different OMCTS flows are summarized in Table I. The deposition rate of the SiO₂ films, as determined by dividing the film thickness by the deposition time, increased linearly with the OMCTS flow up to ~1.12 μm/min for an OMCTS flow of 20 SCCM, as shown in Fig. 2(a). For the highest investigated OMCTS flow of 28 SCCM, the deposition rate of ~1.4 μm/min was lower than expected from this linear relation. The deposition rates are comparable with the values reported by Qi *et al.* for an electron cyclotron resonance (ECR) plasma,¹⁹ although they used a higher OMCTS flow of 50 SCCM. As shown in Fig. 2(a) the refractive index of the SiO₂ films was constant at 1.46–1.47 for an OMCTS flow up to 13 SCCM and nearly equal to the refractive index of thermally grown SiO₂ (*n*=1.46 at 2 eV). When the OMCTS flow rate was increased from 13 to 28 SCCM, the refractive index of the deposited SiO₂-like film gradually increased up to 1.67 for a film deposited with an OMCTS flow of 28 SCCM. This change can be explained by an change in the O/Si ratio to values below 2 and the incorporation of carbon in the film, as determined by means of RBS and summarized in Table II.²⁹ For the SiO₂-like films deposited at the highest OMCTS flow rates, also absorption in the UV part of the spectrum had to be taken into account. However, the extinction coefficient was very moderate with a value of 0.15 at a photon energy of 5 eV for the film deposited with an OMCTS flow of 28 SCCM. This also indicates a change in atomic composition of the films. No significant difference

FIG. 2. (a) Refractive index at a photon energy of 2 eV and (b) the deposition rate as a function of the OMCTS flow. The error bars are an indication in the variation in the obtained values. The line serves as a guide to the eye.

between the refractive index measured *in situ* and *ex situ* was observed, indicating no observable water uptake after exposure to air.³⁰

From the spectroscopic ellipsometry analysis the SiO₂ layers appeared to be very smooth with no significant surface roughness for low OMCTS flows. For higher OMCTS flows the surface roughness was estimated to increase up to ~4 nm. This was verified by atomic force microscopy (AFM) measurements. Samples with a thickness of ~200 nm were deposited for three OMCTS flows. The root mean square surface roughness of a SiO₂ film deposited with low OMCTS flows of 6 and 9 SCCM was found to be ~0.5 nm. However, for a SiO₂ film deposited with an OMCTS flow of 28 SCCM the rms surface roughness increased up to ~2.4 nm.

B. Compositional analysis

To get more insight in the composition and atomic density of the SiO₂ films three samples were analyzed by means of RBS/ERD and SIMS. For this reason SiO₂ films were deposited for three OMCTS flows of 6.3, 9.2, and 28.3 SCCM on HF dipped *c*-Si substrates keeping the other deposition con-

FIG. 3. Infrared transmission spectra of SiO₂ films deposited with various OMCTS flows. The spectra have been offset vertically for clarity.

ditions equal to those used in the optical analysis. The deposition time was chosen such that the resulting film thickness for all films was approximately 200 nm.

From the RBS/ERD measurements, as summarized in Table II, it is observed that the SiO₂ films deposited with a low OMCTS flow are nearly stoichiometric in composition and have a small residual hydrogen content of ~2%. The residual carbon content is below the detection limit of RBS (<3 at. %). For the highest OMCTS flow studied, the SiO₂-like films are Si rich and also higher levels of C (4.5 at. %) and H (17.8 at. %) are incorporated in the film. These results are comparable to the results published by Qi *et al.*¹⁹

For a more quantitative analysis of the carbon content the SiO₂ films were analyzed by means of the SIMS technique. The carbon concentration in the films deposited with a low OMCTS flow (6.3 and 9.2 SCCM) was determined to be below the detection limit of 0.03 at. %. The carbon content of the SiO₂-like film deposited with an OMCTS flow of 28.3 SCCM was easily detectable and in agreement with the results obtained by RBS. Therefore, we can conclude that the SiO₂ films deposited with a low OMCTS flow do not contain a significant amount of residual carbon. However, when using higher OMCTS flow carbon is incorporated into the film.

C. Infrared analysis

Figure 3 shows the infrared transmission spectra in the range of 370–4000 cm⁻¹ of SiO₂ films deposited for various OMCTS flows. The characteristic vibrational rocking, bend-

TABLE II. Atomic composition of three SiO₂ films deposited for various OMCTS flows as determined by Rutherford backscattering (RBS) and elastic recoil detection (ERD).

OMCTS flow (SCCM)	[Si] (at. %)	[O] (at. %)	[H] (at. %)	[C] (at. %)	Atomic density (10 ²² at./cm ³)	Mass density (g/cm ³)
6.3	32.2	65.7	2.1	<3	6.6	2.15
9.2	32.4	65.5	2.1	<3	6.1	2.00
28.3	35.1	42.9	17.8	4±2	6.5	1.83

TABLE III. Infrared peak positions for the Si–O–Si, and silicon hydrides and silicon methyl groups as reported in the literature.

Configuration	Mode peak position (cm ⁻¹)		
	Rocking	Bending	Stretching
Si–O–Si	457 ^a	810 ^a	1076 ^a (AS1) 1200 ^a (AS2)
H–Si(O ₃)	...	860 ^b	2260 ^{b,c}
H–Si(SiO ₂)	...	835 ^b	2195 ^{b,c}
H–Si(Si ₂ O)	...	775 ^b	2108 ^{b,c}
H–Si(Si ₃)	485 ^d	630 ^b	2000 ^{b,c}
Si–CH ₃	...	1260 ^f	...

^aReference 38.^bReference 39.^cReference 40.^dReference 41.^eReference 42.^fReference 18.

ing, and stretching bands of Si–O–Si (as summarized in Table III) were detected in all SiO₂ films. The various absorption peaks were fitted using a Gaussian distribution and the peak position of the in-phase asymmetric stretching mode (AS1 mode) is shown as a function of the OMCTS flow in Fig. 4. The AS1 mode is known to shift as a function of the composition or density of the SiO₂ films.^{31–33} From Fig. 4 we can learn that the peak position of the AS1 mode is approximately constant for OMCTS flows up to 13 SCCM, and then continuously decreases when increasing the OMCTS flow up to 28 SCCM. This is in agreement with the observed increase in the refractive index of the SiO₂ film due to the change in atomic composition as observed by RBS and summarized in Table II. The total normalized absorption in the Si–O stretch mode decreased by approximately 30% when the OMCTS flow was increased from 6 to 28 SCCM, in agreement with the decrease in oxygen content as measured by RBS.

When increasing the OMCTS flow above 13 SCCM also residual carbon and hydrogen were detected in the FTIR spectrum at the peak positions summarized in Table III. The hydrogen and carbon related absorptions increased as a func-

FIG. 4. Si–O–Si in plane asymmetric stretch (AS1) peak position as a function of the OMCTS flow. The typical error in the peak position is indicated for an OMCTS flow of 13 SCCM.

FIG. 5. Effective surface recombination velocity S_{eff} as a function of the injection level for SiO₂ films deposited with OMCTS flows of (a) 6.3 SCCM and (b) 9.2 SCCM prior and after the forming gas anneals (FGAs) at the temperature indicated.

tion of the OMCTS flow rate. No O–H related absorptions (infrared absorption peak position around 3600 cm⁻¹)³⁴ were detected in the films for the FTIR measurement with 20 averages. Using a proportionality constant of 1.8×10^{20} cm⁻² for the Si–H stretching mode,³⁴ a bonded hydrogen concentration of $\sim 8 \times 10^{21}$ cm⁻³ can be calculated for the SiO₂-like film deposited with an OMCTS flow of 28 SCCM. Combining the RBS and FTIR data we can learn that most hydrogen is bonded to silicon for the SiO₂-like film deposited with the highest OMCTS flow. This is remarkable because no Si–H bonds are present in the growth precursor itself.

IV. SURFACE PASSIVATION AND THE IMPACT OF ANNEALING

A. Surface passivation by SiO₂ films

SiO₂ films deposited with OMCTS flows of 6.6 and 9.2 SCCM were selected to test the surface passivation on low resistivity *n*-type *c*-Si. The level of surface passivation was measured prior to and after a post-thermal treatment, as shown in Fig. 5. For both deposition conditions, the surface passivation of the as-deposited SiO₂ films was rather poor with an effective surface recombination velocity of 4×10^3 cm/s. This is comparable to the values reported for SiO₂ prepared by wet oxidation,³ but higher compared to

thermal SiO₂.² However, a 30 min forming gas anneal (10% H₂ in N₂) at 400 °C already improved the surface passivation to effective surface recombination velocities of 7×10^2 and 3×10^2 cm/s for SiO₂ films deposited with OMCTS flows of 6.2 and 9.2 SCCM, respectively. A similar improvement was reported on *p*-type *c*-Si for SiO₂ grown by wet oxidation.³ By adopting even higher annealing temperatures, the level of surface passivation kept improving. The best results were obtained by performing a 15 min forming gas anneal at 600 °C, leading to an optimal effective surface recombination velocity of 54 cm/s for a SiO₂ film deposited with an OMCTS flow of 9.2 SCCM. For higher annealing temperatures the effective surface recombination velocity increased again, for example, for a 15 min FGA at 700 °C, an effective surface recombination velocity of ~ 100 cm/s was obtained for a SiO₂ film deposited with an OMCTS flow of 9.2 SCCM.

The obtained level of surface passivation of plasma-deposited SiO₂ films on low resistivity *n*-type substrates is significantly higher compared to the results previously reported. The best values reported on low resistivity *n*-type substrates were in the 100–400 cm/s range obtained on slightly higher resistivity substrates (3–6 Ω),^{12,13} and it is generally found that the effective surface recombination velocity decreases for increasing wafer resistivity. The surface recombination velocity shows only a limited injection level dependence, similar to what is observed for silicon carbide, amorphous silicon, and silicon nitride on low resistivity *n*-type crystalline silicon.^{35–37} The improvement of the surface passivation with increasing annealing temperature up to 600 °C is not in agreement with results obtained by Chen *et al.*¹⁰ They found that the optimal annealing temperature was 350 °C for their plasma-deposited SiO₂, while for annealing temperatures above 350 °C the level of surface passivation significantly deteriorated. The stability of the surface passivation by plasma-deposited SiO₂ is generally a concern.^{10,12,13} The level of surface passivation of our samples did not deteriorate over time and was tested to remain constant over a period of more than half a year.

For SiO₂ grown by wet or thermal oxidation, an anneal in forming gas or anneal is essential to maximize the level of surface passivation.^{2,3} This improvement is related to a significant reduction of the interface defect density by atomic hydrogen. In our SiO₂ films, however, already 2 at. % hydrogen is present in the films, which can diffuse during the anneal and passivate interface defect states. For this reason, some lifetime samples were annealed in a *nitrogen only* environment to investigate the impact of the presence of H₂ during the forming gas anneal. As shown in Fig. 6, no significant improvement in the effective surface recombination velocity can be observed when the most successful anneal, 15 min at 600 °C, is applied in a nitrogen environment. However, by a subsequent forming gas anneal at 400 °C, similar effective surface recombination velocities were found as before, hence, without the additional anneal at 600 °C. Also the scheme applied by Sivothythaman *et al.*,¹³ a 45 s rapid thermal anneal at 1040 °C, did not yield any improve-

FIG. 6. Effective surface recombination velocity S_{eff} as a function of the injection level for SiO₂ films deposited with 9.2 SCCM after an anneal in a nitrogen environment (closed symbols) for (a) 15 min at 600 °C and (b) 15 s at 1040 °C [rapid thermal anneal (RTA)]. Subsequently the samples received a standard forming gas anneal (10% H₂ in N₂) for 30 min at 400 °C (open symbols).

ment in the level of surface passivation compared to the as-deposited film. A subsequent forming gas anneal for 30 min at 400 °C resulted in a surface recombination velocity of ~ 500 cm/s; hence, no improvement was observed by the additional anneal. It seems that the presence of hydrogen in the annealing environment is essential to improve the level of surface passivation for our SiO₂ film, despite the presence of hydrogen in the film.

Preliminary experiments showed that a 30 min anneal at 400 °C after a forming gas anneal at 600 °C did not yield any improvement in the level of surface passivation. This is in contrast to the results published for thermal oxide where an anneal after a forming gas anneal resulted in a large improvement in the level of surface passivation.²

B. Compositional changes due to annealing

The compositional changes of the SiO₂ film due to the forming gas anneal at 600 °C were investigated by means of FTIR and RBS. For this reason 200-nm-thick SiO₂ films were deposited on single side polished 10–20 Ω cm Cz *c*-Si substrates that had received a HF dip of 1 min prior to deposition. The RBS sample was divided into two parts and one part was treated by a forming gas anneal at 600 °C.

FIG. 7. Differential infrared transmission spectrum of a SiO₂ film with a thickness of ~ 200 nm after a 15 min FGA at 600 °C. The differential spectrum was obtained by dividing the infrared spectrum after the forming gas anneal by the infrared spectrum before the forming gas anneal.

The FTIR spectrum (averaged over 800 scans to increase the sensitivity) of the substrate with the SiO₂ film was taken after a FGA at 600 °C and divided by the spectrum taken prior to the forming gas anneal. The resulting differential infrared transmission spectrum is shown in Fig. 7. From this figure it is clear that both the intensities of the Si–O–Si rocking and stretching modes increased after annealing. Also a peak shift of the asymmetric Si–O–Si stretching mode from 1048 to 1060 cm^{−1} can be observed. Furthermore, by fitting the absorption spectrum by means of multiple Gaussian peaks, we observe a decrease in the peak widths of all the Si–O–Si related absorption peaks. The increased sensitivity (800 instead of 20 averages) also allows detecting an O–H related absorption in the as-deposited SiO₂ film. This O–H related absorption peak is completely removed during annealing and it was not detected in the FTIR spectrum of the sample after the forming gas anneal. The amount of O–H in the deposited film is estimated to be $\sim 1.1 \times 10^{21}$ cm^{−3} (1.8 at. %) using an O–H proportionality constant of 0.44×10^{20} cm^{−2}.³⁴ This is in good agreement with RBS analysis, summarized in Table II, where 1.2×10^{21} cm^{−3} (2 at. %) of hydrogen was detected in the SiO₂ film deposited with an OMCTS flow of 9.2 SCCM. The removal of hydrogen during the forming gas anneal was also confirmed by RBS; the hydrogen concentration decreased from 2.1 down to 0.7 at. % after the forming gas anneal. From spectroscopic ellipsometry measurements a decrease of $\sim 4\%$ in film thickness was observed, indicating a significant densification of the SiO₂ film during the forming gas anneal.

V. CONCLUSIONS

In this article we have shown that SiO₂ films with a low impurity content and a high level of surface passivation can be deposited by the ETP technique at a high rate from an argon/oxygen/OMCTS mixture. From the material analysis we can conclude that SiO₂ films deposited with a low OMCTS to oxygen ratio have a carbon content below 0.03% and

a low hydrogen (~ 2 at. %) content mainly present in the form of O–H groups. When increasing the OMCTS to oxygen ratio the O/Si ratio of the films changes to below 2 and a significant amount of carbon (up to 4.5 at. %) is incorporated into the film. The amount of hydrogen in the film also significantly increases (up to 17 at. %) and the hydrogen is mainly bonded to silicon for the SiO₂-like films deposited with a high OMCTS flow.

The level of surface passivation of the SiO₂ films is significantly improved by a FGA and the best results are obtained with a 15 min FGA at 600 °C. The FGA densifies the SiO₂ film and the bulk hydrogen content of the film is reduced by a factor of 3. The presence of H₂ during the post-deposition anneal is shown to be essential to improve the level of surface passivation. The obtained effective surface recombination velocity of 54 cm/s on 1.3 Ω cm *n*-type *c*-Si is the best reported value so far for PECVD SiO₂ films on low resistivity *c*-Si.

ACKNOWLEDGMENTS

The authors thank M. J. F. van de Sande and J. F. C. Jansen for their skillful technical assistance. Dr. Y. Tamminga and T. Dao (Philips Research) are thanked for the RBS analysis and P. van Hal (Philips Research) for the SIMS measurements. I. Volintiru is acknowledged for her help with the plasma reactor. Dr. M. D. Bijker (OTB Solar) is thanked for the fruitful discussions. This study has been carried out within the EET program “HR-CEL” funded by the Netherlands Ministry of Economic Affairs, the Ministry of Education, Culture and Science and the Ministry of Public Housing, Physical Planning and Environment. The research of one of the authors (W.M.M.K.) has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

- ¹J. H. Zhao, A. H. Wang, M. A. Green, and F. Ferrazza, *Appl. Phys. Lett.* **73**, 1991 (1998).
- ²A. G. Aberle, *Crystalline Silicon Solar Cells: Advanced Surface Passivation and Analysis* (UNSW, Sydney, 1999).
- ³O. Schultz, S. W. Glunz, and G. P. Willeke, *Prog. Photovoltaics* **12**, 553 (2004).
- ⁴A. A. Bright, *J. Vac. Sci. Technol. A* **9**, 1088 (1991).
- ⁵M. Creatore, F. Palumbo, R. d’Agostino, and P. Fayet, *Surf. Coat. Technol.* **142**, 163 (2001).
- ⁶A. S. D. Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemberg-Sapieha, and M. R. Wertheimer, *J. Vac. Sci. Technol. A* **16**, 3190 (1998).
- ⁷Y. Barrell, M. Creatore, M. Schaepkens, C. D. Iacovangelo, T. Miebach, and M. C. M. van de Sanden, *Surf. Coat. Technol.* **180–81**, 367 (2004).
- ⁸W. Kern and R. S. Rosler, *J. Vac. Sci. Technol.* **5**, 1082 (1977).
- ⁹Z. Chen, K. Yasutake, A. Doolittle, and A. Rohatgi, *Appl. Phys. Lett.* **63**, 2117 (1993).
- ¹⁰Z. Chen, S. K. Pang, K. Yasutake, and A. Rohatgi, *J. Appl. Phys.* **74**, 2856 (1993).
- ¹¹A. Ebong, P. Doshi, S. Narasimha, A. Rohatgi, J. Wang, and M. A. El-Sayed, *J. Electrochem. Soc.* **146**, 1921 (1999).
- ¹²C. Leguijt *et al.*, *Sol. Energy Mater. Sol. Cells* **40**, 297 (1996).
- ¹³S. Sivoththaman, P. De Schepper, W. Laureys, J. F. Nijs, and R. P. Mertens, *IEEE Electron Device Lett.* **19**, 505 (1998).
- ¹⁴M. J. Kerr and A. Cuevas, *Semicond. Sci. Technol.* **17**, 35 (2002).
- ¹⁵C. S. Pai and C. P. Chang, *J. Appl. Phys.* **68**, 793 (1990).
- ¹⁶K. Ishii, Y. Ohki, and H. Nishikawa, *J. Appl. Phys.* **76**, 5418 (1994).
- ¹⁷A. D. Ross and K. K. Gleason, *J. Appl. Phys.* **97**, 113707 (2005).
- ¹⁸C. Rau and W. Kulisch, *Thin Solid Films* **249**, 28 (1994).

- ¹⁹Y. Qi, Z. G. Xiao, and T. D. Mantei, *J. Vac. Sci. Technol. A* **21**, 1064 (2003).
- ²⁰L. Zajickova, J. Janca, and V. Perina, *Thin Solid Films* **338**, 49 (1999).
- ²¹M. F. A. M. van Hest, B. Mitu, D. C. Schram, and M. C. M. van de Sanden, *Thin Solid Films* **449**, 52 (2004).
- ²²J. W. A. M. Gielen, W. M. M. Kessels, M. C. M. van de Sanden, and D. C. Schram, *J. Appl. Phys.* **82**, 2643 (1997).
- ²³G. E. Jellison and F. A. Modine, *Appl. Phys. Lett.* **69**, 371 (1996).
- ²⁴J. W. A. M. Gielen, M. C. M. van de Sanden, and D. C. Schram, *Thin Solid Films* **271**, 56 (1995).
- ²⁵Y. Tamminga, F. H. P. M. Willemsen, F. H. P. M. Habraken, and A. E. T. Kuiper, *Nucl. Instr. and Meth.* **200**, 499 (1982).
- ²⁶P. C. Zalm, *Mikrochim. Acta* **132**, 243 (2000).
- ²⁷R. A. Sinton and A. Cuevas, *Appl. Phys. Lett.* **69**, 2510 (1996).
- ²⁸M. Creatore, W. M. M. Kessels, Y. Barrell, J. Benedikt, and M. C. M. van de Sanden, *Mater. Sci. Semicond. Process.* **7**, 283 (2004).
- ²⁹A. Sassella *et al.*, *J. Vac. Sci. Technol. A* **15**, 377 (1997).
- ³⁰M. Creatore, J. C. Cigal, G. M. W. Kroesen, and M. C. M. van de Sanden, *Thin Solid Films* **484**, 104 (2005).
- ³¹Y. H. Kim, M. S. Hwang, H. J. Kim, J. Y. Kim, and Y. Lee, *J. Appl. Phys.* **90**, 3367 (2001).
- ³²D. V. Tsu, G. Lucovsky, and B. N. Davidson, *Phys. Rev. B* **40**, 1795 (1989).
- ³³G. Lucovsky, J. Manitini, J. K. Srivastava, and E. A. Irene, *J. Vac. Sci. Technol. B* **5**, 530 (1983).
- ³⁴A. Ermolieff, T. Sindzingre, S. Marthon, P. Martin, F. Pierre, and L. Peccoud, *Appl. Surf. Sci.* **64**, 175 (1993).
- ³⁵M. J. Kerr and A. Cuevas, *Semicond. Sci. Technol.* **17**, 166 (2002).
- ³⁶I. Martin, M. Vetter, A. Orpella, C. Voz, J. Puigdollers, and R. Alcubilla, *Appl. Phys. Lett.* **81**, 4461 (2002).
- ³⁷M. Schaper, J. Schmidt, H. Plagwitz, and R. Brendel, *Prog. Photovoltaics* **13**, 381 (2005).
- ³⁸C. T. Kirk, *Phys. Rev. B* **38**, 1255 (1988).
- ³⁹L. He, Y. Kurata, T. Inokuma, and S. Hasegawa, *Appl. Phys. Lett.* **63**, 162 (1993).
- ⁴⁰G. Lucovsky, J. Yang, S. S. Chao, J. E. Tyler, and W. Czubytyj, *Phys. Rev. B* **28**, 3225 (1983).
- ⁴¹G. Lucovsky, S. S. Chao, J. Yang, J. E. Tyler, and W. Czubytyj, *J. Vac. Sci. Technol. A* **2**, 353 (1984).
- ⁴²N. Inagaki and M. Taki, *J. Appl. Polym. Sci.* **27**, 4337 (1982).