PROGRESS IN PHOTOVOLTAICS: RESEARCH AND APPLICATIONS
Prog. Photovolt: Res. Appl. 2005; **13**:705–712
Published online 16 June 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/pip.628

Applications

SHORT COMMUNICATION

Industrial High-rate (~5 nm/s) Deposited Silicon Nitride Yielding High-quality Bulk and Surface Passivation under Optimum Anti-reflection Coating Conditions

B. Hoex[1,2], A. J. M. van Erven[1], R. C. M. Bosch[1], W. T. M. Stals[1], M. D. Bijker[1],
P. J. van den Oever[2], W. M. M. Kessels[2*,†] and M. C. M. van de Sanden[2]
[1]*OTB Solar, P.O. Box 7108, 5605 JC Eindhoven, The Netherlands*
[2]*Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands*

High-quality surface and bulk passivation of crystalline silicon solar cells has been obtained under optimum anti-reflection coating properties by silicon nitride (a-SiN$_x$:H) deposited at very high deposition rates of ~5 nm/s. These a-SiN$_x$:H films were deposited using the expanding thermal plasma (ETP) technology under regular processing conditions in an inline industrial-type reactor with a nominal throughput of 960 solar cells/hour. The low surface recombination velocities (50–70 cm/s) were obtained on p-type silicon substrates (8·4 Ω cm resistivity) for as-deposited and annealed films within the broad refractive index range of 1·9–2·4, which covers the optimum bulk passivation and anti-reflection coating performance reached at a refractive index of ~2·1. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS: silicon nitride; deposition rate; solar cells; anti-reflection coating; surface passivation; bulk passivation; industrial reactor

INTRODUCTION

Silicon nitride (a-SiN$_x$:H) has become the state-of-the-art anti-reflection coating for crystalline silicon solar cells as, ideally, this coating not only reduces reflection losses, but simultaneously provides surface and bulk passivation. The current challenges are, however, reaching an optimum level of both surface

* Correspondence to: W. M. M. Kessels, Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
†E-mail: w.m.m.kessels@tue.nl

Contract/grant sponsors: Netherlands Ministry of Economic Affairs; Netherlands Ministry of Education, Culture and Science; Netherlands Ministry of Public Housing, Physical Planning and Environment; Royal Netherlands Academy of Arts and Sciences.

Received 24 December 2004
Revised 29 January 2005

Copyright © 2005 John Wiley & Sons, Ltd.

and bulk passivation under optimum anti-reflection coating performance as well as depositing the a-SiN_x:H at high deposition rates.

The combination of lowering the reflection losses and passivating bulk defects by the a-SiN_x:H is already inevitable for reaching state-of-the-art, optimized efficiencies for multicrystalline silicon solar cells, which dominate today's solar cell market.[1] However, with the current trend towards thinner silicon solar cell substrates and high-efficiency solar cell schemes,[2] passivation of the (front and back) surface will also become important for multicrystalline silicon solar cells. Surface passivation can be achieved by a-SiN_x:H films,[3] but optimal levels of surface passivation are generally achieved for films with a refractive index $n \geqslant 2{\cdot}4$, which, as a consequence, show considerable absorption in the ultraviolet part of the solar spectrum. For this reason, present surface passivation schemes used in industry for monocrystalline silicon solar cells still often involve thermal oxides (requiring a long processing time), possibly combined with an a-SiN_x:H anti-reflection coating to reduce reflection losses.[4,5] Therefore, it is obvious that the photovoltaic community is persistent in their efforts to combine high-quality bulk and surface passivation and optimized anti-reflection properties in one single a-SiN_x:H film.

The second challenge, i.e., depositing the a-SiN_x:H films at high deposition rates, is probably as important from a cost-perspective. To achieve economies of scale, high production throughputs are required for solar cell manufacturing, while these should be obtained with minimal investments in production equipment. Improving throughput by simply duplicating the number of production lines is, consequently, not a preferable option. Instead, by employing a technique with a high deposition rate, high production volumes can be achieved using equipment with a relatively small footprint and decreased (costly) vacuum volume.

In this present work, the main focus will be on obtaining a high-quality surface passivation by depositing a-SiN_x:H in an industrial reactor under conditions applicable for 'standard' industrial-type solar cells such as, e.g., screen-printed multicrystalline silicon solar cells. The level of surface passivation is usually expressed in terms of effective surface recombination velocity S_{eff}, as reached on low-resistivity float zone silicon wafers (generally p-type). In laboratory-scale experiments, values of S_{eff} as low as 4 cm/s have been obtained[6] for Si-rich films ($n = 2{\cdot}3$–$2{\cdot}4$) while higher S_{eff} values are found when going to a lower refractive index.[7,8] An exception to this trend has been found by Schmidt *et al.*[9] who achieved the lowest S_{eff} for stochiometric films (<10 cm/s for $n = 1{\cdot}9$) in a standard laboratory reactor. This different passivation behavior was attributed to the admixing of a significant amount of nitrogen gas to the commonly used reactant mixture of silane and ammonia. For industrial(-like) inline reactors, the general trend of a decreasing S_{eff} with increasing refractive index is also observed. However, recently fairly high levels of surface passivation have also been reported for a-SiN_x:H films with a commercially interesting refractive index (~50 cm/s for $n = 2{\cdot}0$–$2{\cdot}1$) deposited in a reactor with a microwave plasma source.[10,11] In a similar reactor, Winderbaum *et al*.[12] found the highest level of surface passivation for a-SiN_x:H with a low refractive index ($n = 1{\cdot}9$), but only after thermal treatment. Their as-deposited a-SiN_x:H showed almost no surface passivation irrespective of the refractive index of the films. It is important to note that these results[9–12] were all obtained for a-SiN_x:H films deposited at deposition rates well below 1 nm/s.

In this article we will show that a-SiN_x:H films deposited in an *industrial* inline PECVD system employing the expanding thermal plasma (ETP) technique can achieve good surface passivation as well as excellent bulk passivation and reduction of reflection losses with a *single* a-SiN_x:H film deposited at very high deposition rates of ~5 nm/s.

HIGH-RATE DEPOSITION WITH EXPANDING THERMAL PLASMA

The expanding thermal plasma (ETP) technique is renowned for the high deposition rates that can be achieved for films of various materials, including a-SiN_x:H.[13,14] The reason that these high deposition rates can be achieved is due to the fact that plasma production takes place in an upstream plasma source operated at sub-atmospheric pressure. At this high pressure, plasma production is very effective (with ionization degrees up to 10% and dissociation degrees up to 100% when molecular gases are used). This results in large flows of reactive ions and/or neutrals once the plasma expands into a downstream, low-pressure region. In this region, the large 'amount of reactivity' can be used to dissociate large flows of deposition precursor gases such as NH_3 and SiH_4

Copyright © 2005 John Wiley & Sons, Ltd.

for a-SiN_x:H. The downstream pressure is typically 20 Pa (comparable to other plasma techniques) and is sufficiently low to avoid heavy gas phase polymerization. Besides the high deposition rates, the ETP technique has also other advantages: due to the pressure difference, the plasma source is not affected by the downstream conditions, which prevents drift in operation. Also the fact that the source is dc operated is beneficial in this respect. The 'remote' nature of the ETP technique also allows for easier optimization of processing conditions and more freedom in reactor and substrate design and size. Finally, ion bombardment of the substrate is virtually absent as there is no electrical power coupling into the downstream plasma.

The application of the ETP technology for depositing anti-reflection coatings on silicon solar cells has been investigated for N_2–SiH_4 and NH_3–SiH_4 reactant mixtures. Initial studies revealed that the technique was capable of reducing reflection losses[13] and inducing bulk passivation.[14] Evidence for bulk passivation was obtained by local internal quantum efficiency (IQE) measurements, however, the level of bulk passivation still lagged behind compared to state-of-the-art a-SiN_x:H films used as a reference. Apart from poor uniformity (caused by the use of only one plasma source in a non-optimized laboratory reactor), the mass density of the films turned out to be a critical parameter as a clear correlation was observed between the level of bulk passivation reached and the mass density of the a-SiN_x:H.[15] Although increasing the mass density of a-SiN_x:H films is not trivial for high deposition rates, high mass densities (up to 2·5 g/cm^3) have finally been reached after elaborate optimization studies and by implementing the ETP technique in an industrial inline PECVD reactor. This is the so-called DEP*x* system (OTB Solar)[16] that is also used in this study.

As schematically depicted in Figure 1, in the DEP*x* silicon solar cell wafers are placed on carriers which are propelled electromagnetically through different reactor zones. The carriers, which can hold 2×2 solar cell wafers with a size of $15{\cdot}7 \times 15{\cdot}7$ cm each, are first heated to the desired deposition temperature (typically 400–450°C) by infrared radiation in the pre-heating zone. Subsequently, the solar cell wafers enter the deposition zone containing three ETP plasma sources operated on pure Ar and a typical d.c. current of 40–70 A.[16] The process gases NH_3 and SiH_4 are injected into the plasma jet emanating from the ETP source and are cracked down into reactive growth precursors leading to an a-SiN_x:H film with a uniformity of $\pm 2{\cdot}5\%$ over the total carrier width. The deposition zone is kept at a pressure of $\sim$20 Pa by a two-stage rootsblower system with a high pumping capacity. The deposition temperature is maintained constant by infrared radiation until the solar cell wafers enter the cooling zone. The throughput of the system is 960 solar cell wafers/h, corresponding to a typical a-SiN_x:H deposition rate of $\sim$5 nm/s.

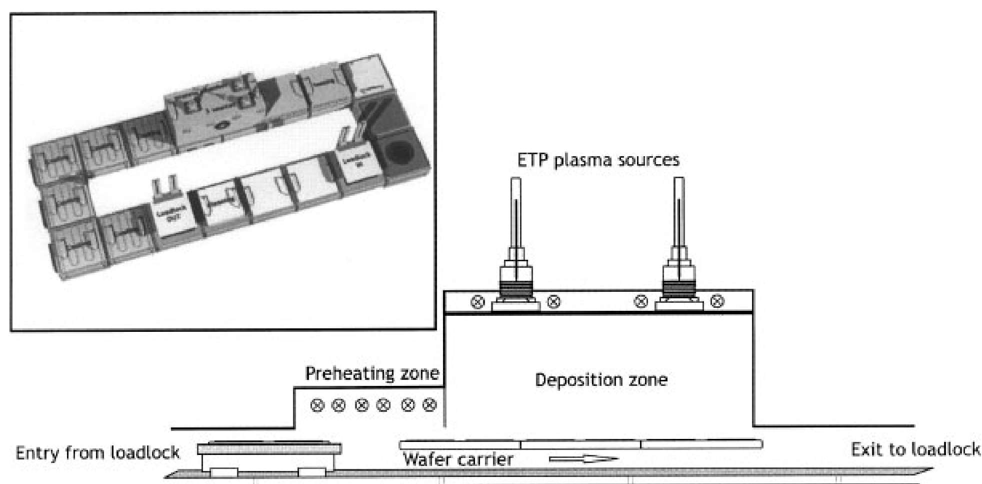

Figure 1. Schematic cross-section of the DEP*x* inline a-SiN_x:H deposition system showing the pre-heating zone, deposition zone with expanding thermal plasma sources, and cooling zone. As indicated in the figure, the wafer carriers are propelled individually, but in the depositing zone the carriers are lined up such that deposition on the carriers takes place in a continuous process. The inset shows a schematic overview of the DEP*x* system

Copyright © 2005 John Wiley & Sons, Ltd.

BULK AND SURFACE PASSIVATION UNDER OPTIMUM ANTI-REFLECTION COATING CONDITIONS

With the DEP*x* system, multicrystalline silicon solar cells with an a-SiN$_x$:H anti-reflection coating have been produced using a standard industrial process involving contact screen-printing, an aluminum back surface field, and surface texturing. In Figure 2 the efficiency of the solar cells is shown for the high-mass-density a-SiN$_x$:H films deposited at deposition temperatures in the range of 300–425°C. This figure shows that efficiencies up to 15·3% have been obtained (as averaged over 10 solar cells) when a-SiN$_x$:H with a mass density of 2·45 g/cm^3 is used.[17] These solar cells results show that the very high-rate deposited a-SiN$_x$:H films can compete with low-rate ($\ll$1 nm/s) a-SiN$_x$:H films yielding a top solar cell efficiency of 15·5% in a reference experiment. Furthermore, Figure 2 again confirms our previous proposition that high mass densities are essential for obtaining a high level of bulk passivation and, therefore, for obtaining high-efficiency multicrystalline silicon solar cells.[15,18]

The surface passivation induced by the a-SiN$_x$:H films deposited by the DEP*x* system has been investigated without further optimization of the deposition process. To this end, the carrier lifetime was measured in double-polished *p*-type float zone silicon wafers with (100) surface orientation, a resistivity of 8·4 Ω cm, and a thickness of 380 μm. The wafers were cleaned using a standard RCA clean, followed by a HF dip, and were coated on both sides with an identical a-SiN$_x$:H film of 50–80 nm thickness. The carrier lifetime was measured using a contactless inductively coupled photoconductance tester (Sinton Consulting, WCT100) that was used in both photoconductance decay mode (PCD) as well as in quasi-steady-state photoconductance (QSSPC) mode in which the reflectivity of the wafers was taken into account.[19] A typical lifetime measurement as a function of the injection level is shown in Figure 3, which reveals that lifetimes up to 350 μs can be reached for the high-rate deposited a-SiN$_x$:H. In this figure also data is given for the lifetimes obtained after a high-temperature (>750°C) firing step of the a-SiN$_x$:H in a standard metallizaton firing furnace revealing the thermal stability of the material. From the lifetime measurements the effective surface recombination velocity S_{eff} was calculated for a typical injection level of 2–5 $\times$ 10^{14} cm^{-3} by assuming a realistic bulk lifetime[20] of 4 ms.[20] Upper and lower error margins for S_{eff} were evaluated assuming an infinite bulk lifetime and the lower lifetime limit of 2 ms for the Si material, respectively. The surface recombination velocity has been determined for as-deposited

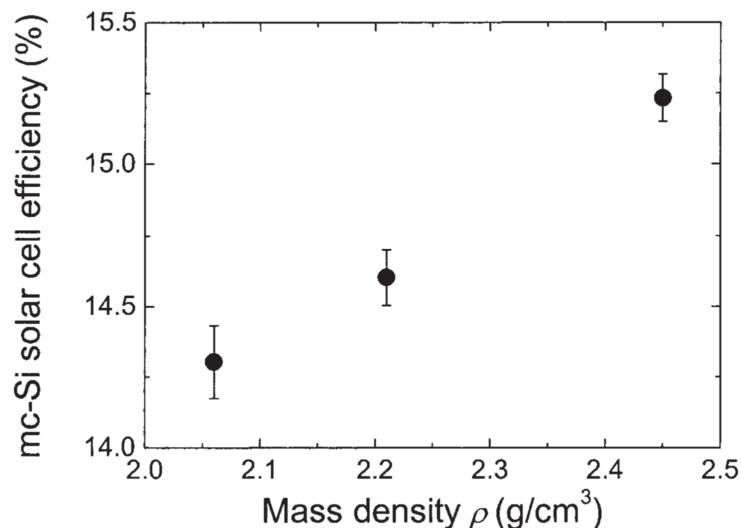

Figure 2. Efficiency of multicrystalline silicon solar cells (averaged over 10 cells) as a function of the mass density ρ of the a-SiN$_x$:H antireflection coating.[17] The mass density of the a-SiN$_x$:H films, measured by Rutherford backscattering analysis, is varied by the changing the deposition temperature of the solar cells from 300 to 425°C. The thickness of the films was tuned such that the reflectivity of the solar cells was minimized for small changes in refractive index

Copyright © 2005 John Wiley & Sons, Ltd.

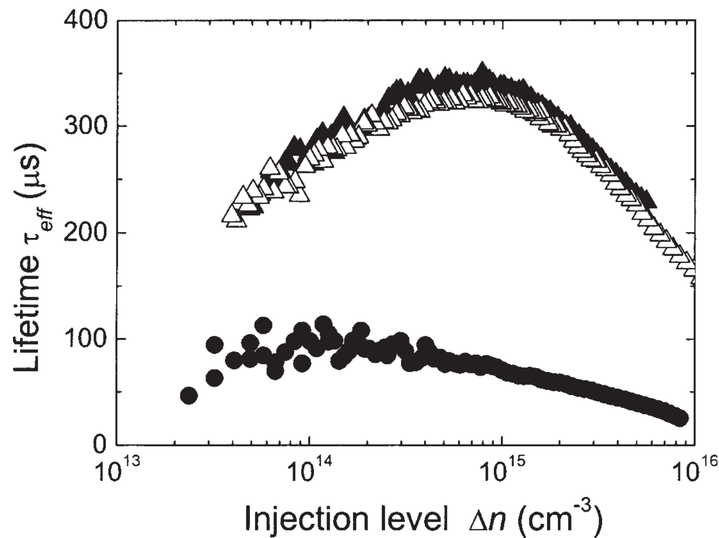

Figure 3. The effective carrier lifetime τ_{eff} as a function of the injection level Δn of a-SiN$_x$:H passivated *p*-type float zone Si wafers (8·4 Ω cm resistivity). Results are given for an a-SiN$_x$:H film deposited at a temperature of ~350°C (closed circles) and for an a-SiN$_x$:H film deposited at a temperature of ~425°C before (closed triangles) and after (open triangles) a standard industrial firing process. The refractive index of both films is ~2·2

a-SiN$_x$:H films with a refractive index ranging from 1·9 to 2·7, obtained by changing the NH_3/SiH_4 ratio in the plasma. The refractive index as well as the absorption coefficient and film thickness were determined by means of spectroscopic ellipsometry (Woollam M2000) over a photon energy range of 0·7–5·0 eV. The ellipsometry data were analyzed by a simple two-layer optical model (bulk film with surface roughness) and using the Tauc–Lorentz formalism.[21] In Figure 4(a) the values of S_{eff} are shown as a function of the refractive index of the films at a photon energy of 2 eV. The corresponding anti-reflection coating performance for optimized film thickness was determined[22] from the films' optical properties by calculating the absorption and reflection losses weighted over the air mass global 1·5 solar spectrum range (360–1100 nm). These results are shown in Figure 4(b).

The surface recombination velocities S_{eff} obtained range from ~50 to ~425 cm/s and are more than one order of magnitude lower compared with the best reported values for ETP deposited a-SiN$_x$:H so far.[13] Interestingly, the lowest S_{eff} values are reached for the refractive index range of $n = 1·95–2·4$ in which S_{eff} is basically constant. This range is the most appropriate for solar cell applications while for the widely applied refractive index of $n = 2·1$ S_{eff} is comparable to the state-of-the-art S_{eff} values obtained in other industrial-type reactors for somewhat lower resistivity wafers.[10–12] An important difference between the a-SiN$_x$:H films is, however, that the films deposited by the ETP technique in the DEP*x* reactor are deposited at significant higher deposition rate of ~5 nm/s. Figure 4(a) also shows directly the impact of the deposition temperature on the level of surface passivation obtained. S_{eff} increases significantly (from 60 to 180 cm/s) when the deposition temperature is decreased from 425 to 350°C. As mentioned earlier, such a large effect was also observed for the level of bulk passivation (see Figure 2)[14] and it possibly indicates that a high mass density is also important for surface passivation. Furthermore, it has to be mentioned that the unexpected increase in S_{eff} when going to a refractive index $n > 2·4$ can possibly be attributed to the fact that no process optimization for the deposition of these high-index a-SiN$_x$:H films has taken place.

When combining the data on the surface recombination velocity with the reflection and absorption losses induced by the a-SiN$_x$:H films under glass, it is clear that a good level of surface passivation can be obtained under conditions where simultaneously optimum antireflection coating performance can be reached ($n = \sim 2·1$). These conditions also yield a high level of bulk passivation for multicrystalline silicon solar cells as recently reported in a separate study.[17]

Copyright © 2005 John Wiley & Sons, Ltd.

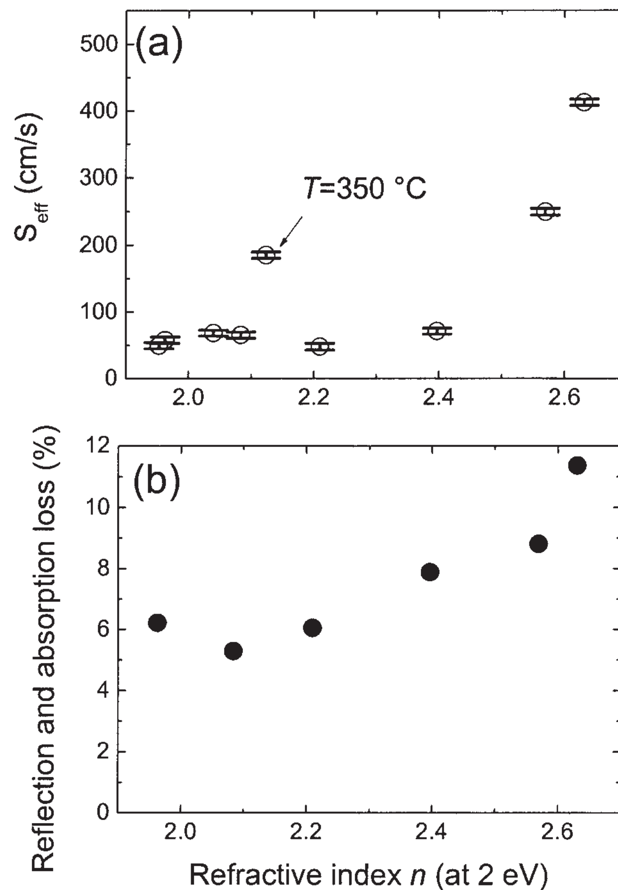

Figure 4. (a) The effective surface recombination velocity S_{eff} at an injection level of $2\text{–}5 \times 10^{14}\,cm^{-3}$; (b) the calculated loss by reflection and absorption of the a-SiN_x:H under glass, using the method of Doshi *et al.*[22] as a function of the refractive index n of the a-SiN_x:H at a photon energy of 2 eV. Due to the small size the error bars are omitted. All a-SiN_x:H films have been deposited on ~425°C, apart from the film for which the temperature is indicated

CONCLUSIONS

It has been shown that a-SiN_x:H films deposited with an industrial inline PECVD reactor employing the expanding thermal plasma technique lead to relatively low surface recombination velocities of 50–70 cm/s on 8·4 Ω cm *p*-type c-Si wafers. These results are achieved for a broad refractive index range of $n = 1{\cdot}95\text{–}2{\cdot}4$ and are not affected by a standard industrial firing process. The combination of these results with the optical properties of the films and with the results on multicrystalline silicon solar cells shows that a good level of surface and bulk passivation can be reached simultaneously under optimal anti-reflection coating conditions, and even for very high deposition rates of ~5 nm/s. Furthermore, the results show once again that a high a-SiN_x:H film density is key for solar cell applications.

Acknowledgements

This study has been carried out within the E.E.T. 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

Copyright © 2005 John Wiley & Sons, Ltd.

Planning and Environment. The research of W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

REFERENCES

1. Willeke GP. The crystalline silicon solar cell—history, achievements and perspectives. *Proceedings of the 19th European Photovoltaic Solar Energy Conference*, Paris, 2004; 383–386.
2. Schultz O, Glunz SW, Willeke GP. Multicrystalline silicon solar cells exceeding 20% efficiency. *Progress in Photovoltaics: Research and Applications* 2004; **12**(7): 553–558. DOI: 10.1002/pip.583
3. Aberle AG. Surface passivation of crystalline silicon solar cells: a review. *Progress in Photovoltaics: Research and Applications* 2000; **8**(5): 473–487. DOI: 10.1002/1099–159X(200009/10)8:5 < 473::AID-PIP337 > 3.0.CO;2-D
4. Zhao JH, Wang AH, Green MA, Ferrazza F. 19·8% efficient 'honeycomb' textured multicrystalline and 24·4% monocrystalline silicon solar cells. *Applied Physics Letters* 1998; **73**(14): 1991–1993. DOI: 10.1063/1.122345
5. Mulligan PM, Rose DH, Cudzinovic MJ, de Ceuster DM. Manufacture of solar cells with 21% efficiency. *Proceedings of the 19th European Photovoltaic Solar Energy Conference*, Paris, 2004; 387–390.
6. Lauinger T, Schmidt J, Aberle AG, Hezel R. Record low surface recombination velocities on 1 Ω cm *p*-silicon using remote plasma silicon nitride passivation. *Applied Physics Letters* 1996; **68**(9): 1232–1234. DOI: 10.1063/1.115936
7. Lauinger T, Moschner J, Aberle AG, Hezel R. Optimization and characterization of remote plasma-enhanced chemical vapor deposition silicon nitride for the passivation of *p*-type crystalline silicon surfaces. *Journal of Vacuum Science and Technology A—Vacuum Surfaces and Films* 1998; **16**(2): 530–543. DOI: 10.1116/1.581095
8. Schmidt J. Measurement of differential and actual recombination parameters on crystalline silicon wafers. *IEEE Transactions on Electron Devices* 1999; **46**(10): 2018–2025.
9. Schmidt J, Kerr M. Highest-quality surface passivation of low-resistivity *p*-type silicon using stoichiometric PECVD silicon nitride. *Solar Energy Materials and Solar Cells* 2001; **65**(1–4): 585–591. DOI:10.1016/S0927-0248(00)00145-8
10. Weeber AW, Rieffe HC, Sinke WC, Soppe WJ. Structural and passivating properties of SiN_x:H deposited under different precursor gases. *Proceedings of the 19th European Photovoltaic Solar Energy Conference and Exhibition*, Paris, 2004; 1005–1008.
11. Moschner JD, Henze J, Schmidt J, Hezel R. High-quality surface passivation of silicon solar cells in an industrial-type inline plasma silicon nitride deposition system. *Progress in Photovoltaics: Research and Applications* 2004; **12**(1): 21–31. DOI: 10.1002/pip.523
12. Winderbaum S, Cuevas A, Chen F, Tan J, Hanton K, Macdonald D, Roth K. Industrial PECVD silicon nitride: surface and bulk passivation of silicon. *Proceedings of the 19th European Photovoltaic Solar Energy Conference*, Paris, 2004; 576–579.
13. Kessels WMM, Hong J, van Assche FJH, Moschner JD, Lauinger T, Soppe WJ, Weeber AW, Schram DC, van de Sanden MCM. High-rate deposition of a-SiN_x:H for photovoltaic applications by the expanding thermal plasma. *Journal of Vacuum Science & Technology A-Vacuum Surfaces and Films* 2002; **20**(5): 1704–1715. DOI: 10.1116/1.1497992
14. Hong J, Kessels WMM, van Assche FJH, Rieffe HC, Soppe WJ, Weeber AW, van de Sanden MCM. Bulk passivation of multicrystalline silicon solar cells induced by high-rate-deposited ($>$1 nm/s) silicon nitride films. *Progress in Photovoltaics: Research and Applications* 2003; **11**(2): 125–130. DOI: 10.1002/pip.468
15. Hong J, Kessels WMM, Soppe WJ, Weeber AW, Arnoldbik WM, van de Sanden MCM. Influence of the high-temperature 'firing' step on high-rate plasma deposited silicon nitride films used as bulk passivating antireflection coatings on silicon solar cells. *Journal of Vacuum Science and Technology B, Microelectronics and nanometer structures: processing, measurement and phenomena* 2003; **21**(5): 2123–2132. DOI: 10.1116/1.1609481
16. Bosch RCM, Stals WTM, Van Erven AJM, Pennings RLJR, Bijker MD. High-throughput PECVD production tool for in-line silicon-nitride deposition on silicon solar cells. *Proceedings of the 19th European Photovoltaic Solar Energy Conference*, Paris, 2004; 1098–1102.
17. Van Erven AJM, Bosch RCM, Toelle R, Voigt O, Petri S, Bijker MD. Ultra high-rate ETP deposited silicon nitride for $>$15% in-line processed multicrystalline silicon solar cells. *Proceedings of the 31st Photovoltaic Specialists Conference and Exhibition*, Lake Buena Vista, 2005; (in press).
18. Kessels WMM, Oever PJ, Hoex B, Bosch RCM, Van Erven AJM, Bijker MD, van de Sanden MCM. Controlling the silicon nitride film density for ultrahigh-rate deposition of top quality antireflection coatings. *Proceedings of the 31st Photovoltaic Specialist Conference and Exhibition*, Lake Buena Vista, 2005; (in press).

Copyright © 2005 John Wiley & Sons, Ltd.

19. Sinton RA, Cuevas A. Contactless determination of current-voltage characteristics and minority-carrier lifetimes in semiconductors from quasi-steady-state photoconductance data. *Applied Physics Letters* 1996; **69**(17): 2510–2512. DOI: 10.1063/1.117723
20. Schmidt J, Aberle AG. Accurate method for the determination of bulk minority-carrier lifetimes of mono- and multicrystalline silicon wafers. *Journal of Applied Physics* 1997; **81**(9): 6186–6199. DOI: 10.1063/1.364403
21. Jellison GE, Modine FA. Parameterization of the optical functions of amorphous materials in the interband region. *Applied Physics Letters* 1996; **69**(3): 371–373. DOI: 10.1063/1.118064
22. Doshi P, Jellison GE, Rohatgi A. Characterization and optimization of absorbing plasma-enhanced chemical vapor deposited antireflection coatings for silicon photovoltaics. *Applied Optics* 1997; **36**(30): 7826–7837.

Copyright © 2005 John Wiley & Sons, Ltd.