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High-rate deposition of $a\text{-SiN}_x\text{:H}$ for photovoltaic applications by the expanding thermal plasma

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Driven by the need for improvement of the economical competitiveness of photovoltaic energy, the feasibility of high-rate (>1 nm/s) amorphous silicon nitride ($a\text{-SiN}_x\text{:H}$) deposited by the expanding thermal plasma (ETP) technique has been explored with respect to the application of the $a\text{-SiN}_x\text{:H}$ as functional antireflection coating on crystalline silicon solar cells. First, the deposition rate and the $a\text{-SiN}_x\text{:H}$ film properties, such as refractive index, Si, N, and H atomic density, and hydrogen bonding configurations, have been mapped for various operating conditions. From ellipsometry, elastic recoil detection, and infrared spectroscopy, it has been shown that deposition rates up to 20 nm/s can be reached with a fair film homogeneity and that the refractive index and the N/Si ratio can fully be tuned by the plasma composition while the hydrogen content can be controlled by the substrate temperature. Good antireflection coating performance of the $a\text{-SiN}_x\text{:H}$ has therefore been observed for monocrystalline silicon solar cells. These cells with ETP $a\text{-SiN}_x\text{:H}$ yielded only slightly lower conversion efficiencies than high-quality reference cells due to a much lower degree of surface passivation. This lack of surface passivation has also been shown in a separate study on the surface recombination velocity. Furthermore, it has been tested whether the $a\text{-SiN}_x\text{:H}$ films lead to silicon bulk passivation, which is essential for solar cells based on cheaper, defective silicon stock material such as multicrystalline silicon. It has been proven that bulk passivation of the cells is indeed induced by the high-rate ETP deposited $a\text{-SiN}_x\text{:H}$ after a high-temperature step in which the metal contacts of the cells are processed. These results make the ETP technique an interesting candidate for high-throughput processing of competitive silicon solar cells. © 2002 American Vacuum Society. [DOI: 10.1116/1.1497992]

I. INTRODUCTION

Hydrogenated amorphous silicon nitride $a\text{-SiN}_x\text{:H}$ deposited by plasma enhanced chemical vapor deposition (PECVD) has, besides a variety of applications in microelectronics,¹ an important application in photovoltaics. For crystalline silicon ($c\text{-Si}$) solar cells (either made from monocrystalline, multicrystalline, or ribbon silicon wafers) the application of a thin $a\text{-SiN}_x\text{:H}$ film can in principle meet three purposes at once.^{2,3} First of all, the combination of the refractive index n of $a\text{-SiN}_x\text{:H}$, which is in the range of $\sim 1.8\text{--}2.5$, together with its relatively high band gap ($\sim 2\text{--}5$ eV) makes the material very well suited as antireflection (AR) coating. The refractive index of $a\text{-SiN}_x\text{:H}$ can easily be optimized for optimal AR performance and it makes the

material a good alternative for the conventionally applied titaniumoxide (TiO_x) AR coatings ($n \sim 2.3$) fabricated by atmospheric pressure CVD (APCVD). Second, $a\text{-SiN}_x\text{:H}$ films can reduce the recombination of charge carriers at the surface of solar cells. This surface passivation effect, which is not obtained by TiO_x films, is especially important for high efficiency and very thin $c\text{-Si}$ solar cells. The $a\text{-SiN}_x\text{:H}$ is therefore preferred over a thermally grown oxide (SiO_2) which leads to excellent surface passivation but which does not provide efficient AR performance because of its low refractive index ($n \sim 1.46$).^{4,5} Furthermore, thermal SiO_2 formation requires high processing temperatures ($>800^\circ\text{C}$) while PECVD of $a\text{-SiN}_x\text{:H}$ can take place at relatively low temperatures ($200\text{--}400^\circ\text{C}$). This reduces production costs and prevents thermal damage to solar cell devices. Third, the application of $a\text{-SiN}_x\text{:H}$ can lead to hydrogen passivation of impurities, defects, and grain boundaries in the Si bulk which is an important issue for multicrystalline silicon mc-Si and ribbon Si solar cells. Despite the lower efficiencies of these

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types of cells compared to monocrystalline Si cells, they are the most promising candidates in $c\text{-Si}$ solar technology for the next decades because of the lower material costs. The hydrogen passivation occurs by atomic hydrogen either present during the deposition process of the $a\text{-SiN}_x\text{:H}$ film itself or by hydrogen released from the $a\text{-SiN}_x\text{:H}$ film during high temperature steps after deposition, e.g., during firing of the metal contacts.^{6–11} It is obvious that this hydrogen bulk passivation does not take place when thermally grown TiO_x and SiO_2 layers are applied.

The nonstoichiometric $a\text{-SiN}_x\text{:H}$ is clearly a very important material for the $c\text{-Si}$ solar cell technology.³ The application of $a\text{-SiN}_x\text{:H}$ with respect to the three above-mentioned purposes has different demands on the properties of the material which depend strongly on the atomic composition of the film in terms of concentrations of N, Si, and H. For AR coatings, $a\text{-SiN}_x\text{:H}$ requires a refractive index between 2.0 and 2.3 while the thickness should be in the range of 70–80 nm (optimum AR coating for unencapsulated cell: 80 nm thick with $n=2.0$; encapsulated cell: 70 nm thick with $n=2.3$).¹² To obtain optimum surface passivation for the cells, generally $a\text{-SiN}_x\text{:H}$ is required with an even higher refractive index ($n \geq 2.3$).^{2,4,13,14} However, for such films considerable light absorption takes place and therefore a compromise between a high surface passivation quality and weak absorbing AR coating is generally obtained for films with $n \approx 2.2$.² So, contrary to the applications of silicon nitride in microelectronics that generally require very N-rich silicon nitride with superior dielectric behavior, a refractive index of ~ 1.8 , and a N/Si ratio equal to the stoichiometric limit of 1.33,^{1,15} photovoltaic applications require generally only slightly N-rich and even Si-rich $a\text{-SiN}_x\text{:H}$ films. For achieving optimum bulk passivation by the $a\text{-SiN}_x\text{:H}$, real requirements for the $a\text{-SiN}_x\text{:H}$ are not yet known for the moment, however, it is evident that the $a\text{-SiN}_x\text{:H}$ films should contain a sufficient hydrogen concentration to make hydrogen diffusion into the mc-Si or ribbon Si cells possible.

Because the application of $a\text{-SiN}_x\text{:H}$ is an additional process step in the production of solar cells, which itself is part of the highly competitive energy market, there are some very strict technological and economic requirements on the $a\text{-SiN}_x\text{:H}$ production techniques. Most plasma-assisted deposition techniques use gas mixtures of silane (SiH_4) and ammonia (NH_3) which are generally decomposed by low-frequency (10–500 kHz, lf-PECVD) or radio-frequency (13.56 MHz, rf PECVD) excitation in a capacitively coupled parallel plate plasma reactor.¹ In addition to these direct plasma techniques, recently also more remote types of plasmas have gained importance, such as microwave plasmas (2.45 GHz)^{13,16} and inductively coupled plasmas.^{9,17} With respect to the AR performance, no clear preferences for a certain plasma technique have been revealed. This is probably due to the fact that only the optical properties and therefore the film composition is of importance for AR coatings and the film composition can usually easily be altered by the plasma composition. Good surface passivation has been obtained with both rf PECVD and remote microwave plasmas,

although remote techniques seem to have some significant advantages over the direct techniques in this respect.^{2,3,16,18} For example, a record low surface recombination velocity of the minority charge carriers has been obtained by a remote microwave PECVD technique (generally denoted as RPECVD).⁴ In this latter technique, microwave excited NH_3 is used to decompose downstream injected SiH_4 . On the other hand, lf PECVD has not yet been successful in depositing $a\text{-SiN}_x\text{:H}$ with good surface passivation properties mainly due to the poor UV stability of the films. This has been attributed to the severe ion bombardment of the film during the lf PECVD process creating interface defects.^{18–20} Bulk passivation has been reported for both direct techniques (lf PECVD²¹ and rf PECVD^{7,8}) as well as for remote microwave techniques.^{16,22,23}

Apart from the performance of the $a\text{-SiN}_x\text{:H}$, a general major economical concern is the processing time of the material, which is directly related to throughput and production costs. The deposition rate of $a\text{-SiN}_x\text{:H}$ is therefore a key issue in the application of the material in large-scale solar cell production.² For the above-mentioned techniques, deposition rates have been obtained of 0.05–0.15 nm/s for lf PECVD in a NH_3/SiH_4 plasma,¹⁹ 0.2 nm/s for rf PECVD in a NH_3/SiH_4 mixture,⁷ 0.25–0.5 nm/s for rf PECVD in a N_2/SiH_4 plasma, and ~ 1 nm/s for RPECVD with NH_3/SiH_4 mixtures.¹³

Increasing the deposition rate well over 1 nm/s has been the motivation for work described in this article. The feasibility of high-rate deposition of $a\text{-SiN}_x\text{:H}$ with a simultaneous fulfillment of the requirements on the film properties with respect to AR performance and surface and bulk passivation will be considered using the so-called “expanding thermal plasma” (ETP) method.²⁴ This is a remote plasma deposition technique which has proven to be capable of depositing good quality $a\text{-C:H}$ and $a\text{-Si:H}$ films (for thin film $a\text{-Si:H}$ solar cells) at rates of 60 nm/s (Ref. 25) and 10 nm/s,²⁶ respectively. These deposition rates are much higher than those obtained by conventional PECVD techniques. The high deposition rates that can be obtained with the ETP technique are directly related to the high production rate of reactive species, which is due to very efficient plasma creation in a high pressure plasma source (a cascaded arc thermal plasma source). Other advantages of the technique are the absence of (energetic) ion bombardment and the fact that N_2 can simply be used instead of NH_3 . The latter is possible because the “strongly bonded” N_2 is easily dissociated in the thermal plasma source. Furthermore, the technique can easily be used in-line, either as a single wafer technique or as a line-source (comprising several cascaded arc plasma sources) for multiple wafer processing.

This article is organized as follows: in Sec. II the experimental setup is described as well as the film analysis techniques used. Section III deals with the results of the work in which first the deposition rate, structural and compositional film properties, and film homogeneity will be treated (Sec. III A). This is followed by investigations on the AR working of the material (Sec. III B) and surface passivation (Sec.

FIG. 1. Expanding thermal plasma (ETP) setup for $a\text{-SiN}_x\text{:H}$ deposition at high rates. The distance between plasma source and substrate holder is either 35 or 70 cm. The figure is not to scale.

III C) and bulk passivation (Sec. III D) performance. The AR performance and surface passivation have been investigated on mono-Si wafers and cells and are compared by reference measurements on $a\text{-SiN}_x\text{:H}$ films deposited at the Institut für Solarenergieforschung Hameln-Emmerthal (ISFH) in Germany. The bulk passivation experiments has been investigated for industrial mc-Si solar cells that were processed by the Energy Research Center of the Netherlands (ECN Solar Energy).

II. EXPERIMENT

A. Experimental setup

The ETP setup is schematically illustrated in Fig. 1. It consists of a dc operated high-pressure cascaded arc plasma source²⁷ and a low-pressure deposition reactor. The cascaded arc has three cathodes and an anode plate with nozzle and these are separated by a stack of ten plates with a central aperture of 4 mm in diameter (plasma channel). The “cascaded” plates are electrically insulated by boron nitride and polyvinylchloride spacers. All other parts are made from copper, except the cathode tips which are made from tungsten with 2% lanthanum. All copper parts are water cooled and o-rings are used for vacuum sealing. The cascaded arc is

TABLE I. Discharge parameters of the ETP for $a\text{-SiN}_x\text{:H}$ deposition at high deposition rates.

Arc current	45 A
Arc voltage	180–210 V
Arc pressure	40 kPa
Ar flow	55 sccs
N ₂ flow	10 sccs
H ₂ flow	0–5 sccs
SiH ₄ flow	1–15 sccs
Downstream pressure	16–21 Pa
Substrate temperature	200–500 °C

operated at subatmospheric pressure with a nondepositing gas mixture of Ar, H₂, and N₂ (99.999% purity) in the plasma channel. Through this channel a current is drawn between the three cathodes and the anode plate. Table I gives an overview of the gas flows [in sccs (standard cm³/s)] and other operating conditions. The plasma expands into the reactor chamber in which the pressure is kept at ~ 20 Pa by means of a stack of two roots blowers and a fore-pump (total pumping capacity at the reactor is ~ 1500 m³/h). The pressure drop at the arc source outlet leads to a supersonic expansion of the plasma into the reactor followed by a stationary shock at ~ 5 cm from the arc outlet. Behind the shock the expansion velocity is subsonic (typically 1000 m/s) and in this region precursor gases, such as SiH₄ in the present case, are injected. This is done by means of a stainless steel injection ring having a diameter of 7.5 cm and containing ten holes with a diameter of 1 mm each. The SiH₄ (99.995% purity) is dissociated by the reactive species emanating from the plasma source (mainly by ionic and atomic species, not by electrons^{28,29}) leading to deposition precursors. The diameter of the deposition reactor is 50 cm while the length can either be 80 or 115 cm by using an additional extension flange. Overnight the reactor is pumped by a turbo molecular pump reaching a base-pressure of $< 10^{-4}$ Pa.

Depending on the length of the chamber, the substrate holder's position is either 35 or 70 cm from the arc outlet. The substrate holder, schematically illustrated in Fig. 2, is a modified version of the one described in Ref. 26. The holder consists of a yoke and aluminum or copper substrate plates that carry the substrates. A substrate plate can be inserted into the reactor without venting it by means of a loadlock

FIG. 2. Schematic of (a) cross-sectional side view and (b) front view of the substrate holder which can handle substrates/wafers up to 10×10 cm². The front view shows a substrate plate onto which three substrates of 2.5×2.5 cm² have been clamped.

Fig. 3. Temperature of the substrate and substrate plate during plasma ignition. The set temperature of the yoke is 400 °C. The plasma is ignited at $t = 260$ s and shut off at $t = 450$ s. The temperature of the substrate plate is determined by a thermocouple in the plate, the temperature of the substrate is determined by ellipsometry.

chamber and magnetic transporter. The substrate plate is thereafter mechanically clamped onto the yoke. A substrate plate can hold substrates (or cells) with a size up to $10 \times 10 \text{ cm}^2$. The plates are also often used to hold three substrates with a size of $2.5 \times 2.5 \text{ cm}^2$ each. The substrates are mounted on the substrate plate by stainless steel clips.

The yoke has a copper head which can be resistively heated up to 500 °C (total heating power is 1 kW) while temperature control is performed by a proportional-integral-derivative (PID) controller. The copper head can also be cooled by means of a liquid N_2 flow and the combination of cooling and heating is used for accurate and fast temperature control of the yoke at relatively low operating temperatures.²⁵ The copper head of the yoke is thermally and electrically insulated from the rest of the yoke by means of a stainless steel heat resistance and ceramic (boron nitride) spacer, respectively. The electrical insulation makes the application of a dc or rf bias possible.

Because the ETP source usually delivers a heavy thermal load to the substrate holder, the thermal contact between yoke and substrate plate on one hand and the substrate plate and substrates on the other hand is optimized by a small helium backflow.^{25,30} The temperature control of the substrates has extensively been checked by means of a thermocouple in the substrate plate and by *in situ* ellipsometry on 0.5-mm-thick Corning 7059 glass substrates. The ellipsometry measurements enable real time monitoring of the substrate temperature after plasma ignition. A possible temperature change is observed by fringes in the ellipsometry data caused by thermal expansion of the substrate due to heating. In Fig. 3, the temperature increase is shown for a yoke temperature set at 400 °C. The figure shows a relatively small temperature rise despite the heavy thermal load delivered by the plasma.²⁵ Measurements at other yoke temperatures have revealed temperature changes of less than 15 °C for all conditions.

The substrates are screened from the plasma during plasma startup and during gas admixture by means of a stain-

less steel retractable shutter. This shutter is full automatically operated by means of a digital timer enabling precise control of the deposition time.

B. Film and solar cell analysis

The structural properties of the $a\text{-SiN}_x\text{:H}$ were analyzed on films approximately 300 nm thick that are deposited on p -type $c\text{-Si}$ substrates ($500 \mu\text{m}$, $2.5 \times 2.5 \text{ cm}^2$, $10\text{--}20 \Omega \text{ cm}$). The film analysis was performed by *ex situ* ellipsometry, infrared absorption spectroscopy, and elastic recoil detection (ERD). From the ellipsometry data the refractive index (at 2 eV) and film thickness were determined. Information on the hydrogen content and on its bonding configurations was obtained by absorption spectroscopy using a Fourier transform infrared (FTIR) spectrometer (Bruker Vector 22). For this analysis, the peak positions ω_0 and calibration constants K for the hydrogen stretching modes as determined from a detailed study for different $a\text{-SiN}_x\text{:H}$ alloys by Bustarret *et al.*³¹ were used: $\text{HSi-N}_2\text{Si}$ and $\text{H}_2\text{Si-NSi}$ at $\omega_0 = 2140 \text{ cm}^{-1}$ ($K = 1.1 \times 10^{20} \text{ cm}^{-2}$), $\text{H}_2\text{Si-N}_2$ at $\omega_0 = 2175 \text{ cm}^{-1}$ ($K = 4.0 \times 10^{20} \text{ cm}^{-2}$), HSi-N_3 at $\omega_0 = 2220 \text{ cm}^{-1}$ ($K = 2.0 \times 10^{20} \text{ cm}^{-2}$), NH at $\omega_0 = 3340 \text{ cm}^{-1}$ ($K = 1.2 \times 10^{20} \text{ cm}^{-2}$), NH_2 at $\omega_0 = 3450 \text{ cm}^{-1}$ ($K = 5 \times 10^{20} \text{ cm}^{-2}$). Information on the N, Si, and H atomic densities in the films was obtained from ERD measurements performed at the Utrecht University using a 54 MeV $^{65}\text{Cu}^{8+}$ beam.³²

The AR performance of the $a\text{-SiN}_x\text{:H}$ was investigated for monocrystalline 0.5 $\Omega \text{ cm}$ float zone Si p/n^+ solar cells with a 100 Ω/sq emitter. The contacts were evaporated and are of Al on the back and of Ti/Pd/Ag on the front. The cells were fabricated from 300- μm -thick 1.5 $\Omega \text{ cm}$ float zone Si substrates and have a size of $2.0 \times 2.0 \text{ cm}^2$. Standard current-voltage measurements under 1.5 AM sun with 100 mW/cm^2 were applied to investigate the solar cell performance.

Surface passivation induced by the $a\text{-SiN}_x\text{:H}$ was examined on float zone p -type $c\text{-Si}$ ($300 \mu\text{m}$, $2.5 \times 2.5 \text{ cm}^2$) with a low resistivity of 1.5 $\Omega \text{ cm}$. Also some substrates with phosphorous diffusion on both sides (sheet resistance 100 Ω/sq) were used for some experiments. All substrates were cleaned with a standard RCA-clean followed by a HF dip (2%, 30 s) and were subsequently deposited with $a\text{-SiN}_x\text{:H}$ at both sides. Information on the effective surface recombination velocity (SRV) was deduced from effective minority-carrier lifetime measurements by means of the microwave-detected photoconductance decay (MW-PCD) under 50 mW/cm^2 bias illumination.³³ Depending on the surface passivation quality this yielded a bulk charge injection level in the range of $10^{13}\text{--}10^{15} \text{ cm}^{-3}$. More details about this analysis and the determination of the effective surface recombination velocity can be found in Refs. 4 and 13.

Bulk passivation experiments were carried out together with ECN Solar Energy on industrial Baysix mc-Si (Bayer Solar GmbH) solar cells with a size of $10 \times 10 \text{ cm}^2$ and a thickness of $\sim 330 \mu\text{m}$. These cells have a diffused emitter with a sheet resistance of 50 Ω/sq . After deposition, the met-

TABLE II. Refractive index, deposition rate, film atomic concentrations of H, Si, and N, mass density and the hydrogen bonding configurations for the α -SiN_x:H films studied. The inaccuracy in the atomic concentrations is less than 5%.

SiH ₄ flow (sccs)	H ₂ flow (sccs)	Substrate temp. (°C)	Refractive index	Deposition rate (nm/s)	[H]		[Si]		[N]		Mass density (g/cm ³)	H bonding type
					(10 ²² cm ⁻³)	(at. %)	(10 ²² cm ⁻³)	(at. %)	(10 ²² cm ⁻³)	(at. %)		
15	5	400	2.7	35.5	1.26	18.4	3.92	57.3	1.67	24.3	2.24	~100% SiH
8	5	400	2.3	19.4	1.23	17.4	3.42	48.4	2.41	34.2	2.19	~100% SiH
4	5	400	2.2	13.2	1.20	16.4	2.83	38.6	3.30	45.0	2.12	~81% SiH ~19% NH
2	5	400	2.1	6.2	2.18	15.4	5.27	37.3	6.68	47.3	4.06	~100% NH _x ^a
1	5	400	2.0	4.0	1.87	16.6	4.32	38.2	5.10	45.2	3.24	~100% NH _x ^a
8	5	200	2.0	21.4	1.37	17.3	3.93	49.6	2.63	33.2	2.47	~80% SiH ~12% SiH ₂ ~8% NH
8	5	300	2.2	20.4	1.68	20.9	3.88	48.2	2.49	30.9	2.42	~67% SiH ~29% SiH ₂ ~4% NH
8	5	500	2.4	19.1	0.90	12.6	3.58	49.9	2.69	37.5	2.32	~100% SiH
8	3	400	2.3	20.4	1.28	18.3	3.26	46.4	2.48	35.3	2.12	~100% SiH
8	1	400	2.4	25.3	1.19	16.3	3.43	46.9	2.70	36.9	2.25	~90% SiH ~10% NH
8	0	400	2.5	31.8	1.39	17.3	3.74	46.5	2.91	36.2	2.45	~90% SiH ~10% NH

^aA quantification of the NH_x bondings in terms of NH and NH₂ has not been possible.

alization was screen-printed on the α -SiN_x:H AR coating and subsequently fired through the coating in an infrared lamp heated belt surface. The cell performance was measured with the class A solar simulator at ECN Solar Energy. Spectral response measurements in combination with reflectance measurements were used to calculate the internal quantum efficiency IQE of the cells.

III. RESULTS AND DISCUSSION

A. Structural and compositional film properties

To obtain insight into the film properties that can be obtained with the ETP technique, the structural and compositional properties of the high-rate deposited α -SiN_x:H films were analyzed for different plasma operating conditions. Three different parameter studies were performed starting from a “standard condition” (i.e., 10 sccs N₂, 5 sccs H₂, 8 sccs SiH₄ and a substrate temperature of 400 °C as decided on from some first experiments): a SiH₄ flow variation, a H₂ flow variation, and a substrate temperature variation. The N₂ flow was kept constant at 10 sccs for all experiments. The distance between cascaded arc plasma source and substrate holder was 35 cm for these experiments. The results of these measurements are summarized in Table II. The refractive index (at 2 eV) and deposition rate, which ranges from 4 to 35 nm/s, were determined by *ex situ* ellipsometry. The deposition rate is in very good agreement with the deposition rate obtained from interference fringes in the FTIR transmission data. The atomic concentrations of H, Si, and N were determined from the ERD analysis and these concentrations were used for the calculation of the mass density of the films. Insight in the H bonding configuration was obtained by the FTIR analysis using the calibration constants from Bustarret *et al.*³¹ given in Sec. II B. The FTIR data will be discussed in

more detail below, but it can already be mentioned that the agreement between the H concentration as determined by FTIR and ERD is within 25%, except for two cases where the samples contain a significant amount of NH₂ (absorption at ~3450 cm⁻¹). In these low-substrate temperature cases, the H content determined from the FTIR data appears to be too high. Such a difference is possibly due to the experimental accuracy and the dependence of the calibration constants on the overall film properties, as also suggested by the discrepancies in calibration constants reported in the literature.^{31,34,35} Furthermore, some weak NH_x absorption peaks observed for conditions with a low SiH₄ flow could not be attributed to a certain H bonding configuration unambiguously. This makes the subdivision of the NH_x bonds in terms of NH and NH₂ impossible for the data presented.

The data in Table II reveal that the SiH₄ flow is a very important parameter for the film properties. In Fig. 4, the deposition rate, refractive index, and N/Si ratio are displayed as a function of the SiH₄ flow. The deposition rate and particularly the Si growth flux (i.e., product of deposition rate and Si atomic film density) shows a linear increase with SiH₄ flow. The refractive index of the films is also strongly dependent on the SiH₄ flow. For both the 300 and 400 °C samples, the refractive index shows the same increasing trend with SiH₄ flow, while the refractive index is somewhat higher for the 400 °C samples as will be discussed below. The data show that the refractive index can be tuned in the range of ~1.8–2.7 by changing the SiH₄ flow. The ERD data in Fig. 4(c) reveal that the refractive index is directly coupled with the N/Si ratio in the film. The refractive index increases with decreasing N/Si ratio showing that the films can be changed from N-rich to Si-rich by increasing the SiH₄ flow for constant N₂ admixture in the arc. Moreover, the general trend is

FIG. 4. (a) Deposition rate, (b) refractive index, and (c) N/Si ratio as a function of SiH₄ flow for films deposited at substrate temperatures of 300 and 400 °C and with a H₂ flow of 5 sccs.

observed that the film density increases with the N/Si ratio.^{34,36}

The hydrogen content of the films is roughly 15%–18% and shows no clear dependence on the SiH₄ flow. The bonding configuration of the hydrogen is however strongly depen-

FIG. 5. Infrared spectra (a) for different SiH₄ flows with a substrate temperature of 400 °C and H₂ flow of 5 sccs and (b) for different substrate temperatures with a SiH₄ flow of 8 sccs and H₂ flow of 5 sccs. The absorption peak around 2350 cm⁻¹ caused by ambient CO₂ during the measurements has been removed. Furthermore, some spectra show influence of absorptions by ambient H₂O around 1600 and 3750 cm⁻¹.

FIG. 6. Atomic hydrogen density as determined from ERD analysis and from FTIR absorption spectroscopy ([SiH], [SiH₂], [NH]) for different substrate temperatures. The H₂ and SiH₄ flow are 5 and 8 sccs, respectively.

dent on the SiH₄ flow as indicated by the infrared vibrational spectra in Fig. 5(a). Concerning the hydrogen stretching modes, at low SiH₄ flows, there are only absorptions due to NH at 3340 cm⁻¹ and NH₂ at ~3450 cm⁻¹ while the origin of the shoulder at ~3230 cm⁻¹ is unclear but appears to be related to NH_x as well. Absorptions are also present around 1540 and 1170 cm⁻¹ due to NH₂ bending and NH wag-rocking modes, respectively.³¹ Furthermore, there appears to be an absorption at 490 cm⁻¹ at low SiH₄ flows, which has been attributed to NSi₃ symmetric stretching^{37,38} but also to distorted Si-Si cluster vibrations.³⁹ Si-N stretching modes are also directly related to the large absorption peak(s) ranging from 700 to 1050 cm⁻¹. In the literature,^{39–41} there is however still controversy about the exact origin of these absorptions and therefore these will not be considered in this article. When going to high SiH₄ flows on the other hand, the NH_x absorptions disappear almost completely and only H bonded as SiH is observed. The center of the SiH stretching absorption peaks shifts to lower wave numbers when going to more Si-rich material. This fact is well known³¹ and can be explained by the decrease in N backbonds for the SiH_x hydrides. It can therefore be concluded that there is a transition from an almost pure NH_x bonding configuration for low SiH₄ flows to an almost pure SiH_x bonding configuration for higher SiH₄ flows. This is in agreement with the transition from N-rich to Si-rich α -SiN_x:H as also observed in other studies.^{31,39} In summary, by changing the SiH₄ flow the refractive index and atomic composition can be fully tuned from N-rich to Si-rich. On basis of these and other data,²⁹ it is also expected that this tuning can be done by changing the N₂ flow for constant SiH₄ flow.

The influence of the substrate temperature was investigated in more detail for Si-rich samples deposited with 8 sccs SiH₄. In Table II, it can be seen that the deposition rate slightly decreases with increasing substrate temperature whereas the refractive index increases. This is not simply due to a densification of the material as follows from the Si and N density as well as from the mass density. The increase of the refractive index is presumably caused by the decreasing H density in the film as shown in Fig. 6. This figure also

shows the bonding configuration of the hydrogen based on the infrared data in Fig. 5(b). In Fig. 5(b), the spectra at temperatures of 200 and 300 °C show the NH wag-rocking mode and stretching mode at 1175 and 3340 cm^{-1} , respectively. For higher substrate temperatures no significant amount of hydrogen bonded to nitrogen can be observed showing that substrate temperatures above 300 °C are necessary to avoid NH bonded hydrogen, even for these “Si-rich conditions.” At lower substrate temperatures, the SiH_x stretching modes show also a shoulder at higher wave numbers which is most presumably due to SiH_2 bonded hydrogen. Furthermore, it is interesting that no absorption around 490 cm^{-1} appears for the low temperature films with a considerable absorption by NH. This is different from the trend observed for the films in Fig. 5(a).

All experiments discussed so far were performed with 5 sccs of H_2 admixed in the cascaded arc. The decision to work with H_2 is based on previous experience with the deposition of $a\text{-Si:H}$. Experiments with this material revealed that H_2 admixture in the arc is crucial for obtaining solar grade quality $a\text{-Si:H}$ for thin film solar cells with the ETP technique.^{26,42} The beneficial working of the H_2 admixture could be attributed to a lower ion flow from the cascaded arc making ion-induced dissociation of SiH_4 less important.^{28,42} In order to investigate whether the use of H_2 is also important for the deposition of $a\text{-SiN}_x\text{:H}$ the structural properties were analyzed for H_2 flows varying from 5 sccs down to 0 sccs. The SiH_4 flow and substrate temperature were kept constant at 8 sccs and 400 °C, respectively. As shown in Table II, lowering the H_2 flow down to zero, yields a slight increase in refractive index and a 50% increase in deposition rate. Furthermore, the atomic densities of Si, N, and H are higher for the condition with 0 sccs H_2 than for the conditions with H_2 admixture. The N/Si ratio is in the range of 0.7–0.8 and increases slightly when going to 0 sccs H_2 admixture. The infrared spectra for the different H_2 flows (data not shown) show no significant changes with H_2 flows except for the fact that the films at 0 and 1 sccs H_2 contain a considerable amount of NH bonded hydrogen (about 10%). This is in agreement with the fact that these films have also a relatively higher N/Si ratio. In summary, some changes of the film properties with H_2 flow are observed, however these changes are not as drastic as for the deposition of $a\text{-Si:H}$. On the basis of measurements and expectations on the plasma chemistry and film growth mechanism^{29,43} it has been decided to work with 5 sccs H_2 admixture throughout the following experiments.

As mentioned, the experiments discussed so far were carried out with a plasma source-substrate distance of 35 cm. This yields a relatively poor homogeneity of the film thickness and the aforementioned analysis of the film properties was therefore done on substrates with a size of only $2.5 \times 2.5 \text{ cm}^2$. However, for the application of the $a\text{-SiN}_x\text{:H}$ on solar cells, the deposition of homogeneous films on larger areas is required. For this reason, experiments on the film homogeneity were carried out with a reactor chamber having an extended plasma source-substrate distance of 70 cm. The

FIG. 7. Homogeneity of the (a) thickness and (b) refractive index as examined by ellipsometry for an $a\text{-SiN}_x\text{:H}$ film deposited on a monocrystalline silicon wafer with a diameter of 10 cm. The film has been deposited with a plasma source-substrate distance of 70 cm with the conditions: 4 sccs SiH_4 , 5 sccs H_2 , and substrate temperature of 400 °C.

$a\text{-SiN}_x\text{:H}$ was deposited onto monocrystalline Si wafers with a diameter of 10 cm and the homogeneity of both the thickness and refractive index was tested by *ex situ* ellipsometry. Figure 7 shows the results for the deposition condition with 4 sccs SiH_4 and the other parameters standard (see Table I, 5 sccs H_2 and substrate temperature of 400 °C). Figure 7(a) shows a thickness homogeneity of <8% within wafer which is considerable better than for a plasma source-substrate distance of 35 cm. As expected, the improvement has taken place at the cost of deposition rate which is now 9 nm/s for this condition instead of 13 nm/s. The homogeneity of the refractive index, which is <2% within wafer [Fig. 7(b)], is much better than the thickness homogeneity. The refractive index has also slightly been affected by increasing the plasma source-substrate distance: $n = 2.05$ instead of $n = 2.16$. Overall, these results on the homogeneity are reasonable and can certainly be used as a starting point. Apart from increasing the plasma source-substrate distance, for future optimization of the homogeneity the utilization of multiple cascaded arc plasma sources yields an interesting opportunity. Multiple cascaded arcs can either be implemented in a single-wafer deposition reactor or as a line-source in a reactor with moving wafers on a conveyor belt.

B. Antireflection coating performance

The reduction of the reflection of light at the solar cells' surface is the most essential feature of an $a\text{-SiN}_x\text{:H}$ AR

TABLE III. Solar cell parameters (100 mW/cm² illumination, AM1.5 spectrum) before and after deposition of the $a\text{-SiN}_x\text{:H}$ AR coating with the ETP technique. The data for every SiH₄ flow is an average value over two cells deposited under identical conditions. Reference measurements with $a\text{-SiN}_x\text{:H}$ deposited with a rf parallel plate capacitively coupled plasma at ISFH are also given.

	Film parameters:		Before antireflection coating:				After antireflection coating:			
	Refractive index	Thickness (nm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η (%)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η (%)
ETP	1.8	93	617	25.8	0.81	12.8	627	34.8	0.81	17.5
	1.9	84	615	25.7	0.81	12.7	628	35.0	0.81	17.7
	1.9	81	617	25.8	0.80	12.8	632	35.4	0.81	18.1
	2.0	75	615	25.3	0.80	12.5	631	34.6	0.80	17.5
			Average ETP:			12.7				17.7
ISFH	1.9	79	615	25.3	0.81	12.6	635	35.3	0.81	18.2
	2.0	75	615	26.2	0.79	12.8	639	35.5	0.81	18.4
	2.1	69	614	25.2	0.82	12.7	636	34.9	0.81	18.1
			Average ISFH:			12.7				18.2

coating because it can yield a gain in the solar cell's efficiency of several percents (absolute). To test the AR performance of the ETP $a\text{-SiN}_x\text{:H}$, a set of small area ($2 \times 2 \text{ cm}^2$) p/n^+ solar cells with a 100 Ω/sq emitter were produced with evaporated metal contacts on front and back (see Sec. II B). The performance of these cells was tested and subsequently the cells were coated with the ETP $a\text{-SiN}_x\text{:H}$. The experiments were carried out with a plasma source-substrate distance of 35 cm explaining the choice of the small area of the cells. During deposition, the substrate temperature was set at 400 °C while 5 sccs H₂, 10 sccs N₂, and four different SiH₄ flows were used. For comparison, three reference cells were produced with $a\text{-SiN}_x\text{:H}$ deposited at a substrate temperature 400 °C in a rf parallel plate reactor at ISFH.¹⁸ The conditions of these reference cells were chosen such that films with different values of the refractive index were obtained.

Table III shows the cell's parameters open circuit voltage V_{oc} , short circuit current I_{sc} , fill factor FF, and efficiency η before and after the application of the $a\text{-SiN}_x\text{:H}$ as measured under standard test conditions. The parameters of the cells coated with ETP deposited $a\text{-SiN}_x\text{:H}$ are averaged over two separate cells processed for each of the four conditions.

All cells in Table III show a large gain in current due to the AR working of the $a\text{-SiN}_x\text{:H}$ films. For the cells coated with the ETP technique, the increase in current is not quite as big than for the reference cells coated at ISFH but the film parameters of the ETP deposited $a\text{-SiN}_x\text{:H}$ coatings are not as well optimized yet. Further optimization is certainly possible and therefore the somewhat lower increase in current does not present a fundamental problem. Furthermore, the increase in V_{oc} , which can be caused by the increase in current as well as by surface passivation of the cell, is also not as large for the cells coated with the ETP as for the references. This seems mainly to be caused by the lower degree of surface passivation achieved with ETP $a\text{-SiN}_x\text{:H}$ (see Sec. III C). It is however clear from Table III that this leads only to a minor difference in cell efficiency. This difference would actually be even smaller on industrial-type solar cells, where a highly doped emitter is typically used to accommodate screen-printed front contacts. It can therefore

be concluded that the ETP deposited $a\text{-SiN}_x\text{:H}$ can successfully be applied as a high-rate deposited AR coating.

C. Surface passivation

The results in the previous section suggest that the ETP deposited $a\text{-SiN}_x\text{:H}$ films on monocrystalline Si solar cells do not lead to a high degree of surface passivation. At the moment, a high degree of surface passivation is mainly important for the very high efficiency solar cells but surface passivation by $a\text{-SiN}_x\text{:H}$ will gain gradually more importance when solar cells become thinner in order to reduce material costs. To test the degree of surface passivation obtained by the ETP deposited $a\text{-SiN}_x\text{:H}$, lifetime experiments were performed: the effective lifetime of the minority charge carriers in high quality, p -type float zone monocrystalline Si substrates with a low resistivity of 1.5 $\Omega \text{ cm}$ was measured after coating the substrates with $a\text{-SiN}_x\text{:H}$ at both sides. All depositions were performed with a H₂ and N₂ flow of 5 and 10 sccs, respectively, while the SiH₄ flow was varied from 1 to 15 sccs. A substrate temperature of 300 °C was used for most depositions but for the condition with 8 sccs SiH₄ also temperatures of 400 and 500 °C were applied. This condition with 8 sccs SiH₄ was explored in more detail because it turned out (see below) that this condition yields similar Si-rich material as the $a\text{-SiN}_x\text{:H}$ deposited at ISFH with a record low surface recombination velocity.⁴

In Fig. 8, the effective minority carrier lifetime is given for the substrates coated with $a\text{-SiN}_x\text{:H}$ under the different conditions. Data as obtained after treatment of the coated substrates with a forming gas anneal for 10 and 20 min at 400 °C are also given. The bias illumination level of the samples was 50 mW/cm². The figure shows that the effective lifetimes obtained are rather low corresponding with a relatively high surface recombination velocity of the charge carriers and therefore with a low degree of surface passivation. The effective lifetime shows however a slight optimum for the samples deposited with 8 sccs SiH₄. As addressed below, the structural properties of the $a\text{-SiN}_x\text{:H}$ under these conditions are comparable to those of the ISFH material with record low surface recombination. The highest effective life-

FIG. 8. Effective minority carrier lifetime under 50 mW/cm² bias illumination for $a\text{-SiN}_x\text{:H}$ films deposited by the ETP technique for different substrate temperatures and SiH_4 flows. The H_2 flow is 5 sccs. The figure shows results (a) for as-deposited films, (b) for films after a 10 min anneal at 400 °C, and (c) for films after 20 min anneal at 400 °C.

time (i.e., 18 μs) obtained for this condition corresponds with an effective surface recombination velocity slightly lower than 10^3 cm/s. This is much higher than the record low surface recombination velocity of 4 cm/s (corresponding to an effective lifetime of 1.6 ms)⁴ obtained with RPECVD coated cells after a forming gas anneal for 10 min at 400 °C.

The results reveal that the ETP $a\text{-SiN}_x\text{:H}$ deposited with a SiH_4 flow of 8 sccs yields the highest effective lifetime. Comparing this film's structural properties with those of the ISFH RPECVD deposited $a\text{-SiN}_x\text{:H}$ with a record low surface recombination velocity yields the following similarities: the refractive index of both the ETP deposited $a\text{-SiN}_x\text{:H}$ as well as of the ISFH material has a refractive index of ~ 2.3 .¹³ The N/Si ratio is 0.7 and the hydrogen content is 17% while for the ISFH $a\text{-SiN}_x\text{:H}$ these are between 0.7–0.8 and 16%–18%, respectively. The total mass density is however lower for the ETP $a\text{-SiN}_x\text{:H}$ (2.2 g/cm³ in comparison with about 2.6 g/cm³) indicating that the ETP deposited films may contain voids which possibly contribute to carrier recombination. The hydrogen bonding configuration is similar for both materials: almost no absorption due to NH vibrations (only very weak peak at the stretching frequencies) is observable and the hydrogen is mainly bonded as H–Si–N₂Si and/or H₂–Si–NSi. The peak positions for the SiH absorptions are somewhat lower in the ETP deposited material indicating that this material contains slightly less nitrogen.^{31,37} The ETP deposited $a\text{-SiN}_x\text{:H}$ is apparently relatively similar to the ISFH material, but despite these similarities, there is a large discrepancy in surface recombination velocities. The main difference is the deposition rate which is 20 nm/s for the ETP deposited material and only 0.25–0.5 nm/s for ISFH material deposited by rf PECVD and ~ 1 nm/s for ISFH $a\text{-SiN}_x\text{:H}$ deposited by RPECVD.

The lack of surface passivation obtained by the ETP deposited $a\text{-SiN}_x\text{:H}$ can either be a interface or bulk effect. To track down this problem, the following experiment has been conducted: samples were coated by a stack of two $a\text{-SiN}_x\text{:H}$

FIG. 9. Effective minority carrier lifetime for $a\text{-SiN}_x\text{:H}$ films consisting of a stack of ETP deposited $a\text{-SiN}_x\text{:H}$ on top of ISFH remote microwave-deposited $a\text{-SiN}_x\text{:H}$ (RPECVD $a\text{-SiN}_x\text{:H}$). The thickness of the RPECVD $a\text{-SiN}_x\text{:H}$ has been varied between 0 and 20 nm, the total $a\text{-SiN}_x\text{:H}$ thickness is ~ 80 nm. The ETP conditions are 5 sccs H_2 , 8 sccs SiH_4 , and a substrate temperature of 400 °C.

films. The bottom film directly on top of the sample, was deposited by RPECVD and has a thickness of either 0, 5, 10, or 20 nm (deposition rate: ~ 1 nm/s). The top film was deposited by the ETP technique using the above mentioned condition with 8 sccs SiH_4 (deposition rate: 20 nm/s) and its thickness was adjusted such that the total silicon nitride film thickness is about 80 nm. Figure 9 shows the effective lifetime obtained for these samples which clearly increases with increasing RPECVD film thickness. The figure shows that an effective lifetime of 238 μs can be obtained by a combination of 20 nm RPECVD and 60 nm ETP deposited $a\text{-SiN}_x\text{:H}$. This corresponds to an effective surface recombination velocity as low as 55 cm/s.

Important is, however, the increase of the effective lifetime with increasing thickness of the RPECVD material. This effect suggests that the lack of surface passivation for the ETP material is a bulk problem and it might therefore be correlated with the above mentioned lower atomic density of the ETP deposited films. An explanation by, e.g., contamination of the film by metal atoms (possibly originating from the cathodes of the plasma source) is unlikely because no metal contamination has been observed by nuclear profiling techniques (Rutherford backscattering with a detection limit $< 10^{13}$ cm⁻²).

As mentioned, for most industrial-type solar cells surface passivation is at the moment a much less important issue than for example antireflection performance and bulk passivation. This is also due to the fact that most of these cells have a diffused emitter for which the effect of surface passivation is already reduced.⁵ To test the effective minority carrier lifetime of the ETP deposited $a\text{-SiN}_x\text{:H}$ under these more industrially relevant conditions, lifetime measurements were carried out on phosphorous-diffused emitter samples having a sheet resistance of 40 Ω/sq (at both sides). The $a\text{-SiN}_x\text{:H}$ was deposited at both sides of the samples using the same conditions as mentioned above (i.e., 8 sccs SiH_4

and at a substrate temperature of 400 °C). This yielded an effective lifetime of 23 μs which is now indeed much closer to lifetime of the RPECVD deposited samples of 200 μs .

D. Bulk passivation

After the antireflection working, bulk passivation of the silicon is the most important feature of $a\text{-SiN}_x\text{:H}$ coatings for industrial-type solar cells so far. To reduce material costs, these type of cells are (in the future) mostly not made from good quality monocrystalline-silicon but from lower quality casted multicrystalline and edge-defined film fed grown (EFG) silicon ribbons. These silicon materials contain crystallographic defects such as grain boundaries and intra-grain defects (e.g., dislocations, twins) which act as carrier recombination centers and consequently reduce the minority carrier lifetime significantly. Hydrogen in the $a\text{-SiN}_x\text{:H}$ coating can passivate these defects when the hydrogen is made mobile by thermal activation of the film, e.g., in the firing process of the cell's screen printed metallization.^{6,7,44}

Although previous measurements have suggested bulk passivation by ETP deposited $a\text{-SiN}_x\text{:H}$,⁴³ a new experiment was carried out to obtain more evidence. Two groups of 10 Baysix mc-Si wafers (10×10 cm²) were selected such that adjacent positions in the ingot (neighbor wafers) were equally divided over the two groups. One group of wafers was processed into solar cells using the standard process scheme at ECN Solar Energy: saw damage etch, emitter diffusion (50 Ω/sq emitter), phosphorous glass removal, $a\text{-SiN}_x\text{:H}$ deposition, Ag-front side and Al-rear side metallization by screen printing, and simultaneous firing of the metal contacts at both sides in a belt furnace. The deposition process of the $a\text{-SiN}_x\text{:H}$ was carried out by the ETP technique using the conditions: 45 A arc current, 55 sccs Ar, 5 sccs H₂, 10 sccs N₂, 4 sccs SiH₄, and a substrate temperature of 350 °C. The distance between cascaded arc plasma source and substrate was 70 cm and the resulting refractive index and deposition rate of the $a\text{-SiN}_x\text{:H}$ were 2.11 and 9.2 nm/s, respectively. The second group of wafers was processed by the same scheme except for the fact that the $a\text{-SiN}_x\text{:H}$ deposition (with the same deposition conditions) was carried out after the screen-printing and firing of the metallization. This is the so-called reverse-scenario process and it serves as a reference: the $a\text{-SiN}_x\text{:H}$ coating leads in principle to a similar antireflection coating performance but it cannot induce bulk passivation because the $a\text{-SiN}_x\text{:H}$ is not thermally activated in the firing process.

The bulk passivation was examined by internal quantum efficiency (IQE) measurements and not by considering the solar cell performance parameters (often the open-circuit voltage V_{oc} of the cell is used as a fingerprint of bulk passivation of mc-Si solar cells) because the homogeneity of the coatings is reasonable but not yet sufficient for this (see Sec. III B). The IQE was determined by quantum efficiency and reflectivity measurements at the 5×5 cm² center region of the cells. Results of one set of cells (neighbor wafers) are given in Fig. 10(a). In Fig. 10(b) the IQE of both cells is displayed relative to the IQE of the reverse-scenario cells

FIG. 10. (a) Internal quantum efficiency (IQE) measurements of mc-Si cells made from neighbor mc-Si wafers and coated with an ETP $a\text{-SiN}_x\text{:H}$ anti-reflection coating. For the fired through cell, the $a\text{-SiN}_x\text{:H}$ has been deposited before screenprinting and firing of the front and rear side metallization. The $a\text{-SiN}_x\text{:H}$ has therefore been thermally activated during the firing step in a belt furnace. For the reverse scenario cell, the $a\text{-SiN}_x\text{:H}$ has been deposited after the screenprinting and firing of the front and rear side metallization. The $a\text{-SiN}_x\text{:H}$ for this cell has therefore not been thermally activated. (b) IQE of both cells relative to the IQE of the reverse scenario cells.

showing the difference between two different cells. The figure shows an enhancement of the red response for the “fired through” cell compared to the reverse-scenario cell which clearly shows that bulk passivation is obtained for the high-rate deposited $a\text{-SiN}_x\text{:H}$. This is confirmed by the other cells in the group which have revealed similar data. On the other hand, the blue response of the fired through cell has decreased significantly compared to the reverse-scenario cell. This is an interesting effect which is of course unfavorable to the performance of the cells. It appears that the $a\text{-SiN}_x\text{:H}$ coating used is very sensitive to heat treatment and on the basis of the reflectivity measurements of the cells it is deduced that the decrease in blue response is most probably due to densification of the material in the firing step. This causes an increase of the absorption coefficient of the $a\text{-SiN}_x\text{:H}$ and leads therefore to a lower internal quantum efficiency in the lower wavelength region.⁴⁵ In summary, it can be concluded that bulk passivation has been observed for the very high-rate deposited $a\text{-SiN}_x\text{:H}$. Nonetheless, the application of the bulk passivating, high-rate deposited $a\text{-SiN}_x\text{:H}$ antireflection coating on large, industrial-type cells appears still to be hindered by insufficient homogeneity and significant light absorption after firing. These problems might however relatively easily be solved technologically. In future work, we will address these remaining problems of the ETP deposited $a\text{-SiN}_x\text{:H}$ by a deeper analysis of the optical properties and by investigation of the influence of the thermal activation of the $a\text{-SiN}_x\text{:H}$, as well as by the application of NH₃ as nitrogen source gas instead of N₂.

IV. CONCLUSIONS

The feasibility of high-rate deposition of $a\text{-SiN}_x\text{:H}$ by the expanding thermal plasma technique has been examined with respect to its potential of high-throughput processing of

functional antireflection coatings on crystalline silicon solar cells. For gas mixtures of Ar, H₂, N₂, and SiH₄, the structural and compositional properties that can be obtained for the $a\text{-SiN}_x\text{:H}$ have been mapped and the film homogeneity, antireflection performance, and surface and bulk passivation have been investigated. The most important conclusions in this respect are:

- (1) Very high deposition rates (10–20 nm/s) of the $a\text{-SiN}_x\text{:H}$ can be obtained by the expanding thermal plasma.
- (2) The refractive index and the N/Si ratio in the film can fully be tuned for optimum antireflection coating performance by varying the SiH₄ flow with respect to the N₂ flow.
- (3) The hydrogen content is mainly determined by the substrate temperature and is in the range of 16%–18% for films deposited at 400 °C. This hydrogen concentration is similar in magnitude compared to $a\text{-SiN}_x\text{:H}$ films deposited by other techniques and which induce bulk passivation of multicrystalline or ribbon silicon solar cells.
- (4) Investigation of the film homogeneity has revealed that the homogeneity can be improved by increasing the plasma source-substrate distance at the expense of the deposition rate (30% decrease when going from 35 to 70 cm). For the increased plasma source-substrate distance the thickness homogeneity is <8% within wafer for 10 × 10 cm² cells and <2% within wafer for the refractive index. Although this thickness homogeneity is reasonable, it is not yet sufficient, but can be improved by other reactor designs.
- (5) Good antireflection coating performance has been observed for the $a\text{-SiN}_x\text{:H}$ as has been tested for small area monocrystalline silicon solar cells. The solar cells' average efficiency increased from 12.7% to 17.7% by application of the ETP deposited $a\text{-SiN}_x\text{:H}$. This is only 0.55% (absolute) lower than for ISFH reference cells with high-quality $a\text{-SiN}_x\text{:H}$ and this difference can be attributed to lack of surface passivation of the ETP deposited $a\text{-SiN}_x\text{:H}$.
- (6) The lack of surface passivation has also been revealed by lifetime measurements on both float zone, low-resistivity silicon and diffused emitter samples. For the float zone silicon samples, the lowest effective surface recombination velocity obtained is slightly lower than 1000 cm/s which is far above the record-low surface recombination velocity of 4 cm/s. On the more industrial-type diffused emitter samples this difference is significantly smaller. The lack of good surface passivation of the $a\text{-SiN}_x\text{:H}$ coatings, which have rather similar structural and compositional film properties as the material with very good surface passivation, has been investigated. This has indicated that this lack is due to a problem in the $a\text{-SiN}_x\text{:H}$ bulk material instead of an interface problem.
- (7) Bulk passivation experiments in which cells with thermally activated $a\text{-SiN}_x\text{:H}$ have been compared to cells without thermally activated $a\text{-SiN}_x\text{:H}$ have revealed a clear enhancement of the internal quantum efficiency in

the high-wavelength region. Bulk passivation has therefore been observed for the high-rate $a\text{-SiN}_x\text{:H}$ although an insufficient film homogeneity and a decrease of the blue response in the internal quantum efficiency (due to the thermal activation of the material) pose still some (technological) problems.

The potential of $a\text{-SiN}_x\text{:H}$ deposited at very high rates by the expanding thermal plasma has therefore been demonstrated by this first study and will be explored more extensively in future work.

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