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Ion-induced effects on grain boundaries and a-Si:H tissue quality in microcrystalline silicon films

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Microcrystalline silicon films have been deposited by means of the remote expanding thermal plasma. The effect of ion bombardment on the microcrystalline silicon film properties has been investigated by applying an RF bias to the deposition substrate. The application of the RF substrate bias resulted in the formation of an additional plasma in front of the substrate holder. Neither the SiH\textsubscript{4} depletion nor the growth flux was significantly enhanced upon substrate biasing, which suggests that the composition of the growth precursor flux is unaffected and that the ion-film interaction mechanisms were responsible for the observed material changes. Moderate bias conditions (i.e., dc bias voltages up to \(~70\) V) led to an improved grain boundary passivation and densification of the amorphous silicon tissue, as concluded from the analysis of the infrared Si-H\textsubscript{x} stretching modes. These improvements have been ascribed to ion-induced Si surface atom displacement, which enhances the surface diffusion length of the growth precursors. More-energetic ion bombardment (i.e., under applied dc bias voltages of \(~60\) V and higher) resulted in enhanced (di)vacancy incorporation via ion-induced Si bulk atom displacement. The film crystallinity was found not to be affected by the ion bombardment, although a reduced crystallite size was observed under ion bombardment conditions where Si bulk displacement had been sufficiently activated. The extent of the ion-film interaction mechanism has been enhanced by increasing the ion-to-Si deposition flux ratio. Under specific ion bombardment conditions, i.e., dc bias voltage in the range of \(40–70\) V and ion/Si arrival rate \(\sim0.20\), microcrystalline silicon films have been obtained which, on the basis of the Si-H\textsubscript{4} stretching modes, are qualified as solar-grade, i.e., the intergranular space is filled with a dense amorphous silicon tissue which completely passivates the crystalline grain boundaries. © 2012 American Vacuum Society. [http://dx.doi.org/10.1116/1.4766193]

I. INTRODUCTION

Microcrystalline silicon (\(\mu\)c-Si:H) is extensively used as light-absorbing layer in thin-film tandem solar cells. It is a mixed-phase material consisting of crystalline silicon grains, hydrogenated amorphous silicon (a-Si:H) tissue, and voids. Microcrystalline silicon combines the advantage of a low (indirect) band gap (\(1.1\) eV), which results in an enhanced absorption of red and (near)infrared light, with an improved stability under light exposure (reduced Steabler–Wronski effect).\textsuperscript{1} However, the \(\mu\)c-Si:H absorption coefficient in the energy range below \(1.5\) eV is relatively low. Therefore, to achieve sufficient light absorption relatively thick layers are necessary (\(1–2\) \(\mu\)m), even when light-trapping techniques are applied. From a cost-perspective point of view high growth rates are required (\(>1\) nm/s), preferably in combination with large-area roll-to-roll processing.

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It is in this respect that the expanding thermal plasma (ETP) has been employed for the deposition of \(\mu\)c-Si:H films.\textsuperscript{2–6} The ETP has proven to be a viable deposition technique for amorphous silicon (a-Si:H), silicon nitride, and silicon dioxide at very high growth rates (\(2–20\) nm/s).\textsuperscript{7–9} In addition, the setup is compatible with large-area deposition: for example, OTB-Solar/Roth&Rau (member of the Meyer Burger group) applies multiple ETP sources to achieve a uniform deposition over an area as large as \(\sim0.3\) m\textsuperscript{2}.\textsuperscript{10} Both the high growth rates and the possibility of large-area deposition make the ETP technique an ideal candidate for \(\mu\)c-Si:H film deposition.

Previous work, however, has shown that the \(\mu\)c-Si:H material properties are rather poor. The material is characterized by a network (of interconnected) pores linked to an insufficient amount of a-Si:H tissue;\textsuperscript{2,3,5,6} a-Si:H tissue is necessary to fill the intergranular space and ensures grain boundary passivation. Consequently, the films are prone to postdeposition oxidation. It has been investigated if preferential etching of the a-Si:H tissue by atomic hydrogen, which is abundant in the (expanding thermal) plasma and
recognized as the main parameter to promote $\mu c$-Si:H film growth.\textsuperscript{11–13} was responsible. However, our study pointed out that at high growth rates (>1 nm/s) H-induced etching could not compete with film deposition.\textsuperscript{3} Therefore, in the present work we investigated if the application of an ion bombardment can improve the $a$-Si:H tissue quality and/or the grain boundary passivation.

For $a$-Si:H films grown by means of the ETP, moderate ion bombardment conditions have led to a reduced nanosized void content, a reduced defect density, and an improved photoresponse.\textsuperscript{14,15} These improved material properties have been ascribed to enhanced surface species migration and Si surface atom displacement,\textsuperscript{15} both processes being enhanced by ion-film interactions. Therefore, we investigated if these ion-induced processes can improve the $a$-Si:H tissue quality and/or the grain boundary passivation, and thereby improve the ETP-grown $\mu c$-Si:H film quality.

Up to now, negative side effects of ion bombardment on the $\mu c$-Si:H film properties have been reported in literature, i.e., amorphization of the crystalline phase (i.e., a reduced crystal fraction,\textsuperscript{16–19} smaller crystallite sizes,\textsuperscript{18–20} and an increased void fraction\textsuperscript{(19)}) and an increased defect density.\textsuperscript{16,21} for films deposited by means of a capacitively coupled plasma (CCP), which is the most widely used, and so far the most successful, $\mu c$-Si:H deposition technique. In fact, the so-called high-pressure-depletion (HPD) regime and the use of very high excitation frequencies (VHF) have been employed not only to increase the growth rate,\textsuperscript{20,22–25} but were hypothesized to be necessary to suppress a (potentially uncontrolled) ion bombardment effect associated with high plasma power regimes. Although ion energy measurements under these deposition conditions are lacking, reduction of ion bombardment, by, e.g., working at higher pressures and/or using higher excitation frequencies, resulted in improved material properties,\textsuperscript{18,19} and consequently in an improved solar cell performance.\textsuperscript{25,26}

However, the extent of an ion bombardment effect depends on the ion energy, the ion flux, and the chemical nature of the ions. Therefore, ion-surface interactions can be beneficial, e.g., via the enhancement of the surface diffusion length of the growth precursors, or detrimental, e.g., due to sputtering. Recent measurements performed under HPD conditions showed an ion per deposited Si atom ratio of \textasciitilde0.30,\textsuperscript{27} whereas under ETP conditions this ratio is much lower (\textasciitilde0.05) (this ion to Si deposition flux ratio has been estimated from the growth flux under standard $\mu c$-Si:H deposition conditions (1–2 \texttimes 10\textsuperscript{16} part/cm\textsuperscript{2}s)\textsuperscript{3} and ion flux measurements performed under these conditions by means of a capacitive probe (5–8 \texttimes 10\textsuperscript{14} ions/cm\textsuperscript{2}s), leading to an ion-to-Si growth flux ratio of \textasciitilde0.05). In addition, the ion energy in the ETP is extremely low, 1–2 eV, whereas in CCP under HPD conditions ion energies in the range of 3–20 eV have been estimated.\textsuperscript{26,28} The extremely low-energetic ion bombardment in remote plasmas is advantageous for the study of an ion bombardment effect on the film growth: the application of an external bias in remote plasmas allows for a manipulation of the ion energy under conditions in which the neutral radical flux toward the substrate is not significantly affected.

This work addresses whether the $\mu c$-Si:H quality can be improved, via densification of the $a$-Si:H tissue and improvement of the grain boundary passivation while maintaining the crystal quality, by inducing and/or enhancing ion-film interactions. The ion bombardment energy is enhanced (and controlled) by applying an external RF substrate bias (ERFSB). The application of an ERFSB can lead to the creation of an additional plasma in front of the substrate holder. Therefore, the effect of an ERFSB on the (composition of the) growth flux is addressed. The microstructure of the ETP+ERFSB-grown $\mu c$-Si:H films is studied with infrared absorption spectroscopy on the basis of the Si-H\textsubscript{x} stretching modes, following Smets \textit{et al.}\textsuperscript{31,32} The Si-H\textsubscript{x} stretching modes provide information on the $a$-Si:H tissue quality as well as on the grain boundary passivation. In addition, Raman spectroscopy and x-ray diffraction (XRD) have been employed to probe the quality of the crystalline silicon grains.

II. EXPERIMENTAL SETUP

The experimental setup is depicted in Fig. 1. It consists of a plasma source, a so-called cascaded arc, and a low-pressure, stainless-steel deposition chamber. A detailed description of the plasma source and the ETP technique can be found elsewhere.\textsuperscript{29–31} Operating conditions can be found in Table I. For the deposition of $\mu c$-Si:H films, an Ar/H\textsubscript{2} plasma is created in the cascaded arc; typical electron densities and electron temperatures in the arc are 10\textsuperscript{22} m\textsuperscript{–3} and 1 eV, respectively.\textsuperscript{32} The plasma expands supersonically into the deposition chamber due to the large pressure difference between the source (~200 mbar) and the chamber. After the onset of the expansion, a fast reduction in the electron density is observed due to charge–exchange reactions followed by electron-induced dissociation, $R1$ and $R2$, respectively in Table II.\textsuperscript{33} Hence, under these operating conditions the arc acts as an atomic hydrogen source.\textsuperscript{29,34} Downstream, the

![Fig. 1. (Color online) Experimental setup.](image)
typical electron densities and electron temperatures are $10^{17}$–$10^{19}$ m$^{-3}$ and 0.3 eV, respectively. Silane gas is injected downstream via an injection ring. The SiH$_4$ gas flow rates are chosen such as to obtain $\mu$-Si:H films located at the so-called amorphous-to-microcrystalline transition regime, where empirically the best $\mu$-Si:H film quality is obtained. Due to the low electron temperature, the main dissociation mechanism of SiH$_4$ is via H abstraction reactions forming SiH$_3$ (R3, Table II), which is the dominant growth radical. However, subsequent dissociation of SiH$_3$, via H abstraction reactions (R4, Table II), can occur under $\mu$-Si:H growth conditions. Hence, in addition to SiH$_3$, SiH$_2$, SiH, and Si radicals are expected to contribute to the growth. This subsequent dissociation of SiH$_3$ into SiH$_2$ (x $\leq$ 2) radicals is undesirable because of their near-unity sticking coefficients. In order to minimize SiH$_2$ (x $\leq$ 2) formation, the SiH$_3$ injection ring is placed close to the substrate ($\sim$30 cm from the source outlet). Film deposition occurs on a heated substrate (250 °C) positioned $\sim$40 cm from the source outlet.

The additional ion bombardment is created by applying 13.56 MHz RF power to the substrate holder. Details on the ERFSB setup can be found elsewhere.14,15,44 The RF power (P$_{RF}$) is varied from 0 to 50 W, which results in typical bias voltages (V$_{dc}$) in the range of $-20$ to $-140$ V. Application of an ERFSB resulted in the formation of an additional plasma in front of the substrate holder. The emission near the substrate is collected via a lens focused onto the optical fiber of an Avantis optical emission spectrometer, which has a wavelength detection range of 150–1300 nm and a resolution of 1.3 nm. Spectra were recorded every 2000 ms. The emission lines of interest are H$_2$ (656.308 nm), H$_\beta$ (486.276 nm), the dominant line of the H$_2$ Fulcher band (H$_2$* 603.103 nm), and Ar* (763.251 nm). In addition, residual gas analysis (Balzers QMS 200 Prisma) is used to measure the SiH$_4$ depletion.30,31

A capacitive probe, built in the substrate holder, is used to measure the ion flux ($\Gamma_{ion}$). The working principle of the capacitive probe has been described in detail by Petcu et al.45,46 Basically, the ion flux is determined from the voltage drop across an external capacitor ($C = 1.5$ nF):

$$C \frac{dV}{dt} = eA\Gamma_{ion},$$

in which $dV/dt$ is the time derivative of the voltage drop across the external capacitor, $e$ is the elementary charge ($1.6 \times 10^{-19}$ C), and $A$ is the area of the probe (2 cm$^2$). This technique has already proven to be tolerant toward insulating film deposition on the probe surface45,46 and recently also toward $\alpha$-Si:H and $\mu$-Si:H film depositions.27 Still, to verify the influence of a film deposited on the probe surface in H$_2$/SiH$_4$ plasmas, a procedure analogously to one used by Petcu et al.45 has been followed in which before and after every measurement performed in an Ar/H$_2$/SiH$_4$ plasma a measurement in a nondepositing Ar/H$_2$ plasma has been carried out; for details on this procedure, we refer to the literature.27,45

The $\mu$-Si:H film deposition was carried out simultaneously on glass (Corning 7059) and on crystalline silicon ($c$-Si) [n-type (100)]. Since glass is an insulator, this could result in a slightly different $V_{dc}$ on the glass substrate with respect to the $c$-Si substrate under the same ERFSB conditions employed. However, analogously to Smet et al.15 under the conditions used in this paper ($-200$ V $< V_{dc} < 0$ V) the difference in $V_{dc}$ on glass compared to $c$-Si can be considered insignificant. The films deposited on $c$-Si have been analyzed using Fourier transform infrared (FTIR) spectroscopy to determine the film thickness, the H concentration (c(H)), and the Si-H$_4$ bonding configurations. In addition, Rutherford backscattering (RBS, using 2 MeV $^4$He$^+$ ions) and elastic recoil detection (ERD) analysis have been carried out to obtain the Si and H atomic concentrations. The growth flux, or Si deposition flux ($\Gamma_{Si}$), has been calculated from the Si concentration and the deposition rate.

FTIR spectroscopy is carried out using a Bruker Vector 22. The resolution of the spectrometer was set at 4 cm$^{-1}$ and

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**Table I. Experimental conditions and corresponding ion/Si atom arrival ratio ($\Gamma_{ion}/\Gamma_{Si}$) (sccs stands for standard cubic centimeter per second).**

<table>
<thead>
<tr>
<th>Ar</th>
<th>H$_2$</th>
<th>SiH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (sccs)</td>
<td>I$_{arc}$ (A)</td>
<td>P (mbar)</td>
</tr>
<tr>
<td>I</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>II</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

**Table II. Most important dissociation and excitation reactions.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Branching ratio (%)</th>
<th>Rate constant (cm$^3$/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Ar$^+$ + H$_2$ $\rightarrow$ ArH$^+$ + H</td>
<td>$\sim$10$^{-9}$</td>
<td>38</td>
</tr>
<tr>
<td>R2</td>
<td>ArH$^+$ + e $\rightarrow$ Ar + H$^*$</td>
<td>$\sim$10$^{-7}$</td>
<td>38</td>
</tr>
<tr>
<td>R3</td>
<td>SiH$_4$ + H $\rightarrow$ SiH$_3$ + H$_2$</td>
<td>2.68 $\times$ 10$^{-12}$</td>
<td>39</td>
</tr>
<tr>
<td>R4</td>
<td>SiH$_3$ + H $\rightarrow$ SiH$_2$ + H$^*$</td>
<td>1 $\times$ 10$^{-10}$</td>
<td>40</td>
</tr>
<tr>
<td>R5</td>
<td>SiH$_4$ + e $\rightarrow$ SiH$_2$ + 2 H$^+$</td>
<td>46</td>
<td>1.59 $\times$ 10$^{-10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>R6</td>
<td>H + e $\rightarrow$ H$^+$ + e</td>
<td>42 and 43</td>
<td></td>
</tr>
<tr>
<td>R7</td>
<td>H$_2$ + H$_2$ $\rightarrow$ H$_3$ + H</td>
<td>2.1 $\times$ 10$^{-9}$</td>
<td>42 and 43</td>
</tr>
<tr>
<td>R8</td>
<td>H$_2$ + e $\rightarrow$ H + H + H$^<em>$ $\rightarrow$ H$_2$ + H$^</em>$</td>
<td>$\sim$10$^{-7}$</td>
<td></td>
</tr>
</tbody>
</table>
spectra were collected in the range of 450–750 cm\(^{-1}\). The film thickness and refractive index in the infrared are estimated by fitting the interference fringes in the 3000–4000 cm\(^{-1}\) range.\(^{47}\) The hydrogen content is defined as \(c_{H} = N_{H}/(N_{Si} + N_{H})\), where \(N_{Si} + N_{H} \approx 5 \times 10^{27} \text{ cm}^{-3}\) (Ref. 48) and \(N_{H} = A_{H} n_{i}\), where \(n_{i} = \int_{0}^{\infty} A(\omega)d\omega\) is the integrated absorption of a mode at position \(\omega\). The total hydrogen content \((c_{H})\) is determined from the integrated absorption of the Si-H wagging mode at 640 cm\(^{-1}\), using \(A_{H} = 1.6 \times 10^{10} \text{ cm}^{-2}\).\(^{48}\) The absorption peak at \(\sim 640 \text{ cm}^{-1}\) arises due to Si-H wagging vibrations. For \(a\)-Si:H films, this can be fitted with a single Gaussian function. For \(\mu\)-Si:H films, however, this peak splits into several contributions and needs to be fitted with three Gaussians, in agreement with Refs. 49–51. The cause for this splitting is not yet clear, but the presence of crystalline silicon grains is believed to be responsible. The SiH\(_{x}\) stretching mode is fitted with at maximum nine Gaussians following Smets et al.\(^{52,53}\) [see Fig. 5(a)]: three extreme low stretching modes (ELSMs) are positioned at \(-1895, -1925, \text{ and } -1950 \text{ cm}^{-1}\), one low stretching mode (LSM) at \(-2025 \text{ cm}^{-1}\), one medium high stretching mode (MSM) at \(-1925 \text{ cm}^{-1}\), two high stretching modes (HSMs) at \(-2100\) and \(-2120 \text{ cm}^{-1}\), and three narrow high stretching modes (NHSMs) at 2083, 2103, and 2135 cm\(^{-1}\). Analogously to \(a\)-Si:H films, the LSM represents hydrogen bonded in divacancies and the HSM represents hydrogen bonded on the surface on nanosized voids. For \(\mu\)-Si:H films, this peak splits into several contributions and needs to be fitted with three Gaussians.\(^{54}\) The assignment of the ELSMs is still under discussion. However, as the best solar cell performance is obtained when the absorption spectra show no NHSMs and the combined area of ELSMs, LSM and MSM is maximum, it is speculated that the ELSMs and/or MSM reflects “a thin hydride-dense \(a\)-Si:H tissue, which either passivates the grain boundaries or fills the small pores.”\(^{55}\)

The film crystal structure has been investigated by means of Raman and XRD spectroscopy. The crystal fraction has been determined, for films deposited on glass, by means of Raman spectroscopy following the method of Smit et al.\(^{55}\) using a Raman microscope (Renishaw) in a backscattering geometry equipped with a 514.5 nm Ar ion laser. The corresponding penetration depth of the laser in \(\mu\)-Si:H is about 100 nm. The deposited films have a thickness in the range of 500–600 nm. As there is often a gradient in crystallinity with film thickness, the crystallinity probed by the 514.5 nm Ar ion laser might be overestimated. X-ray diffraction spectra have been obtained, for films deposited on \(c\)-Si, with an x-ray diffractometer (PanAlytical X’pert PRO MRD) measured under grazing incidence with Cu-K\(_{\alpha}\) x rays using a graphite crystal monochromator. Three crystal orientations can be observed in the XRD spectra, i.e., the (111), (220), and (311) orientations at, respectively, 28\(^{\circ}\), 47\(^{\circ}\), and 56\(^{\circ}\) (see Fig. 8). Information on a preferred (or random) crystal orientation is obtained by comparing the peak intensities of the different crystal orientations after normalization with a powder spectrum. The full width half maximum of the (111) peak in the diffraction spectrum is used to determine the crystallite size using the Scherrer formula. This crystallite size reflects the crystal length (along the growth direction, i.e., not lateral dimensions of the grains), which is free of lattice defects. We use the crystallite size as a measure for the grain quality.

III. RESULTS AND DISCUSSION

A. Effect of ERFSB on the growth and ion fluxes

Figure 2 shows the developed dc bias voltage \((V_{dc})\) as function of the applied RF power \((P_{RF})\). The nonlinear relationship between \(V_{dc}\) and \(P_{RF}\) indicates that not all the RF power is used to accelerate the ions, but that a considerable fraction of the RF power is used to create an additional plasma in front of the substrate holder, possibly resulting in additional dissociation of H\(_{2}\), SiH\(_{4}\), and perhaps SiH\(_{x}\) \((x = 1–3)\) radicals. The SiH\(_{4}\) depletion, depicted in Fig. 3(a), shows no significant increase with increasing \([V_{dc}]\). However, we should note that the mass spectrometer samples the background gas and may not be sensitive enough to detect (slight) changes in SiH\(_{4}\) depletion close to the substrate holder. In addition, only a slight enhancement of the Si deposition flux in the presence of an ERFSB is observed [Fig. 3(b)], which does not change considerably with \([V_{dc}]\).

The change in growth flux composition has been studied for \(a\)-Si:H growth conditions (i.e., at least a ten times higher SiH\(_{4}\) flow rate) using pulsed ERFSB.\(^{56,57}\) This study showed a factor of 5–6 increase in Si density (measured in front of the substrate holder) which is lost in gas phase reactions, and a 60–80% increase in SiH\(_{3}\) density, which is predominantly lost at the surface.\(^{56,57}\) The increased SiH\(_{3}\) density resulted in a correspondingly increased deposition rate. Since under ETP growth conditions SiH\(_{3}\) is the dominant growth radical and remains the dominant contributor to \(a\)-Si:H film growth under ETP+ERFSB conditions, it was concluded that the composition of the radical flux was not significantly affected by the application of an ERFSB.\(^{15}\) Similar to \(a\)-Si:H, under ETP growth conditions for \(\mu\)-Si:H films SiH\(_{3}\) is the

![Fig. 2. (Color online) dc bias voltage \((V_{dc})\) measured at the substrate vs applied RF power \((P_{RF})\) for Ar/H\(_{2}\) and Ar/H\(_{2}/\text{SiH}_{4}\) plasmas, as measured under condition I (Table I). The solid lines serve as a guide to the eye.](image-url)
dominant growth radical, which is formed in H abstraction reactions with SiH$_4$ (R3, Table II). In addition, SiH$_2$, SiH, and Si are expected to contribute to the growth of l-c-Si:H films due to (1) the excess of atomic H, which can dissociate SiH$_3$ into SiH$_2$ (R4, Table II) and, subsequently, SiH$_2$ into SiH, etc., and (2) due to a reduced gas phase loss of SiH and Si with SiH$_4$ under µc-Si:H growth conditions, i.e., low SiH$_3$ densities compared to a-Si:H growth conditions. With the application of an ERFSB, SiH$_4$ dissociation may occur via electron impact reactions (R5, Table II), due to a possibly (locally) increased electron temperature. This reaction may even compete with H abstraction due to the higher rate coefficient. The reaction products, however, are similar. Therefore, we can likely conclude that the composition of the growth radical flux is not significantly affected by the application of an ERFSB.

At high bias voltages, $|V_{dc}| > 60$ V, an increased H* emission can be observed. Figure 4(a) shows the H* emission normalized to the Ar* emission line at 763 nm. The Ar* emission intensity was used to probe the electron energy distribution function, shown in the inset of Fig. 4(a). By normalizing the H* emission to the Ar* emission, the effect of an increasing electron density with increasing RF power can be canceled out; the electron temperature was found not to depend on the RF power, as determined from the constant H$_2$/H$_a$ and H$_2^*/Ar^*$ emission intensity ratios [Fig. 4(b)]. Hence, the increased H* emission suggests an increasing H flux at high bias voltages. It is unclear whether this increased H density is due to a different plasma chemistry (e.g., a competition between H abstraction of SiH$_4$ producing H$_2$ (R3, Table II) and electron impact dissociation of SiH$_3$ forming H (R5, Table II), or if it involves ions like ArH$^+$ (R1 followed by R2, Table II) or H$_3^+$ [R8, Table II]) or if it is due to ion-bombardment assisted desorption of surface-bonded atomic H.

Since the atomic H-to-Si deposition flux is recognized as the key parameter describing the phase transition toward µc-Si:H films growth,

FIG. 3. (Color online) (a) SiH$_2$ depletion and (b) the Si deposition flux vs $|V_{dc}|$ using experimental conditions I (Table I). The solid lines serve as a guide to the eye.

FIG. 4. (Color online) (a) H$_a$ emission intensity normalized to the Ar* emission intensity (763 nm) and (b) the H$_2$/H$_a$ and H$_2^*/Ar^*$ emission intensity ratios vs $|V_{dc}|$, as measured under conditions I (Table I). The inset in (a) shows the Ar* emission intensity (763 nm). The solid lines serve as a guide to the eye.

FIG. 5. (Color online) (a) Gaussian fit of the Si-H$_x$ stretching mode region of µc-Si:H deposited without ERFSB and (b) infrared absorption spectra showing the Si-H$_x$ stretching mode region of µc-Si:H deposited under various ERFSB conditions under condition I (Table I).
affecting the surface species migration. However, due to the large H flux the surface coverage is expected to be rehydrogenated if ion-assisted desorption takes place. Furthermore, a recent study on the interaction of atomic H with α-Si:H showed, for α-Si:H films with a microstructure similar to the α-Si:H tissue in the here-presented μc-Si:H films (i.e., μc-Si:H films characterized by a dominant HSM in absorption spectra as will be discussed in Sec. III B), that atomic H does not influence the material properties.3

The extent of an ion bombardment effect depends on the ion energy, the ion flux, and the chemical nature of the ions. The ion energy distribution (IED) has not been measured (yet) under current experimental conditions. The IED at the RF biased electrode is expected to have a bimodal shape, with a maximum and minimum ion energy, respectively, above and below a mean ion energy ($E_{ion}$), which is not necessarily symmetrical with respect to $E_{ion}$. In a collisionless plasma, the mean ion energy is given by $E_{ion} = eV_p - V_{dc}$. In our experimental setup, the grounded electrode (i.e., the reactor wall) is much larger (at least a hundred times) than the biased substrate electrode. Due to this extreme asymmetry the plasma potential is low, 1–2 eV, compared to the dc bias voltage. Therefore, we can approximate the average ion energy by $E_{ion} = eV_{dc}$, in line with Refs. 15 and 59. In this paper, however, we present and discuss the data in terms of $|V_{dc}|$, which only reflects an averaged energy.

The chemical nature of the ions has not (yet) been measured under current experimental conditions. In an Ar/H$_2$ plasma, when no ERFSB is applied, the dominant ion is H$^+$ followed by H$_2$+29. This is expected not to change when a small amount of SiH$_4$ is added, i.e., highly hydrogen diluted deposition conditions. Under slightly different ETP conditions without ERFSB, used for the deposition of α-Si:H films (i.e., at least a ten times higher SiH$_4$ flow), hydrogen-poor ion clusters contribute for a maximum of 5% to the growth. These cationic clusters contain on average about three to six Si atoms, leading to an ion/Si atom arrival ratio of about ~0.02 to ~0.008, respectively. Under our experimental conditions, the ion flux ($\Gamma_{ion}$) showed no dependence with $|V_{dc}|$, $\Gamma_{ion} = (1.0 \pm 0.1) \times 10^{14}$ cm$^{-2}$ s$^{-1}$, leading to an ion/Si atom arrival ratio ranging from 0.08 in the absence of ERFSB to 0.06 in the presence of ERFSB [under ERFSB conditions the ion/Si arrival ratio is slightly lower because the Si growth flux is slightly higher, see Fig. 3(b)], indicating that other ions than large cationic clusters are responsible for the energy transfer. The additional ions created in front of the substrate are most probably $H^+$, $H_2^+$, $H^-$, $Ar^+$, $ArH^+$, and Si$H_n^+$ ($n = 0–3$).

B. Ion-induced material modification

Figure 5(b) shows the Si-H$_2$ stretching mode region of μc-Si:H films deposited with and without RF substrate bias. For all conditions NHSMs are present in the absorption spectra, indicating that not all the grain boundaries are passivated by α-Si:H tissue. With increasing $|V_{dc}|$ an increase in the lower stretching mode region (~1900–2050 cm$^{-1}$) and a decrease in the higher stretching mode region (~2070–2100 cm$^{-1}$) can be seen, pointing out a densification of the α-Si:H tissue. The deconvolution of the Si-H$_2$ stretching mode region, following the approach of Smets et al.,53 provided more-quantitative information on the changes in intensities with $|V_{dc}|$. Figure 6 shows the integrated peak areas of the NHSMs (c), HSMs (d), and LSM (e), as well as the total hydrogen content (a) and the film density (b). With increasing $|V_{dc}|$ the NHSM peak intensity reduces, which is an indication of an improved grain boundary passivation and suggests a filling of the intergranular space. In addition, with increasing $|V_{dc}|$ the HSM peak area reduces. Since the HSM represents hydrogen bonded on the surface of nanosized voids, a reduction in the HSM peak area implies a reduced void content and is therefore an indication of the α-Si:H tissue densification. Only at high $|V_{dc}|$ (~133 V) the void content increases, causing the total hydrogen content to increase. The LSM increases with increasing $|V_{dc}|$, especially for $|V_{dc}| > 60$ V, which indicates an increased (di)vacancy incorporation.

Despite the decrease in HSM and NHSM and increase in LSM areas, which point toward a film densification with increasing $|V_{dc}|$, the film density, as quantified by RBS and shown in Fig. 6(b), does not increase. This is an indication that the void content is limited, although significant since the films are prone to postdeposition oxidation.

The crystal fraction, shown in Fig. 7(a), shows no dependence on $|V_{dc}|$. This indicates that the potentially higher H flux under ERFSB conditions does not affect the film crystallization, under current experimental conditions, which suggests
that the ERFSB-enhanced H flux is small compared to the already present H flux in the H-rich deposition environment. Figure 7(b) shows the crystallite size as determined from the (111) peak of the XRD spectra, which are shown in Fig. 8. The XRD spectra of the μc-Si:H films show three peaks at 28°, 47°, and 56° originating from (111), (220), and (311) oriented c-Si crystallites, respectively. Normalization of the peak intensities corresponding to the different crystal orientations of Fig. 8 to the respective intensities of the powder peak intensities resulted in similar peak heights, indicating that the crystallites exhibit no preferred crystal orientation. With increasing $|V_{dc}|$ the width of the peaks increases, which is an indication of a reduced crystallite size. Figure 7(b) shows that the crystallite size reduces for $|V_{dc}| > 40$ V, implying that more defect planes are present within the crystalline grains.

C. On the role of ions

Analogously to a-Si:H films deposited by means of the ETP+ERFSB, the observed changes in the microstructure of the μc-Si:H films can be ascribed to specific ion-surface interactions. The effect of ion-surface interactions depends on the chemical nature of the ion and its energy. For significant material changes to occur an energy per deposited atom of 1–10 eV is required. Low-energetic ion-surface interactions can result in an energy transfer to the surface in the form of a thermal spike. Molecular dynamic simulations showed that $H_2^+$ ion bombardment with an energy above 20 eV can enhance the reactivity of the surface by the creation of dangling bonds. Heavier ions, e.g., $SiH_2^+$ and $Ar^+$, can result in the displacement of Si atoms; threshold ion energies of 18 and 40 eV have been reported for ion-induced Si surface and bulk atom displacement, respectively. At even higher energies, the Si atoms can be physically removed from the surface via sputtering ($E_{ion} > 50$ eV).

For bias conditions where Si surface atom displacement is significantly activated, i.e., $|V_{dc}| > 18$ V, we observe a densification of the a-Si:H tissue, deduced from the decrease in HSM [Fig. 3(c)], and an improved grain boundary passivation and filling of the intergranular space, deduced from the decrease in NHSM [Fig. 3(b)]. These improvements are therefore related to ion-induced Si surface atom displacement. At higher $|V_{dc}|$, i.e., $|V_{dc}| > 40$ V, Si bulk atom displacement is activated. Analogously to a-Si:H, we observe an increase in divacancy incorporation, and therefore we ascribe these changes to Si bulk atom displacement. The increased nanosized void content at $|V_{dc}| = 133$ V is ascribed to sputtering.

Under the current experimental conditions, we did not observe an ion-induced amorphization effect, i.e., no reduced crystal fraction. We did, however, notice a disruption in the crystalline lattice, i.e., for $|V_{dc}| > 40$ V, the crystallite size decreased. As Si bulk atom displacement is activated at these ion energies, this process may be responsible for disrupting the crystal growth.

The optimal microstructure is obtained for a $|V_{dc}|$ of 40–70 V, i.e., at these bias voltages both the NHSM and HSM areas have decreased with, respectively, a factor of 5 and 1.5 with respect to the ETP deposited layers; note that this $|V_{dc}|$ only reflects an averaged energy. Similar optimum bias voltages have already been reported for μc-Si:H and a-Si:H films grown by means of ETP+ERFSB. Application of an ERFSB during the growth of μc-Si:H by means of the remote matrix distributed electron cyclotron resonance (MDECR) plasma resulted in a film densification at low $|V_{dc}|$ (<15 V) and reduced grain size at higher $|V_{dc}|$. That the optimum material properties by MDECR+ERFSB are obtained at lower $|V_{dc}|$ compared to ETP+ERFSB, is due to the higher plasma potential.

![Fig. 7. (Color online) (a) Crystal fraction and (b) the crystallite size vs $|V_{dc}|$ of films deposited using experimental condition I (Table I). The solid lines serve as a guide to the eye.](image)
data in an ion-film interaction diagram, adopted from Smets
grain boundary passivation was not yet achieved under the
and improved grain boundary passivation, a quantitative
range of 40–70 eV.

The ion-film interaction diagram is depicted in Fig. 9, in
which the ion/Si atom arrival rate is plotted versus the average
ion energy. The range in which 1–10 eV per deposited atom is available, needed to induce significant material modifications, 60 is depicted in the ion-film interaction diagram between the two solid lines. Also shown is the range of typical ion energies and ion/Si arrival rates measured in a radio frequency excited CCP under conditions where solar-grade μc-Si:H can be obtained. 27 The ETP deposition conditions without ERFSB are depicted by the orange area in Fig. 9. Under these conditions radical-surface interactions dominate film growth, and not ion-surface interactions. The application of the ERFSB results in an additional energy of 2–10 eV per deposited Si atom, compared to ETP deposition without ERFSB.

By enhancing the ion-to-Si atom arrival ratio, achieved by reducing the deposition rate, and tuning the ion energy to ~50 eV, a solar-grade μc-Si:H film could be deposited, as deduced from the infrared Si-H, stretching modes. Figure 10 shows the absorption spectrum of the solar-grade μc-Si:H film grown by ETP+ERFSB at enhanced ion/Si arrival rate conditions (Γion/ΓSi = 0.20). For comparison, the absorption spectra of an ETP+ERFSB-grown μc-Si:H film (Γion/ ΓSi = 0.06) and of a CCP-grown solar-grade μc-Si:H film are shown. Notice the absence of NHSMs and the increased absorption in the low frequency stretching mode region (1850–2050 cm⁻¹). This result indicates that by tuning the ion energy the kind of ion-film interaction can be tuned and that by tuning the Γion/ΓSi the interaction mechanism can be enhanced.

IV. SUMMARY AND CONCLUSIONS

In the present contribution, it has been investigated whether ion-film interaction mechanisms can lead to the improvement of ETP-deposited μc-Si:H film quality. For this purpose, μc-Si:H films have been deposited under the application of an externally applied RF substrate bias. Furthermore, the plasma was studied to discern whether the observed material changes were due to a change in growth precursor flux and/or due to an ion bombardment effect.

From the plasma study, it has been concluded that the application of an ERFSB did not significantly affect the growth flux and its composition. It did result, however, in the creation of an additional H flux. The film crystallinity was not affected by this higher flux, probably because the additional H flux is small compared to the high H flux already developed within the Ar/H₂/SiH₄ plasma chemistry. Therefore, the changes in microstructure were ascribed to an ion bombardment effect.

The type of ion-film interaction depends on the ion energy, which has been tuned by the dc bias voltage. A moderate ERFSB (|Vdc| = 40–70 V) resulted in improved grain boundary passivation and a Si:H tissue densification, as deduced from the infrared Si-H, stretching modes. This improvement has been ascribed to ion-induced Si surface atom displacement. At higher |Vdc|, i.e., for |Vdc| > 70 V, ion-induced Si bulk atom displacement starts to play a role, which enhances the incorporation of (di)vacancies and may be responsible for the creation of the crystal lattice defects.
The extent of ion-film interactions has been enhanced by increasing the ion/Si atom arrival rate. Under specific ion bombardment conditions, i.e., dc bias voltage in the range of 40–70 V and ion/Si arrival rate \( \sim \)0.20, \( \mu \)-Si:H films have been obtained which, on the basis of the Si-H\(_2\) stretching modes, are qualified as solar-grade, i.e., the intergranular space is filled with a dense amorphous silicon tissue which completely passivates the crystalline grain boundaries. Thus, by tuning of the ion energy and ion/Si atom arrival rate, good \( \mu \)-Si:H films have been obtained for the first time by means of the remote expanding thermal plasma.

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