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Formation of cationic silicon clusters in a remote silane plasma and their contribution to hydrogenated amorphous silicon film growth

W. M. M. Kessels,^{a)} C. M. Leewis, M. C. M. van de Sanden,^{b)} and D. C. Schram
Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The formation of cationic silicon clusters Si_nH_m^+ by means of ion-molecule reactions in a remote Ar-H₂-SiH₄ plasma is studied by a combination of ion mass spectrometry and Langmuir probe measurements. The plasma, used for high growth rate deposition of hydrogenated amorphous silicon (*a*-Si:H), is based on SiH₄ dissociation in a downstream region by a thermal plasma source created Ar-H₂ plasma. The electron temperature, ion fluence, and most abundant ion emanating from this plasma source are studied as a function of H₂ admixture in the source. The electron temperature obtained is in the range of 0.1–0.3 eV and is too low for electron induced ionization. The formation of silicon containing ions is therefore determined by charge transfer reactions between ions emanating from the plasma source and SiH₄. While the ion fluence from the source decreases by about a factor of 40 when a considerable flow of H₂ is admixed in the source, the flux of cationic silicon clusters towards the substrate depends only slightly on this H₂ flow. This implies a strong dissociative recombination of silicon containing ions with electrons in the downstream region for low H₂ flows and it causes the distribution of the cationic silicon clusters with respect to the silicon atoms present in the clusters to be rather independent of H₂ admixture. The average cluster size increases, however, strongly with the SiH₄ flow for constant plasma source properties. Moreover, it leads to a decrease of the ion beam radius and due to this, to an increase of the ion flux towards the substrate, which is positioned in the center of the beam. Assuming unity sticking probability the contribution of the cationic clusters to the total growth flux of the material is about 6% for the condition in which solar grade *a*-Si:H is deposited. Although the energy flux towards the film by ion bombardment is limited due to the low electron temperature, the clusters have a very compact structure and very low hydrogen content and can consequently have a considerable impact on film quality. The latter is discussed as well as possible implications for other (remote) SiH₄ plasmas.
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I. INTRODUCTION

The possibility of applying hydrogenated amorphous silicon (*a*-Si:H) successfully and at relatively low costs in devices such as thin film solar cells and thin film transistors by means of SiH₄ dissociation by a plasma, has initiated numerous studies to reveal the underlying plasma and surface chemical aspects of the film growth. In most of the work now done in this field, it is assumed that the dominant species contributing to film growth is the silyl (SiH₃) radical. The dominance of SiH₃ is either concluded from experimental results,^{1–4} in which the arguments are usually based on measured densities instead of net fluxes towards the substrate, or from more or less indirect deductions from other experiments.^{5–8} Presently usually only little or even no attention is paid to the contribution of positive ions to the deposition process. In, e.g., the model for *a*-Si:H growth in rf and very high frequency, VHF discharges proposed by Ganguly, Matsuda, *et al.*, and Perrin *et al.*⁴ no contribution of positive ions to film growth is included. Neglecting the contribution of positive ions is frequently based on the low electron density usually found in these types of plasmas. However in this

reasoning it is passed over that the ions have presumably unity sticking probability^{9,10} and that the ions can also contain more than one silicon atom.¹¹ Moreover, apart from this direct contribution to film growth, the positive ions can also have an indirect contribution. They have a much higher kinetic energy than radicals do as they are accelerated in the plasma sheath. This can lead to ion bombardment and, consequently, in possible film densification and/or growth site creation.¹² In the deposition of hydrogenated amorphous carbon (*a*-C:H) for example, ions are even often expected to be inevitable for dense film growth.^{13–15} Furthermore, Ganguly and Matsuda¹⁶ and Kato *et al.*¹⁷ have observed an increase in room temperature hole drift mobility in their material of 2 orders of magnitude compared to the conventional value when the ions have an energy between 23 and 24 eV. Recently, Hamers *et al.*^{18,19} concluded from mass resolved ion energy measurements that the best structural properties, in terms of hydrogen bonding configuration and film density, are obtained above an ion threshold energy of 5 eV per deposited atom. Moreover, they estimated that the ion flux in a conventional rf/VHF SiH₄ discharge can at least account for 10% of the observed growth rate. Accordingly, the contribution of ions to *a*-Si:H film growth in SiH₄ plasmas is still a matter of debate.

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

^{b)}Electronic mail: m.c.m.v.d.sanden@phys.tue.nl

The contribution of ions to film growth has also been investigated in so-called remote plasmas. As a matter of fact these plasmas, in which plasma generation, plasma transport, and film deposition are spatially separated, even facilitate the study of the flux of ions as well as of other reactive species towards the substrate. Theil and Powell²⁰ observed rather large positive silicon containing ions in 13.56 MHz and 2.45 GHz generated helium discharges in which SiH₄ was injected downstream. On the other hand, Jasinski¹⁰ reports only on positive ions containing one Si atom in a He–SiH₄ afterglow plasma created by a microwave discharge in pure helium. Assuming unity sticking probability for the ions Jasinski estimates a contribution of 10% to the growth rate. In an expanding Ar–H₂–SiH₄ plasma, the remote plasma which is the subject of this article, also large positive silicon ions or, more appropriate, positive cluster ions have been observed.^{21,22} This plasma is created by the so-called expanding thermal plasma technique and uses a thermal Ar–H₂ plasma to dissociate SiH₄ in a downstream region. The high efficiency plasma source, a cascaded arc, enables the use of high SiH₄ flows and solar grade *a*-Si:H can be deposited at a rate of 10 nm/s.^{23,24} Apart from the interesting properties as good film quality at a high growth rate, the technique is well suited for studies concerning *a*-Si:H film growth. From such studies it was concluded that in this plasma *a*-Si:H deposition is dominated by SiH₃ radicals.⁸ However, we have to admit that the influence of positive ions on the SiH₄ dissociation and film growth in our deposition technique was formerly dealt with on an inaccurate basis: neglecting ion–molecule reactions and expecting that silane ions created by a charge transfer reaction between hydrogen and/or argon ions with SiH₄ would immediately recombine dissociatively with electrons it was estimated that the total contribution of species created by ionic processes was about 6% of the growth rate and mainly in the form of SiH_{*x*} radicals (*x* < 3) and Si₂H_{*y*} radicals (*y* < 6).⁸

Recent experiments revealed that positive ions themselves can possibly contribute significantly to film growth as ions containing several Si atoms were observed.²¹ Their formation, attributed to sequential ion–molecule reactions, has already been addressed in another article²² as well as their hydrogen poverty, the reaction rates for the ion–molecule reactions and the discrepancy between these rates and rates determined from ion cyclotron resonance mass spectrometry. In this article more data obtained from ion mass spectrometry and Langmuir probe measurements will be given for a variety of plasma conditions. The Langmuir probe measurements and the calculated ion fluxes replace thereby previous measurements^{25,26} in which the nature of the ions in the plasma was not revealed and which were performed for less appropriate plasma conditions with respect to film quality obtained. Furthermore the contribution of the cationic clusters to *a*-Si:H film growth is determined emphasizing the implications of the ion chemistry in SiH₄ plasmas.

II. EXPERIMENT

A. Deposition setup

The expanding thermal plasma setup consists of two parts: a thermal plasma source, a cascaded arc, and a low-

pressure deposition chamber. The cascaded arc consists of three cathodes, a stack of ten copper plates with a central bore of 4 mm, and an anode plate with a conical shaped nozzle. All parts are water cooled and made of copper except the cathode tips, which are of tungsten with 2% lanthanum. The plates are separated by boron–nitride and PVC spacers. Under the conditions of interest, pure Ar or a mixture of Ar and H₂ is introduced into the arc. The Ar flow is fixed at 55 sccs (1 standard cubic centimeter per second corresponds to 2.5 × 10¹⁹ particles per second) and the H₂ flow is varied between 0 and 15 sccs (purity of both gases >99.9995%). The dc discharge is current controlled at 45 A and the voltage over the arc ranges from 70 to 140 V depending on the H₂ concentration in the mixture. The pressure in the upstream part of the arc is about 400 mbar and varies only slightly with gas mixtures used. Typical arc plasma parameters are an electron density of about 10²² m⁻³ and an electron temperature of about 1 eV. Due to the high electron density there is a good energy coupling between the electrons and the heavy particles, which leads to a high heavy particle temperature (~1 eV).²⁷ As a result of the high pressure gradient between the plasma source and the deposition chamber (at 0.20 mbar) the plasma expands supersonically from the nozzle into this chamber. After a stationary shock front at about 5 cm behind the nozzle, the plasma expands subsonically and the electron temperature and electron density are heavily reduced in comparison with those in the arc.²⁸ As will be shown in this article, the electron temperature is in the range of 0.1–0.3 eV and the electron density in the range of 10¹⁶–10¹⁹ m⁻³ depending on the gas mixture used. The typical directed velocity of the particles downstream is 1000 m/s.²⁹ Pure SiH₄ (Praxair Silane Ultraplus, purity >99.995%) is admixed to the expanding plasma by a stainless steel injection ring located 5 cm from the nozzle. The injection ring has a diameter of 7.5 cm and contains eight holes with a diameter of 1 mm each. Throughout this article, SiH₄ flows in the range of 0–25 sccs are used. All flows are controlled by mass flow controllers. The deposition chamber has a volume of 180 ℓ and is pumped by a stack of two root blowers and one fore-pump. The pumping capacity at the reactor chamber is ~1500 m³/h for a pressure of 0.20 mbar. The residence time of stable particles in the low-pressure chamber is typically 0.4–0.5 s as concluded from mass spectrometry measurements. Overnight the reactor is pumped by a 450 ℓ/s turbopump reaching a base pressure of 10⁻⁶ mbar. Films are deposited on a substrate holder located at 38 cm from the arc exit, which is replaced by a mass spectrometer (see Sec. II C) for the current study.

B. Langmuir probe measurements

Cylindrical single and double Langmuir probe measurements have been applied to determine the ion and electron density, the electron temperature, and, where possible, the effective mass of the ions in the downstream region (i.e., in the deposition chamber). The probes consist of tungsten wires with a diameter of 0.2 mm and a length of 3 mm protruding from a ceramic (Al₂O₃) tube. The two probes in the double probe configuration are separated about 3 mm.

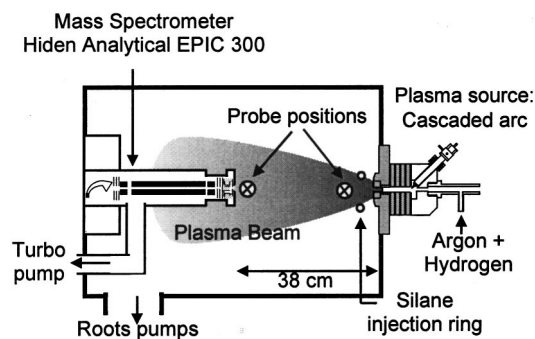


FIG. 1. Expanding thermal plasma deposition setup. The axial positions of the Langmuir probe are indicated. The mass spectrometer is situated at the usual position of the substrate holder.

The voltage on the single probe, or between the probes in the double probe, is swept between -10 and 10 V with a step size of 0.05 – 0.2 V by means of a Keithley 2400 source-measure unit.

In the Ar–H₂ plasma, single probe measurements have been performed at axial positions of ~ 6 cm from the arc nozzle and at ~ 2 cm from the substrate (see Fig. 1). At both positions, radial profiles of the electron and ion density are obtained by moving the probe in a radial direction. The plasma sheath thickness in the plasma under investigation is in the range 10^{-4} – 10^{-5} m which means that the sheath is collisionless (ions' mean free paths $\sim 10^{-1}$ – 10^{-3} m). The thin sheath limit,³⁰ which has been assumed in previous studies using cylindrical probes,^{8,31} is not completely valid within the total range of the above mentioned electron densities. Therefore the probe measurements have not been analyzed by applying linear extrapolation of the saturation currents to plasma potential, but by the procedure proposed by Peterson and Talbot.^{32,33} This yields somewhat lower electron densities than reported in previous studies for similar plasma conditions.⁸ The procedure gives the electron and ion saturation current at plasma potential, the electron temperature, the plasma potential, and the ratio of probe radius and Debye length. The electron density is calculated from the electron saturation current at plasma potential.³⁴ From the ratio of electron and ion saturation current the effective ion mass is calculated, giving an indication which ions are dominantly present in the plasma.³⁴ The latter procedure has been verified in different types of plasmas as Ar, (Ar–)H₂, Ar–D₂, (Ar–)N₂^{34,35} by comparison with ion mass spectrometry.

In the Ar–H₂–SiH₄ plasma only double probe measurements have been performed. The reason is that the electron saturation current collected by a single probe cannot be measured appropriately due to the formation of a resistive layer on the probe during deposition. The *a*-Si:H film deposited on the probe has a limited conductivity, which can generate a considerable voltage drop over the film. In simplified terms, the voltage V_{probe} applied to the probe is lowered by the product of current I drawn and the resistance R of the film, i.e., the voltage on the surface exposed to the plasma is equal to $V_{\text{probe}} - IR$. This means that depending on the current drawn and the resistivity of the film, the voltage on the surface exposed to the plasma can deviate considerably from the

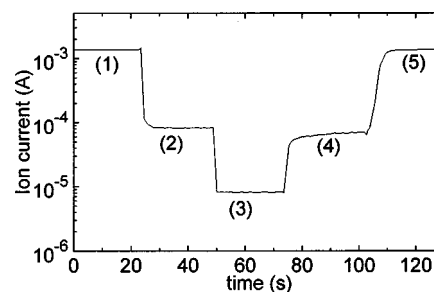


FIG. 2. Time-dependent ion current scan with single cylindrical probe at -10 V for Ar plasma (1) and (5), Ar–H₂ plasma (2) and (4) and Ar–H₂–SiH₄ plasma (3). The gas flows used are 55 sccs Ar, 10 sccs H₂, and 10 sccs SiH₄.

voltage applied.³⁰ This is of course most pronounced at higher currents, like the electron saturation current. The ion saturation current does not necessarily suffer from a voltage drop over the film, as it is relatively small. This was already addressed by Mosburg *et al.*³⁶ They showed that the voltage drop over the film at low currents can be insignificant due to a decreased resistivity of the *a*-Si:H caused by irradiation with photons, and/or by an increased probe temperature. The latter is easily obtained in the expanding thermal plasma as the gas temperature is relatively high compared to other plasmas.^{37,38} Whether the ion saturation current does not suffer from a serious voltage drop has been checked by performing time-resolved measurements at a fixed negative potential of 10 V in single probe configuration. Starting with a clean probe the current is measured in an Ar plasma to which, successively, H₂ and SiH₄ are introduced. Subsequently the SiH₄ is removed and then the H₂. In Fig. 2 such a scan is shown and it is clear that the ion current is constant for all conditions including the plasma in which deposition takes place. Moreover, when the SiH₄ is switched off the current rises immediately to almost the usual level of the current in an Ar–H₂ plasma. This shows that the current in the plasma with SiH₄ is not limited by the deposited film. However the fact that it does not rise immediately to the full current drawn in the Ar–H₂ plasma (before admixing SiH₄) shows that the probe suffers slightly from the *a*-Si:H film in that case. This time-dependent scan was checked for all conditions, while in between the probe was cleaned. The cleaning of the probes was performed by applying $+10$ V to the probes in an Ar plasma for 30 s, resulting in a large current of about 0.7 A. This cleaning procedure has been executed before every measurement. The currents drawn with the double probe and in the time-dependent measurements showed good agreement. The double probe measurements were again analyzed by an appropriate procedure proposed by Peterson and Talbot,³² yielding the electron temperature, the ion saturation current at plasma potential, the voltage difference between floating and plasma potential, and the ratio of probe radius and Debye length. Comparison of single and double probe measurements in Ar and Ar–H₂ plasmas revealed an agreement in electron density within 15%. Analysis of double probe measurements yields no information on the effective mass of the ions, however, the latter is required to analyze the double probe measurements. Infor-

mation on the effective mass of the ions in SiH_4 plasmas is therefore deduced from ion mass spectrometry as will be dealt with in more detail in Sec. II C. The total error in ion saturation current is estimated at 25% as also suggested by the reproducibility measurements. The error in electron density is larger as it is relatively more sensitive to the effective ion mass. Fortunately, knowledge of the ion saturation is sufficient to determine the flux of silicon containing ions to the *a*-Si:H film as will be shown in Sec. III.

C. Ion mass spectrometry

To obtain information on the different ions present in the plasma ion mass spectrometry has been applied at the position of the substrate holder. The mass spectrometer used is a Hiden Analytical EPIC 300,³⁹ whose outer geometry is adjusted such that it roughly resembles the geometry of the substrate holder. Gas extraction takes place by a 50 μm thin, knife-edged extraction orifice with a diameter of 50 μm . The ionizer, located just behind the orifice, is switched off in the present study. The mass filter is preceded and followed by only an rf driven pre- and postfilter. The mass range of the mass spectrometer is 300 amu. Mass filter transmitted particles are finally accelerated to a DeTech 415 channeltron with the first-dynode voltage set at -1200 V and which is operated in the pulse-counting mode. The masses are scanned in steps of 0.02–0.1 amu and the integration time at every step is typically 100 ms. The mass spectrometer is differentially pumped by a turbopump leading to a pressure of 5×10^{-7} mbar during processing (reactor pressure ~ 0.20 mbar) and a base pressure of 10^{-9} mbar.

The diameter of the orifice for gas extraction is much smaller than the mean free path of the species present in the plasma and therefore the flow of particles into the mass spectrometer is effusive. It is only for a pure Ar plasma that the thickness of the plasma sheath does not exceed half the orifice diameter, and therefore only in this case can the plasma in front of the orifice as well as the ion extraction be disturbed to some extent. The physical acceptance angle of the mass spectrometer for the ions is limited to 12.7° with respect to the normal of the orifice flange. During processing the extraction hole can become plugged due to deposition and therefore a plasma clean is applied regularly using an Ar- CF_4 plasma followed by an Ar- H_2 plasma.

A problem with the interpretation of mass spectrometry data is mass discrimination by the mass spectrometer as both the mass filter transmittance and detector efficiency are usually mass dependent.⁴⁰ The transmittance of the mass filter was estimated for masses up to 132 amu by comparing an ion spectrum with a so-called “rf-only” spectrum.^{41–43} In the rf-only case the dc voltage on the mass filter rods is omitted and the mass spectrometer acts as a high pass filter. Although only information up to 132 amu was obtained and although the data showed considerable scattering, it turned out that the transmittance of the mass filter is best estimated by a decrease with ion mass M proportional to $M^{-1/2}$. This rather small mass discrimination can possibly be attributed to the presence of a pre- and postfilter reducing the influence of the dc fringing fields. Furthermore, it turned out that the

detection efficiency of the channeltron used decreases approximately in a way similar to the mass.⁴⁴ This leads to an overall mass discrimination proportional to M^{-1} . Throughout this article mass spectrometry data are given uncorrected for this mass discrimination unless stated otherwise.

Another complication in this study is the presence of a signal at the spectrometer detector generated by plasma photons: the cascaded arc plasma source, which produces a large photon flux covering the total spectral range,⁴⁵ is perfectly aligned with the mass spectrometers orifice (see Fig. 1). This leads to a background signal in the mass spectra (see Fig. 6) which depends on the plasma created in the cascaded arc (the photon signal decreases for increasing H_2 admixture). For the present case it is much smaller than the signals created by plasma ions. Therefore it does not disturb the measurements and in fact enables monitoring the plugging of the gas extraction orifice by *a*-Si:H deposition.

III. RESULTS

A. Argon–hydrogen plasma

Different plasmas generated by the cascaded arc have been investigated thoroughly by spectroscopic diagnostics^{28,29,46–49} and Langmuir probe measurements^{31,34,35} as they are used to dissociate precursor gases like SiH_4 for thin film deposition. In this section, the knowledge of the Ar and Ar- H_2 plasma is enlarged by applying Langmuir probe measurements and ion mass spectrometry to the specific conditions used for *a*-Si:H deposition. Furthermore, the probe measurements have been analyzed by a more appropriate and accurate method in comparison with a previous study⁸ (see Sec. II B). The electron temperature obtained by the single probe at 6 cm from the arc exit is given in Fig. 3(a) and is about 0.3 eV for pure Ar and decreases for increasing H_2 admixtures. This is in good agreement with Thomson scattering results.^{28,46–48} The low electron temperature arises from the fact that no power is coupled to the plasma in the downstream region and it makes electron induced ionization of the atomic and molecular species in this region improbable.⁸ The plasma is therefore recombining and this means that the ion fluence in the downstream region is totally determined by the ion fluence emanating from the arc. Ionization in the downstream region occurs by means of charge transfer reactions between ions emanating from the arc and the species downstream like SiH_4 .⁸ In order to investigate the formation of silicon containing ions, the ion fluence and the type of ions emanating from the arc have been determined.

The total ion fluence, expressed in standard cubic centimeters per second, is given in Fig. 3(b). It has been derived by integrating Gaussian fits applied to the radial electron density profiles at an axial position of 6 cm from the arc exit and assuming a directed velocity of the ions of 1000 m/s.²⁹ Electron density profiles are given in Fig. 4 for an Ar plasma and an Ar- H_2 plasma with 10 sccs H_2 . The expansion of the plasma is clearly observable: at 6 cm from the arc the electron density shows a clear Gaussian profile, whereas nearby at 2 cm from the substrate holder the electron densities are smeared out due to expansion. They are only slightly peaked

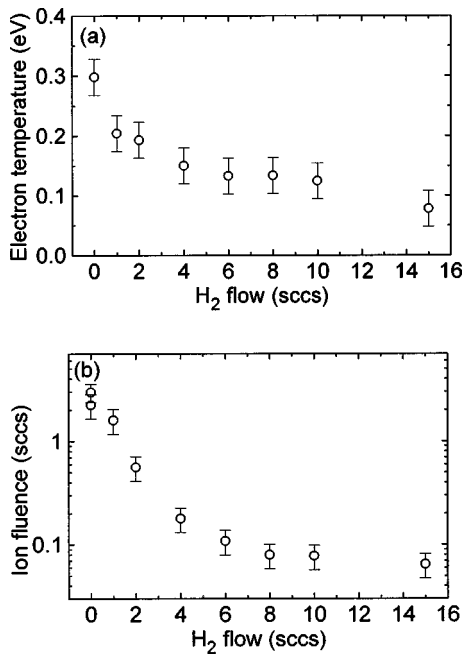


FIG. 3. (a) Electron temperature in the downstream region and (b) the ion fluence emanating from the arc determined at 6 cm from the arc exit for an Ar flow of 55 sccs and varying H₂ flow.

at the source axis. The electron densities for the pure Ar plasma show a good correspondence with Thomson scattering^{28,49} after correction for differences in pressure. The accuracy of the ion fluence is mainly limited by the accuracy of the Gaussian fits applied and by the assumptions of the ion directed velocity. Furthermore, this method has also been applied in Ref. 8, although less appropriate analysis of the Langmuir probe data (see Sec. II B) lead to a too high ion fluence in that case (up to ~50%).

In agreement with earlier observations the ion fluence decreases strongly for increasing H₂ flow due to charge transfer and dissociative recombination reactions.⁴⁷ The ion fluence decreases less drastically as suggested by electron densities determined at the plasma source axis due to a slight increase of the width of the profiles with increasing H₂ flow. The latter can be understood from Fig. 5(a), which shows the effective mass of the ions as obtained from the ratio of electron and ion saturation current. For pure Ar the ion mass is

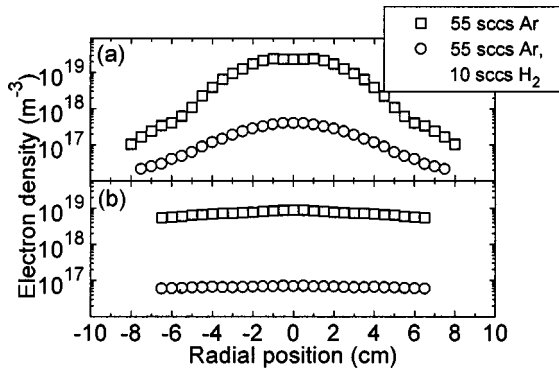


FIG. 4. Radial profiles of electron density determined at (a) 6 cm from the arc exit and (b) 2 cm from the substrate.

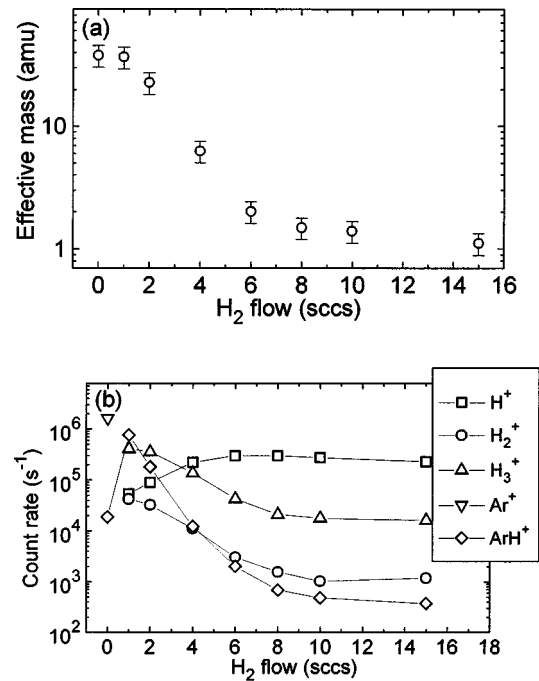


FIG. 5. (a) Effective mass (in amu) of ions emanating from the arc determined from the ratio of electron and ion saturation current and (b) ions measured by mass spectrometry at a distance of 38 cm from the arc exit for different H₂ flows.

equal to about 40 amu corresponding to Ar⁺. For increasing H₂ admixture, the effective ion mass decreases, finally down to about 1 amu corresponding to H⁺. This behavior is confirmed by ion mass spectra, obtained at an axial position of 38 cm, as shown in Fig. 5(b). The ArH⁺ present in the spectrum when H₂ is admixed is created by associative charge exchange between Ar⁺ and H₂.⁴⁷

In summary, it can be concluded that for a pure Ar plasma the ion fluence is large and that the dominant ion is Ar⁺. The dissociation and ionization of the SiH₄ is therefore governed by Ar⁺ emanating from the arc leading to a high dissociation degree.⁸ It should be noted that the argon metastable density is of little importance,⁸ as the metastable density is about a factor of 10 lower than the ion density.⁵⁰ When H₂ is admixed in the arc the most abundant ion changes from Ar⁺ or ArH⁺ to H⁺, while at the same moment the ion fluence is strongly reduced. Subsequently, for larger H₂ flows the dissociation of SiH₄ is therefore not dominated by ions but by the large fluence of H atoms emanating from the arc leading to an overall smaller dissociation degree of SiH₄.⁸ However for the formation of silicon containing ions the relative small ion fluence under these conditions is still important as will be shown in Sec. III B.

B. Argon–hydrogen–silane plasma

As already reported, adding SiH₄ to the Ar–H₂ plasma leads to the observation of large and hydrogen-poor positive silicon ions as shown in Fig. 6.^{21,22} These ion mass spectra consist of raw data without any correction for mass discrimination. In the spectra the signal generated by plasma photons can be clearly seen. Furthermore, ion peaks are observed

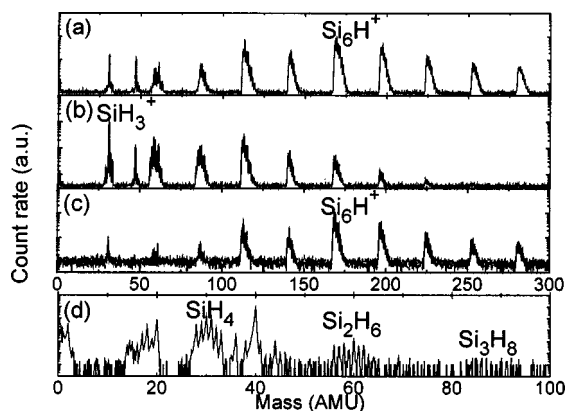


FIG. 6. Mass spectra for different SiH_4 and H_2 flows: ion spectrum for (a) 10 sccs SiH_4 and 10 sccs H_2 , (b) 3 sccs SiH_4 and 10 sccs H_2 , (c) 10 sccs SiH_4 and 3 sccs H_2 (most abundant ions are indicated), (d) neutral mass spectrum showing SiH_4 and polysilanes for plasma with 10 sccs SiH_4 and 10 sccs H_2 .

around mass 47 due to silanol ions $\text{SiH}_n\text{OH}_2^+$ ($0 \leq n \leq 3$). The oxygen in these ions probably comes from contamination as at first the deposition chamber was cleaned with an $\text{Ar}-\text{CF}_4-\text{O}_2$ plasma. After omitting O_2 in the gas mixture, silanol ions were hardly observable.

To draw conclusions about the relative abundance of ions throughout different plasma conditions and to avoid problems by day-to-day changes in the absolute count rates so-called multiple-ion detection (MID) scans have been performed. This means that the most abundant ion within every major peak was selected and the combination of these masses was monitored as a function of time wherein the plasma conditions were varied. Changes of the relative distribution of hydrogen within the different clusters with plasma conditions have been neglected, justified by the ion mass spectra. Furthermore, corrections have been applied for decreasing signals due to plugging of the gas extraction orifice. A finally obtained multiple-ion-detection scan is given in Fig. 7 as a function of SiH_4 flow at a constant H_2 flow of 10 sccs.

From Figs. 6(a), 6(b), and 7 it is very clear that the cluster size increases with increasing SiH_4 flow and consequently downstream SiH_4 density. For low SiH_4 flows,

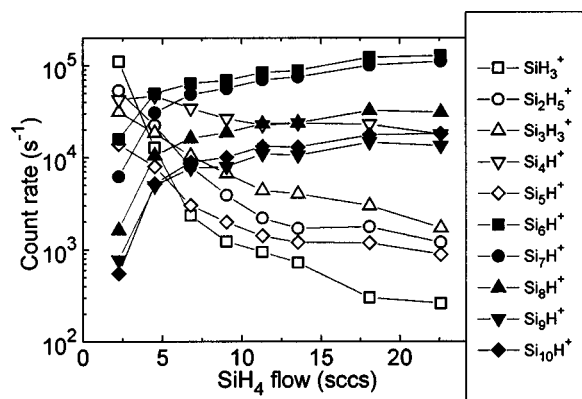
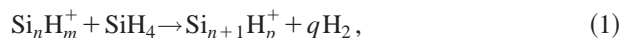


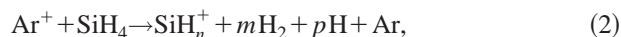
FIG. 7. Multiple-ion-detection scan as a function of SiH_4 flow for a H_2 flow of 10 sccs.

mainly clusters with only a few Si atoms are observed and their signals decrease drastically when the SiH_4 flow is increased. On the other hand, the signals due to clusters containing six or more Si atoms increase rapidly. Unfortunately, the mass range of the mass spectrometer limits the observation of the cluster ions for large SiH_4 flows.

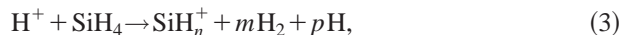
The results of Figs. 6 and 7 confirm the earlier proposed reaction pathway for the formation of cationic silicon clusters under the plasma conditions considered, i.e., the ion-molecule chain reactions^{21,22}



with $n \geq 1$ and $m + 4 = p + 2q$, neglecting endothermic reactions leading to the formation of H atoms.⁵¹ The possibility that the cluster ions are created by ionization of polysilanes present in the plasma can be ruled out as only a small amount of Si_2H_6 and a hardly observable amount of Si_3H_8 are present in the plasma beam [see Fig. 6(d)]. The sequential ion-silane reactions of Eq. (1) are initiated by Ar^+ or H^+ emanating from the arc (see Sec. III A). These ions undergo charge transfer reactions with SiH_4 admixed by ring injection



with $n + 2m + p = 4$ and, respectively,



with $n + 2m + p = 5$. For reaction (2) the reaction rates are still the subject of debate but on the order of $10^{-16} - 10^{-17} \text{ m}^3 \text{ s}^{-1}$, leading probably dominantly to ions with $n = 3$.⁵² For reaction (3) only a reaction rate is proposed for the reaction leading to ions with $n = 3$ which is $5 \times 10^{-15} \text{ m}^3 \text{ s}^{-1}$.⁵² Reaction rates for the sequential ion-molecule reactions have been estimated from a simple one-dimensional model. It revealed near-collisional rates ($10^{-16} - 10^{-17} \text{ m}^3 \text{ s}^{-1}$), which are rather independent of silicon and hydrogen content of the clusters.²² However Fig. 7 indicates that the ion-molecule reactions of Eq. (1) cannot be as straightforward as proposed and that also another kind of reaction must take place. This is suggested by the remarkable fact that the count rate due to clusters containing four Si atoms decreases only slightly with increasing SiH_4 flow, whereas the count rate due to clusters containing five Si atoms behaves rather similar to the clusters containing less than four Si atoms. For the moment no information is available on an underlying reaction and no conclusive information can be distracted from fundamental ion-molecule reaction studies, e.g., performed by Mandich and Reents,⁵³ as discussed in Ref. 22. Therefore, a computer code is applied to obtain more insight.⁵⁴

Quantitative information on the total ion flux arriving at the substrate has been obtained from Langmuir probe measurements (see Sec. II B). The ion flux towards the substrate as a function of SiH_4 flow is given in Fig. 8. Also the total sum of the count rates (in arbitrary units) of Fig. 7 is displayed for a SiH_4 flow up to about 15 sccs. For larger SiH_4 flows cluster ions containing more than ten Si atoms are probably very important. Apart from the simple integrated count rate, the integrated count rate with a correction for the overall mass discrimination of the mass spectrometer is also

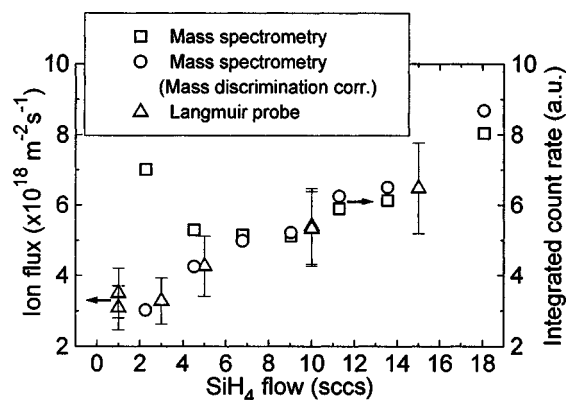


FIG. 8. Ion flux as obtained from Langmuir probe measurements and mass spectrometry (in arbitrary units) for a H₂ flow of 10 sccs and a varying SiH₄ flow.

shown. Despite the doubts about the accuracy of this correction, it shows a much better correspondence to the probe data. Both methods show an increase of ion flux towards the substrate for increasing SiH₄ flow. As the initial ion fluence is independent of the amount of SiH₄ injected, at first sight the difference could be accounted for by differences in recombination rates of the different cluster ions with electrons. However, another effect becomes clear from radial scans of the single Langmuir probe in front of the substrate holder. Figure 9 shows the radial ion current scans normalized to their center value for different SiH₄ flows injected. It is clear that the ion current scans are profiled and that the width of the profiles decrease for increasing SiH₄ flow. It has been carefully checked that the observed profile is not due to probe contamination. From the profiles and from a comparison with the scans obtained in Ar(-H₂) plasmas (see Fig. 4), it is suggested that the width of the ion current profiles is determined by the mass of the ions present in the plasma. For an Ar-H₂ plasma with H⁺ as the dominant ion, the ion current is not significantly peaked. The current profiles for small SiH₄ flows have an approximately similar width to the ion current profile in a pure Ar plasma, whereas the profiles for larger SiH₄ flows and consequently large cluster ions are considerably more pronounced. An increase of ion current due to the slightly increasing pressure with SiH₄ flow appeared to be insignificant. This leads to the conclusion that

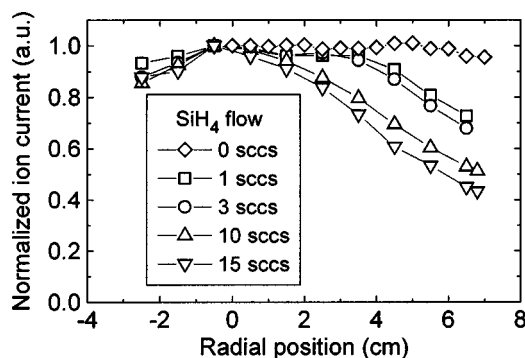


FIG. 9. Normalized radial scans of ion current for different SiH₄ flows at 2 cm in front of the substrate holder. The ion current scan for the Ar-H₂ plasma (55 sccs Ar, 10 sccs H₂) is given for comparison.

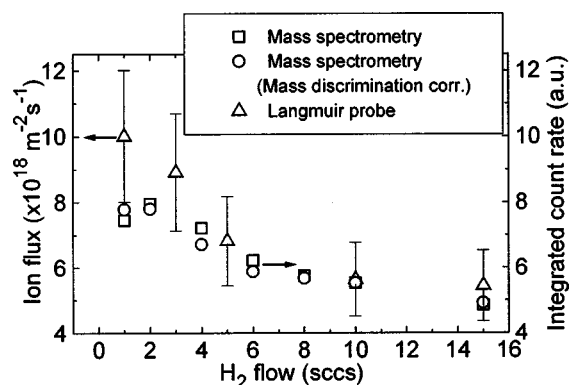
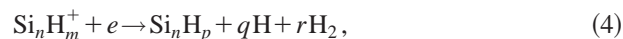


FIG. 10. Ion flux as obtained from Langmuir probe measurements and mass spectrometry (in arbitrary units) for a SiH₄ flow of 10 sccs and a varying H₂ flow.

the expansion of the ion beam is limited by the outward diffusion of the ions. Hereby the directed velocity of the ions towards the substrate, estimated at 900 m/s,²² is inevitably coupled to the one of the neutral species.²⁹ When, for example, both the diffusion velocity as well as the directed velocity would scale with the ion mass no difference in profile width should be observed.

The ion flux towards the substrate as a function of H₂ flow admixed in the arc is given in Fig. 10. The ion flux shows a slight decrease for increasing H₂ flow. Furthermore, MID scans for varying H₂ flow (data not shown) yield that the relative abundance of the ions does not considerably change with H₂ flow. This is also suggested by radial scans of the ion current, similar to those in Fig. 9, which show no significant dependence of the profile width on the H₂ flow. This fact, which leads to an almost constant average ion mass, prevents us from drawing conclusions about the spectrometer mass discrimination correction in this case. The slight decrease of the ion flux and the rather similar mass spectra for all H₂ flows are surprising as the ion fluence from the arc decreases drastically when H₂ is admixed [see Fig. 3(b)] and the dominant ion emanating from the arc changes from Ar⁺ or ArH⁺ to H⁺ (see Fig. 5).⁵⁵ It can be explained by a competition of the ion-molecule reactions (1) with dissociative recombination reactions of the ions with electrons:



with $p + q + 2r = m$ and whereby in fact it is not excluded that the silicon cluster breaks apart. Analogous to hydrocarbon ions, the reaction rate of dissociative recombination is estimated at $10^{-13}T_e^{-1/2}$ (in m^6s^{-1} with T_e the electron temperature in eV),⁵² while the rate can possibly increase slightly with ion size.⁵⁶ Depending on the proportion of this reaction rate to the reaction rates for the ion-molecule reactions and on the proportion of the density of electrons to the density of SiH₄ either dissociative recombination or ion-molecule reactions are more favored. This means that at high electron density, i.e., for a low H₂ flow in the arc, first dissociative recombination is more probable and when the electron density is decreased to a sufficient extent by recombination, the ion-silane reactions become as important. This most probably causes the apparent small influence of H₂ ad-

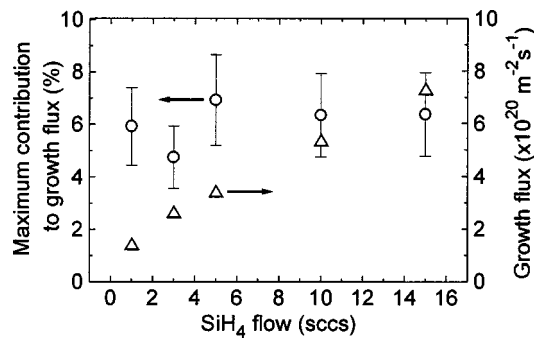
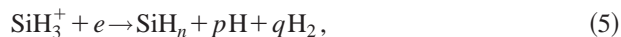


FIG. 11. Total growth flux and maximum contribution of cationic silicon clusters to this growth flux as a function of SiH_4 flow (10 sccs H_2).

mixture in the arc on the ion spectrum [see Figs. 6(a) and 6(c)], although the amount of ions emanating from the arc is strongly changed. The recombination presumably takes place in the initial region where SiH_4 is admixed immediately after charge transfer with Ar^+ or H^+ has occurred by the reaction



with $n \leq 2$ and $n + p + 2q = 3$. The radicals created in this way are very reactive both with SiH_4 as with surfaces.

The electron temperature and ion density in the depositing plasma have also been determined from the Langmuir double probe measurements, yet with limited accuracy. The electron temperatures obtained are about 0.3 eV for the H_2 flow series. For the SiH_4 flow variation it is in the range of 0.2–0.3 eV, with the electron temperature increasing slightly with SiH_4 flow. The electron density is on the order of 10^{16} m^{-3} and shows roughly the same trend as the ion fluxes in Figs. 8 and 10. For all SiH_4 flows the electron density is smaller than for the plasma without SiH_4 , despite a smaller beam radius for the conditions with SiH_4 . This can be attributed to dissociative recombination of the cluster ions with electrons [Eq. (4)].

From the ion flux towards the substrate,⁵⁷ the contribution of the cationic clusters to *a*-Si:H film growth in the expanding thermal plasma can be determined. To calculate this contribution in terms of the number of Si atoms deposited, the ion fluxes have to be multiplied by the average number of Si atoms in the clusters. These averages have been estimated from ion mass spectra as given in Fig. 6. In this reasoning, it is essential that hydrogen ions do not contribute significantly to the ion flux measured by the Langmuir probe. Under any condition, hydrogen ions have not been observed in ion mass spectra for SiH_4 plasmas. This was checked by changing the admixed H_2 for D_2 , neither showing a peak corresponding to deuterium ions.

To calculate the contribution of the cationic clusters, knowledge of their sticking probability is also necessary. As no data are available yet, unity sticking probability is assumed following the literature.^{9,10} For this reason the contribution calculated and depicted in Figs. 11 and 12 is called the maximum contribution of the cluster ions to film growth. In Fig. 11 and 12 the growth fluxes obtained at a substrate temperature of 400 °C are also shown, i.e., the net flux of Si atoms contributing to growth and leading to the deposition

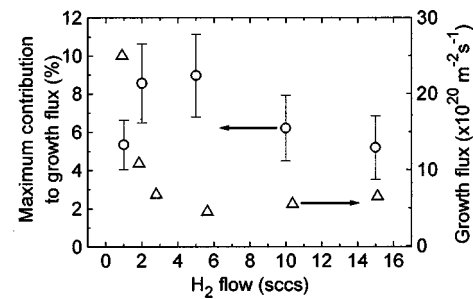


FIG. 12. Total growth flux and maximum contribution of cationic silicon clusters to this growth flux as a function of H_2 flow (10 sccs SiH_4).

rate. The growth flux is calculated by the product of deposition rate (in the range of 2–60 nm) and silicon density in the film obtained for the particular plasma condition.⁵⁸

The maximum contribution of the cationic silicon clusters ranges from 4% to 7% for varying SiH_4 flow (cf. Fig. 11) and from 5% to 9% for varying H_2 flow (see Fig. 12). The contribution is rather independent of both the SiH_4 and H_2 flow. The latter case is again surprising because for no or small H_2 admixture in the arc the ion fluence into the chamber is very large and the dissociation is mainly governed by charge exchange reactions with the Ar^+ and ArH^+ ions emanating from the arc. The H atom fluence is still low under these conditions and the charge exchange reactions have a relatively high reaction rate compared to the reaction rate of H atoms with SiH_4 as well.⁸ So the peculiar situation occurs that a high ion fluence from the arc is used for efficient SiH_4 dissociation, consequently leading to a high growth rate but with only a relatively small contribution of positive ions. As already mentioned this requires a strong dissociative recombination of molecular ions finally creating very reactive radicals and leading presumably to the rather poor film properties (e.g., low film density) obtained at low H_2 flows. The best material so far has been obtained under conditions (H_2 and SiH_4 flow both 10 sccs) in which the film growth is dominated by SiH_3 radicals⁸ and where the cluster ions have a maximum contribution of about 6%. The *a*-Si:H obtained under this condition fulfills the demands for its application in thin film solar cells.^{23,24} The impact of the cationic clusters on the film quality will be discussed in Sec. IV, but it is already mentioned that the energy flux of the clusters to the film in the expanding thermal plasma is limited. Due to the low electron temperature the difference between plasma potential and floating potential is only 1.5–2 V and the ions are therefore not highly energetic when they hit the surface in contrast with, e.g., ions in rf SiH_4 plasmas.^{16,18,19}

IV. DISCUSSION

In Sec. III it is shown that the maximum contribution of the cationic silicon clusters to the growth flux is in the range of 4%–9% for the conditions investigated. As already mentioned, especially the fact that the contribution is rather independent of the H_2 flow is very interesting: the ion fluence emanating from the source is heavily dependent on the H_2 flow and for no or small H_2 flows the initial chemistry is totally determined by this ion fluence. This apparent contra-

diction has been explained by dissociative recombination reactions, Eq. (4) and in particular, Eq. (5). These reactions are favored over clustering as long as the electron density is high. Now it is interesting to examine what happens with the reaction products created by this dissociative recombination as they are in fact also generated by ion-silane reactions. When a silane ion immediately recombines with an electron most probably very reactive silane radicals SiH_n with $n < 3$ are created, which can react rapidly with SiH_4 . The reaction of SiH_2 with SiH_4 can lead, for instance, to Si_2H_6 or to disilane radicals. The production of Si_2H_6 requires a stabilization reaction, favorably by collisions with SiH_4 .^{8,59} However when such a stabilization reaction does not occur, reactive disilane radicals are created, such as Si_2H_4 , which can possibly react with SiH_4 again. In this way, silane radicals created by dissociative recombination of silane ions can induce also clustering reactions by means of sequential radical-silane reactions (the few rates reported for these reactions have the same order of magnitude as the ion-silane reactions⁵²). Unfortunately, the detection of such radicals at relative low densities is difficult due to their reactive nature and due to the fact that they need to be ionized in the mass spectrometer. But it shows that the role of ion chemistry is not limited to the contribution of cationic clusters to the growth flux. In Ref. 8 it was shown that approximately two SiH_4 molecules are consumed per Ar^+ when a pure Ar plasma is used. This is an average value and does not exclude that (cationic) clusters are created with more than two Si atoms: a part of the Ar^+ can be lost by reactions with H_2 generated by SiH_4 dissociation, a part of the SiH_4 can be dissociated by H atoms created by other SiH_4 dissociation reactions and some of the reactive silane radicals will react at the chamber walls before clustering with SiH_4 . In Ref. 8 it was also shown that the polysilanes and particularly the Si_2H_6 creation, which are low in this type of plasma, are even lower when a pure Ar plasma is used instead of an Ar- H_2 plasma. This can be attributed to failing stabilization reactions as more SiH_4 is consumed in a pure Ar plasma leading to a lower SiH_4 density. Another possibility is that the Si_2H_6 is immediately dissociated by either ions from the source or by H atoms created by SiH_4 dissociation. The latter reaction, which has a larger reaction rate than the reaction between H atoms and SiH_4 ,⁵² leads most probably to SiH_3 and SiH_4 and consumes in fact only one SiH_4 because SiH_3 is unreactive with SiH_4 . Consequently, sequential radical-silane reactions cannot be excluded, especially under conditions in which dissociative recombination is important, and the importance of ion induced reactions is most probably not limited to cationic clusters contributing to growth. A significant contribution of reactive (poly)silane radicals can therefore be a reason for the relatively poor properties of the films produced when no or a small H_2 flow is admixed in the arc.

For higher H_2 flows the deposition is dominated by SiH_3 and under these circumstances the best quality material is obtained. For a SiH_4 and H_2 flow both of 10 sccs, solar grade material is deposited while the maximum contribution of cationic silicon clusters is about 6%. Also under these conditions the total contribution of reactive species generated by ion induced reactions can be larger as inferred from the same

reasoning as above. Dissociative recombination will relatively occur more for cationic clusters and less for silane ions, especially due to the already low electron density. This most probably leads to a relative larger contribution of polysilane radicals.

A rough estimate of the total contribution of ion-silane interactions to the SiH_4 dissociation and *a*-Si:H film growth for this condition can be obtained by considering the initial ion flux emanating from the arc (about 0.08 sccs). A lower limit is obtained if it is assumed that on the average two SiH_4 molecules are dissociated per ion as is the case for the pure Ar plasma.⁸ This assumption leads to a dissociation of ~ 0.16 sccs SiH_4 ($\sim 13\%$ of the SiH_4 dissociated under this condition). This is a lower limit because an average value, obtained in a plasma in which relatively more reactions will occur consuming only one SiH_4 per ion (as discussed above) is used. Furthermore, the contribution to film growth at the substrate is probably larger than 13% due to a preferentially more directed velocity of the heavier particles towards the substrate holder (see Sec. III B). An upper limit can be obtained by assuming that all the ions emanating from the source lead to clusters containing on the average six Si atoms, as is the case for the cationic clusters. This would mean that dissociatively recombined ions and recombined cationic clusters continue to react with SiH_4 at the same rate as for the ion-silane reactions. In this case, 40% of the SiH_4 flow is dissociated due to reactions initiated by ions. In conclusion, the real part of SiH_4 dissociated by ion induced reactions will probably be somewhere in between these percentages, while the growth is still dominated by SiH_3 . Yet the contribution of species created by ion induced processes to film growth can still be important for, e.g., the film quality as will be discussed next.

It is generally accepted that the deposition of *a*-Si:H in most types of SiH_4 plasmas is dominated by SiH_3 . Furthermore, a correlation between the high film quality and dominance of SiH_3 is often suggested. A relatively small contribution of cationic clusters (and possibly reactive polysilane radicals) to film growth can have important implications for the film quality. First of all the clusters have a very compact structure as discussed in Ref. 22 and can possibly create disturbances in the *a*-Si:H film stoichiometry. The clusters do not have the perfect tetrahedral crystalline structure to create nano- or microcrystalline sites,⁶⁰ which is in agreement with the fact that this has also not been observed by Raman scattering on the films.⁵⁸ Furthermore the clusters are hydrogen-poor and consequently contain many overcoordinated or unsaturated bonds.²² Therefore they can have a significant contribution to the dangling bond density in the film. Their contribution to film growth is on the order of 10^{-1} – 10^{-2} , while a defect density on the order of 10^{-6} – 10^{-7} of the film density is required for solar grade material. Nonetheless, as already mentioned the defect density of the material deposited with a considerable flow of H_2 in the arc is sufficiently low ($< 10^{16} \text{ cm}^{-3}$) for the application in solar cells. So it is still difficult to draw conclusions on detrimental or possibly even advantageous influences of the cationic clusters on the film quality up to now.

The possible implications mentioned above depend strongly on the sticking probability of the clusters, which is of no importance when the energy flux towards the film is considered. Due to the low electron temperature in the expanding plasma the energy flux of the clusters is small compared to other types of plasmas. In, for example, rf plasmas the energy flux of the ions could even be very important for the film quality. For example, the structural properties of the α -Si:H films deposited by an rf SiH₄ plasma, which improve with ion energy as observed by Hamers,^{18,19} might be totally explained by the additional energy supplied to the film by the ions. The absence of this additional energy supply in the expanding Ar-H₂-SiH₄ plasma can be one reason for the relatively high substrate temperature required to obtain good quality α -Si:H. The best solar grade properties are obtained at substrate temperatures in the range of 400–450 °C which are at least 150 °C higher than the optimum substrate temperature in rf SiH₄ plasmas. This can possibly be clarified by the application of an external bias voltage.

The observation of cationic clusters in the expanding Ar-H₂-SiH₄ plasma and their formation mechanism has some possible implications for other SiH₄ plasmas. Especially in remote SiH₄ plasmas where the product of geometrical path length between source and substrate is usually relatively high, the creation of reactive species by ions and sequential ion-molecule reactions cannot be neglected. Even when the ion or metastable fluence from the source is relatively small in comparison with, e.g., the H atom fluence (as in the expanding Ar-H₂-SiH₄ plasma) the clustering reactions can lead to clusters with a considerable size and can have a significant contribution to the growth flux or impact on film properties. The fact that for a certain technique α -Si:H deposition is dominated by SiH₃ is therefore most probably no guarantee for a good film quality. A reduction of the contribution of large (cationic) clusters in remote SiH₄ plasmas can possibly be obtained by putting the substrates not in line-of-sight with the source. The fact that the substrate in the microwave setup of Jasinski¹⁰ is placed in a tube at 90° with the plasma source is perhaps the reason that he only observes small silane ions, whereas Theil and Powell do observe large cationic clusters.²⁰

V. CONCLUSIONS

It has been shown that the combination of ion mass spectrometry and Langmuir probe measurements is very powerful to study ion formation and ion fluxes in a reactive plasma. Both techniques are in principle ion flux measurements, yet the interpretation of their data separately can lead to problems, whereas their combination yields complementary information. Furthermore, it is shown that probe measurements in depositing plasmas can very well be possible although great care is required.

The results obtained in the expanding Ar-H₂-SiH₄ plasma confirm that the observed cationic clusters are created by sequential ion-molecule clustering reactions and not by direct ionization of polysilanes. After charge exchange reactions between ions emanating from the plasma source and SiH₄ these reactions compete with dissociative recombina-

tion reactions with electrons. Especially when the electron density is sufficiently low (or reduced) they can lead to large cationic clusters whose average size depends on the product of SiH₄ density and distance between plasma source and substrate holder.

The ion flux towards the substrate has distinct beam properties for larger SiH₄ flows. The width of the ion beam decreases with increasing SiH₄ flow and consequently increasing cluster size. This leads to an ion flux towards the substrate increasing with SiH₄ flow. The influence of the H₂ flow admixed in the arc on the ion flux to the substrate and on the cluster size is small, although the initial ion flux emanating from the arc is strongly dependent on this H₂ flow. This is attributed to a strong dissociative recombination of the initially created silane ions with electrons at the position of SiH₄ injection.

The maximum contribution of the cationic clusters to the silicon growth flux is in the range of 4%–9% and rather independent of SiH₄ and H₂ flow. It has been discussed that cationic clusters and reactive species created by ion induced processes in general can still have a significant impact on the film growth. In (remote) silane plasmas they cannot be simply neglected both in terms of contribution to growth flux or influence on α -Si:H film quality.

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