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Plasma chemistry aspects of *a*-Si:H deposition using an expanding thermal plasma

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The plasma chemistry of an argon/hydrogen expanding thermal arc plasma in interaction with silane injected downstream is analyzed using mass spectrometry. The dissociation mechanism and the consumption of silane are related to the ion and atomic hydrogen fluence emanating from the arc source. It is argued that as a function of hydrogen admixture in the arc, which has a profound decreasing effect on the ion-electron fluence emanating from the arc source, the dissociation mechanism of silane shifts from ion-electron induced dissociation towards atomic hydrogen induced dissociation. The latter case, the hydrogen abstraction of silane, leads to a dominance of the silyl (SiH_3) radical whereas the ion-electron induced dissociation mechanism leads to SiH_x ($x < 3$) radicals. In the pure argon case, the consumption of silane is high and approximately two silane molecules are consumed per argon ion-electron pair. It is shown that this is caused by consecutive reactions of radicals SiH_x ($x < 3$) with silane. Almost independent of the plasma conditions used, approximately one H_2 is produced per consumed SiH_4 molecule. Disilane production is observed which roughly scales with the remaining silane density. Possible production mechanisms for both observations are discussed. © 1998 American Institute of Physics. [S0021-8979(98)06917-5]

I. INTRODUCTION

Hydrogenated amorphous silicon (*a*-Si:H) solar cells are a promising efficient and clean energy source for the near future. To compete with other kinds of energy production, *a*-Si:H solar cell research is aimed at the reduction of production costs and improvement of the cell efficiency and stability. Recent results by Yang *et al.* have shown that triple *a*-Si:H junction solar cells with initial efficiency of 14.1% and a stable efficiency of 13% are possible.¹ One way of reducing the costs is to increase the deposition rate of intrinsic hydrogenated amorphous silicon.

Hydrogenated amorphous silicon (*a*-Si:H) is a material that exhibits good electronic properties and photoconductivity.²⁻⁴ Usually *a*-Si:H is deposited using a silane containing plasma, possibly diluted in hydrogen. The presence of hydrogen in *a*-Si:H drastically reduces the defect density, which originates from coordination defects (unpaired Si-Si bonds). It is the properties of *a*-Si:H, i.e., photoresponse, photoconductivity, defect density, hydrogen content, etc., that determine the applicability of *a*-Si:H in optoelectronic devices such as thin film solar cells and transistors.²⁻⁴

In this article we will discuss an example of remote plasma deposition of *a*-Si:H using an expanding thermal argon/hydrogen plasma.⁵⁻⁸ It has been shown that this type of plasma is capable of obtaining high growth rates while maintaining *a*-Si:H quality. In the past other types of remote plasmas have been used to deposit high quality *a*-Si:H films.⁹⁻¹³ The major advantage of remote plasma is the absence of direct plasma contact with the substrate and there-

fore absence of ionic species (with possible high energy ions) and ultraviolet (UV) radiation. This leads to less surface damage and bulk defects which could be advantageous for radical dominated plasma deposition processes such as *a*-Si:H deposition. Lucovsky and co-workers,⁹ Anthony *et al.*¹⁰ and Theil and Powell¹¹ have utilized a rf inductively coupled plasma whereas Jasinski¹² and Johnson and co-workers¹³ utilized a microwave induced remote plasma for the deposition of *a*-Si:H. Major drawbacks of these plasma sources are the reported low *a*-Si:H growth rates, usually in the range of 0.01–0.05 nm/s.⁹⁻¹³

In the literature discussion about the possible precursor for growth from remote rare gas (He, Ar) diluted silane plasmas has ranged from exotic precursors as highly excited silane¹⁴ to silicon centered radicals.^{12,15} The situation seems more clear for hydrogen diluted microwave plasmas where atomic hydrogen is the reactive specie which abstracts hydrogen from silane to form mainly silyl radicals (SiH_3) and molecular hydrogen.¹³ There is a distinct difference between argon and helium diluted remote plasmas. The recent appearance of potential mass spectrometry measurements of a He/ SiH_4 remote rf inductively coupled plasma has revealed that the dominant specie in this type of plasma is the silyl radical,¹⁰ in agreement with modeling results by Kushner.¹⁵ On the other hand Ar/ SiH_4 remote plasmas seem to favor higher silanes and powder formation which might explain the bad *a*-Si:H quality deposited utilizing this type of plasma.^{16,17}

In other papers we have demonstrated that the expanding thermal plasma is a convenient plasma source to study the deposition mechanism by varying both growth rate and substrate conditioning.^{18,19} This article will be focused on the

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FIG. 1. The plasma setup for fast deposition of hydrogenated amorphous silicon.

plasma chemistry of this source as determined from quadrupole mass spectrometry. The influence of hydrogen dilution of the argon carrier gas will be interpreted in view of previously published results obtained by Thomson-Rayleigh scattering and Langmuir probe measurements and related to the depletion of silane downstream.^{20–26} The results will be compared to the results obtained using other types of remote plasmas and conventional plasma enhanced chemical vapor deposition (PECVD) of *a*-Si:H.

II. EXPERIMENTAL SETUP

An argon/hydrogen plasma is created in a dc thermal arc (cascaded arc) operated at high pressure (≈ 0.5 bar).^{5–8} The deposition chamber, with a length of 0.5 m and a radius of 0.25 m, is pumped by a pump stage consisting of a large Roots blower (2600 m³/h) which is backed by a small Roots blower (400 m³/h) and a fore pump (100 m³/h) (see Fig. 1). The pressure in the deposition chamber is approx 20 Pa and a plasma jet is thus created. Samples can be transferred in the substrate holder by means of a load lock chamber pumped by a turbopump (100 ℓ /s). Near the plasma source, typically 10 sccs (i.e., 0.6 slm) silane is injected symmetrically into the jet by means of an injection ring. The active plasma species dissociate the silane in radicals and ions which can deposit on the substrate positioned 30 cm from the arc outlet. The substrate is accurately temperature controlled (within 5 °C) and can be rf biased externally. A list of setup parameters is given in Table I. A similar setup was used in the past to

TABLE I. Setup parameters for the expanding thermal plasma.

Parameter	Processing values
Ar flow	30–100 sccs
H ₂ flow	0–20 sccs
SiH ₄ flow	0–17 sccs
Arc current	30–75 A
Arc voltage	45–120 V
Arc pressure	0.4–0.6 bar
Vessel pressure	0.15–0.5 mbar
Substrate temperature	50–500 °C
Substrate bias	0–150 V

FIG. 2. The ion fluence and atomic hydrogen fluence vs H₂ flow 6 cm from the arc outlet. Plasma conditions are argon flow 55 sccs, arc current 45 A and chamber pressure 20 Pa.

deposit hydrogenated amorphous carbon at high rates.²⁷

Background gas is sampled from the plasma by a Balzers QMS 200 Prisma residual gas analyzer (RGA) through an orifice of 100 μ m. The RGA is pumped by a turbopump (60 ℓ /s), positioned directly under the quadrupole. The operating pressure during measurements is in the 10^{−6} mbar range, depending on the chamber pressure. The mass spectrometer samples stable gases (H₂, SiH₄, Si₂H₆, etc.) in the plasma background as evidenced by comparing the cracking pattern under plasma conditions with the cracking pattern for H₂, SiH₄, and Si₂H₆ gas for the electron energy used (around 90 eV).

III. RESULTS

The expanding thermal plasma can be considered as a high density remote plasma, because there is no direct interaction between the arc source and the chamber due to the large pressure difference ($> 10^4$ Pa). Therefore the properties of the plasma expansion are fully determined by the upstream properties of the arc source in interaction with the accumulated background gases in the plasma chamber. The properties of reactive species (ions, hydrogen atoms, metastables, etc.) emanating from the arc are fixed and only depend on the arc conditions. For example, for a pure argon plasma the fluence of argon ions can be determined from electron and ion density measurements by means of Thomson-Rayleigh scattering and Langmuir probe.^{20–26} This fluence of ions and electrons then interacts with, e.g., silane or hydrogen injected in the chamber. The silane injected is dissociated and deposits on the wall. During dissociation of silane or deposition of *a*-Si:H other gases, such as H₂, are formed and in turn react with the plasma expansion. It is an important feature of the expanding thermal plasma that the reactivity of the initial expanding plasma is fixed and cannot be influenced by downstream conditions.

In Fig. 2 the ion and atomic hydrogen fluence emanating from the arc are given as a function of the hydrogen flow for an argon flow of 55 sccs, arc current of 45 A and a vessel pressure of 20 Pa. The ion fluence was determined from radial profiles of the ion density as obtained from Langmuir probe measurements, taking into account the correct ion mass^{21,23} and the directed velocity of the ion as determined

FIG. 3. Silane depletion vs H_2 flow injected in the arc as determined using the quadrupole mass spectrometer for the different mass peaks of the cracking pattern of silane. The peaks at $M/Z=28$ and $M/Z=32$ are corrected for the influence of oxygen and nitrogen. Plasma conditions are argon flow 55 sccs, silane flow 10 sccs, arc current 45 A and chamber pressure 20 Pa.

from Doppler shifted two photon atomic laser induced fluorescence (TALIF).²⁸ In the calculation of the atomic hydrogen fluence we assumed a constant dissociation degree of 80% of the injected H_2 flow, a value confirmed by recent flow modeling studies of the arc.²⁹ The dissociation degree of course depends on the hydrogen flow: it is higher at lower hydrogen flow and probably around 80% for the highest hydrogen flow. Since good experimental data are lacking it will suffice here use the estimated H fluence for our discussion of silane injection.

What is particularly clear from Fig. 2 is that at 10 sccs of H_2 injection the reactivity of the arc is mainly contained in hydrogen atoms emanating from the arc. Furthermore, the ion fluence decreases rapidly by two orders of magnitude as more hydrogen is injected into the arc. As discussed in our previous papers this is due to efficient wall association of atomic hydrogen and a less efficient arc operation at high hydrogen admixture.^{21,22,24–26}

In Fig. 3 the silane depletion (=relative consumption) D as calculated for the various mass peaks of the cracking pattern of silane is shown as a function of the hydrogen flow admixed in the arc. The plasma conditions were similar to the conditions used in Fig. 2. A difference is the injection of silane through an injection ring directly into the expanding argon/hydrogen plasma. The silane depletion is defined by the relative flow of dissociated SiH_4 and is obtained by

$$D = \frac{I(i)_{SiH_4,off} - I(i)_{SiH_4,on}}{I(i)_{SiH_4,off}}, \quad (1)$$

where $I(i)_{SiH_4,off}$ and $I(i)_{SiH_4,on}$ are the channeltron current signals measured at the different mass peaks i of the SiH_4 cracking pattern. The silane cracking pattern was in good agreement with the cracking pattern of silane gas for our mass spectrometer and resembles the one reported in the literature, unless the depletion was close to 100%. In the latter case deviations were observed of the silane gas cracking pattern due to improper background signal correction, especially for the signals which can be polluted by oxygen ($M/Z=32$) and nitrogen ($M/Z=28$).

The depletion D is a well defined ratio of the partial pressures in the plasma chamber if the temperature of the gas which is sampled from the background is not significantly changed between plasma on and off. This was checked by monitoring the argon partial pressure at $M/Z=40$. No significant change of this signal was observed when the plasma was on, confirming that the depletion as measured using Eq. (1) is proportional to the consumption of silane. Another concern is that consumption of silane can lead to changes in the residence time and specific conductivities of the different species and consequently to difference in partial pressures.³⁰ For example, hydrogen is generated when silane is consumed. Equation (1) remains valid as long as the total flow entering chamber remains more or less constant. Since we use large flows of argon and as we will show below for every silane molecule which is consumed one hydrogen molecule is produced, the difference in residence time between plasma on and off is minimal and at maximum 5%. We did not attempt to correct for these small differences.

Under the conditions measured the residence time is long (typically $\tau_{res} \approx 0.5$ s) compared with a typical loss time for radicals at the wall or in the gas phase (typically $\tau_{loss} \approx 0.05$ –5 ms). The wall loss time depends on the microscopic loss probability on the wall and the typical transport time by means of convection or diffusion to the wall which depends on the dimensions of the deposition chamber. Since $\tau_{res} \gg \tau_{loss}$ silane radicals or ions formed out of silane will be lost at the wall or substrate holder or react in the gas phase and have a minimal chance of being pumped away. As a result, the depletion as measured using the quadrupole mass spectrometer equals the loss of silane, i.e., the silane injected is converted into either radicals or ions which stick to the wall and substrate or react in the gas phase and form higher silanes and possibly dust. Concerning the latter, we expect, due to the short transport time of radicals and ions inside the plasma expansion, that significant dust formation in the plasma expansion can be excluded: respectively, around 7.5% and 1.5% of the consumed silane are converted into disilane and trisilane. This limits the contribution of dust formation to the depletion of silane to approximately 9%, if we assume that higher silanes are a necessary first step for cluster growth.

As can be observed in Fig. 3 the depletion of silane decreases, goes through a minimum, after which it increases slightly with increasing hydrogen admixture. The behavior of the silane depletion as a function of the hydrogen admixture reflects the two different ways of silane dissociation using an expanding argon/hydrogen plasma (cf. Fig. 2): when no hydrogen is admixed silane is dominantly dissociated by an argon plasma containing ions and electrons. At a high hydrogen admixture dominantly hydrogen atoms remain as the specie to dissociate the injected silane. First we will discuss the ion-electron dominated region after which we will analyze the region dominated by hydrogen atoms.

A. Electron-ion dominated region

In active plasmas such as a rf capacitively coupled plasma the dissociation and ionization of silane is in first approximation dominated by electrons.³¹ In rf or dc dis-

charges the mean electron temperature is around 2–5 eV. Moreover, the electron energy distribution is strongly non-Maxwellian leading to an underpopulated tail of the electron energy distribution function.³² As is known for the expanding thermal arc plasma, the electron temperature in the region where silane is injected, as measured using Langmuir probes and Thomson scattering, is around 2000–3000 K, i.e., much lower than the mean electron temperatures in active plasmas.^{20–25} In fact the dissociation of silane in the pure argon case shows similarities with the reported results on helium and argon remote plasmas by the group of Lucovsky *et al.*,⁹ Anthony *et al.*,¹⁰ Jasinski,¹² Theil and Powell¹¹ and modeled by Kushner.¹⁵ Here we will develop the analysis as proposed by these researchers further by a systematic analysis of the silane dissociation channels possible.

To compare the different dissociation mechanism we introduce the mechanism interaction length L_{int} . Since we are dealing with a remote plasma we can interpret this length as the $1/e$ length over which an electron or ion has an interaction with silane. The definition of this length is given by (K_{int} is the reaction rate of the interaction of electrons or ions with silane molecules)

$$L_{\text{int}} = \frac{\nu}{n_{\text{SiH}_4} K_{\text{int}}} = \frac{\nu k_B T}{p_{\text{SiH}_4} K_{\text{int}}} \quad (2)$$

We will assume that we can treat the interaction of the expanding argon/hydrogen plasma with the silane injected downstream in a partial pressure picture. Within this assumption we can determine the silane partial pressure p_{SiH_4} if we know the flow ratio and the total pressure. Note that this assumption is obviously invalid since we actually measure a silane consumption of, e.g., 80% for a pure argon plasma (cf. Fig. 3 with H_2 flow=0 sccs and $I_{\text{arc}}=45$ A) which means that only 20% of the silane flow injected contributes to the silane partial pressure. The interaction length L_{int} therefore should be compared with the distance between the injection ring and the substrate (around 30 cm). If the interaction length is much smaller than this distance the mechanism is very efficient and as a result the partial pressure is not determined by the flow ratio times the total pressure. In this case the interaction length should be determined self-consistently by adjusting the partial pressure until the silane consumed given a certain partial silane pressure results exactly in the partial silane pressure put in. Of course this simple iteration scheme is complicated by the fact that products formed in the dissociation of silane also decompose silane. Hence, to keep the analysis simple, we will only compare the first dissociation step of silane using argon ions and electrons to determine the dominant dissociation mechanism in the pure argon case.

In Table II the interaction length for four possible dissociation mechanisms using argon ions and electrons is shown. In the discussion of the dissociation we will neglect pyrolysis of silane.³³ The reason is that unimolecular dissociation of silane depends only on the temperature of the silane gas. Therefore, since we observe that the depletion of silane depends on both arc current and H_2 admixture (cf. Fig. 3), this would mean that these different plasma conditions lead to

TABLE II. Cross section, threshold energy, rate coefficient and interaction length L_{int} for the different possible dissociation mechanism. To calculate L_{int} we took a silane density of $7 \times 10^{19} \text{ m}^{-3}$ corresponding to approximately $p_{\text{SiH}_4} = 2$ Pa and a drift velocity of 1000 m/s. Mechanism (1) electron induced dissociation Eq. (3), (2) electron induced ionization Eq. (4), (3) dissociative attachment and ion-ion recombination Eqs. (7), and (4) dissociative charge exchange and dissociative recombination Eqs. (8).

Mechanism	Cross section ($\text{\AA}^2$)	Threshold (eV)	Rate ($\text{m}^3 \text{s}^{-1}$)	L_{int} (m)
1	≈ 10	≈ 4	$\approx 10^{-20}$	$\approx 10^3$
2	≈ 4	≈ 12	$\approx 10^{-34}$	$\approx 10^{17}$
3	≈ 0.01	≈ 6.5	$\approx 10^{-27}$	$\approx 10^{10}$
4	≈ 13	exotherm	$\approx 10^{-16}$	$\approx 10^{-1}$

vastly different temperatures of silane by interaction with the argon/hydrogen plasma. The high rovibrational temperature reported for the SiH radical in previous work of around 1500–3000 K should not be confused with the gas temperature of silane which is expected to be in the range of 800–1000 K.¹⁷ The rovibrational temperature of the SiH radical is high but also highly nonequilibrium because it is produced following the interaction of argon ions with silane. Hence, we think that the depletion of silane is initially caused by interaction with the active species, electrons and ions, emanating from the arc.

The first dissociation mechanism discussed is electron induced dissociation of silane (only the dominant process is given here with the lowest threshold energy)^{31,34}

The cross section and the threshold energy for this process are around $10 \text{ \AA}^2$ and 4 eV, respectively. Due to this relatively high threshold energy in comparison with the thermal energy of the electrons, the resulting Maxwellian rate coefficient at $T_e = 3000$ K is small and around $10^{-20} \text{ m}^3 \text{s}^{-1}$. Similar arguments hold for the second mechanism, electron induced ionization of silane (again the dominant channel is given with the lowest threshold energy)^{31,34}

possibly followed by a fast dissociative recombination of the molecular ion formed. The cross section and threshold energy for this reaction are around $6 \text{ \AA}^2$ and 12 eV. Consequently the Maxwellian rate at 3000 K is extremely small.

Although the Maxwellian rate for dissociation and ionization are small one has to be careful. A recent paper by Capitelli *et al.*³⁵ illustrated that the assumption of Maxwellian velocity distribution in the first expansion of an expanding thermal argon plasma might be in error. The basis for this kinetic calculation of the electron energy distribution is the heating of the electron gas by superelastic collisions between electrons and metastables leading to an overpopulated high energy tail. The argon metastable particles Ar^M are generated by three particle recombination process (either directly or after several optical and electron induced de-excitation processes from higher excited states)^{35,36}

The process, Eq. (5), is very slow in comparison with transport processes.³⁷ From the measurements of the metastable density by Buuron *et al.*³⁶ we deduce that the fluence of high energy electrons is at least a factor of 10 lower than the ion fluence. In this respect it is clarifying to realize that we are dealing with a remote plasma: since the high energy electron is capable of dissociating or ionizing only one silane molecule, after which it has lost most of its kinetic energy, and since it got its energy from the recombining electron-ion pair, it is the recombination process Eq. (5) which effectively determines the rate of dissociation and ionization by fast electrons. Hence, the production of fast electrons is not significant and can be neglected here in comparison with ion induced processes which we will discuss below. Similar arguments as for the fast electron induced processes hold for the frequently speculated, metastable induced dissociation of silane in remote plasmas (again we only consider the dominant channel),^{31,34}

It is known that these processes have very large rates of around $5 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$.³⁸ However, as discussed above, the metastables are produced by three particle recombination in the first expansion. Thus as in the case of the fast electron induced processes it suffices therefore to effectively compare the three particle recombination rate with other silane dissociation mechanism. As can be concluded from Table II ion induced dissociation of silane is more likely than metastable or fast electron induced dissociation.

Another possible dissociation mechanism of silane which needs to be discussed here is electron dissociative attachment and consecutive dissociative recombination of the negative molecular ion formed with the abundant argon ions (again we only discuss the dominant channel)^{31,34,39}

followed by

The cross section for the first process is around $10^{-2} \text{ \AA}^2$ and has an appearance potential of approx 6.5 eV. The resulting rate for this process at 3000 K is approx $10^{-27} \text{ m}^3 \text{ s}^{-1}$, i.e., much smaller than the electron induced dissociation Eq. (3) and can therefore be neglected. The recombinative step has probably a much larger rate coefficient since it is a Coulomb controlled process. Reaction Eq. (7a) could have a much larger rate coefficient in case silane is significantly rovibrational excited. However, the enhancement should be on the order of 10^7 to make the process comparable with electron induced dissociation. Moreover, the enhancement of the rate should be even larger in comparison with the dominant dissociation mechanism: dissociative charge exchange and consecutive dissociative recombination of the molecular ion formed^{31,34,40}

followed by

The cross section for the dissociative charge exchange step has been measured by Haaland⁴⁰ and found to be in the range of $13 \text{ \AA}^2$, a value which is higher by approximately a factor of 2 than measured by others.⁴¹ The cross section reported by Haaland leads to a reaction rate of approx $1.6 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ at 3000 K.⁴⁰ Whereas Haaland found that SiH_3^+ is the dominant product, others have reported production of smaller molecular ions SiH_n^+ ($n < 3$) too, albeit in small quantities.⁴¹ Similar to the process of dissociative attachment, it is uncertain what the influence is of rovibrational excitation of silane on the magnitude of the rate coefficient for process Eq. (8a). The dissociative recombination of the molecular ion formed is very fast with rates in the $10^{-13} \text{ m}^3 \text{ s}^{-1}$ range at 3000 K so that the first step can be considered to be the rate limiting step. Since it is well known that silane molecular ions have a large reaction rate with silane (typically $10^{-15} - 10^{-16} \text{ m}^3 \text{ s}^{-1}$), the dissociative recombination of molecular ions with electron is dominant as long as the electron to silane ratio is well above 1%.^{31,34} Note that the electrons emanating from the arc source are used to recombine with the molecular ion formed. As a result of Eqs. (8) the ion density decreases as a function of silane flow, as evidenced by Langmuir probe measurements.¹⁷

As can be seen from Table II the rate coefficient for the dissociative charge exchange reaction Eq. (8a) of an argon ion with a silane molecule is by far the largest rate in comparison with the other processes discussed above. Furthermore as can be seen from Table II only the interaction length for mechanism 4 is smaller than the distance between injection of silane and the substrate ($\Delta L \approx 30 \text{ cm}$). The three particle recombination length $L_{\text{rec}} = \nu / (n_e^2 K_{\text{rec}})$ for $T_e \approx 2000 \text{ K}$ and $n_e \approx 10^{19} \text{ m}^{-3}$ is around 2 m for electrons and argon ions, i.e., much longer than the interaction length for process Eqs. (8). Therefore we believe that silane in an expanding pure argon plasma is mainly dissociated by means of the processes given in Eqs. (8).

The latter conclusion is in sharp contrast with the conclusions derived by Parsons *et al.* and Tsu *et al.*¹⁴ from a mass spectrometric analysis of silane injected in a remote He plasma. They concluded that no real dissociation of silane occurs (although their measured silane consumption is over 50%) but that instead the silane is excited and deposited onto the walls. This hypothesis was derived from the fact that no radical fragments were observed using an appearance potential mass spectrometer down to a detection limit of 0.5%. However, their analysis is erroneous. First of all they used a so-called sniffer tube of considerable length between reaction chamber and mass spectrometer which could obscure the detection of radicals below the percentage level simply because they will stick to the wall of the sniffer tube before being detected by the mass spectrometer. The latter conclusion was also reached by Theil and Powell¹¹ and more or less confirmed by Jasinski¹² who in fact detected silyl radicals in a similar remote helium plasma. The amount of silyl radicals detected could explain the observed deposition rate using a well established sticking probability of around 10%.⁴² Another main comment on the interpretation by Parsons *et al.* and Tsu *et al.*¹⁴ is that they confuse depletion of silane with the actual radical and ion density corresponding with this

depletion. Since the loss time for radicals and ions formed by dissociation and ionization of silane is much shorter than the residence time of the silane gas, the reactive species density is much smaller than the silane density during plasma on. The latter statement even holds for SiH_3 which has the smallest loss probability reported which is 25%–37%.^{42–45} Jasinski¹² concludes that under some circumstances the He ions emanating from the microwave source are quenched downstream and in this way dissociate silane. Apart from this, Jasinski¹² conjectures that He metastables could play a role too. Calculations by Kushner¹⁵ indicate that the metastable density in both Ar/ SiH_4 and He/ SiH_4 rf inductively coupled remote plasma is higher than the ion density by at least a factor of 10. Hence, in view of the fact that the cross section for dissociative ionization by He ions is larger by a factor of 10 in comparison with the cross section for dissociative charge exchange by He metastables,^{40,41,46} we conclude that in the case of He/ SiH_4 remote rf inductively coupled plasmas both ions and metastables are important. On the other hand, the situation in Ar/ SiH_4 is reversed since the cross section for dissociation by metastables is a factor of 10 higher than the cross section for ion induced dissociation.^{38,40,41} This leads to the conclusion that in the case of an Ar/ SiH_4 rf inductively coupled remote plasma dissociation of silane occurs mainly by metastables. In contrast, and following the arguments given above, we believe that in an expanding thermal argon plasma the dominant process of dissociation is given by Eqs. (8).

Subsequent reactions of the silane products formed in the dissociative charge exchange and dissociative recombination reaction Eqs. (8) can be the insertion reaction of SiH_x ($x < 3$) into SiH_4 or the reaction of atomic hydrogen with silane. The insertion reactions have reported high reaction rates.^{31,34,47} An example is the reaction of silylene with silane

or

with reported total reaction rate constants of around $10^{-16} \text{ m}^3 \text{ s}^{-1}$. The first reaction needs a stabilizing third body and the reaction rate for this reaction shows a clear pressure dependence. The reaction probability of Si_2H_4 with silane is large and can contribute to the depletion of silane too.³⁴ Also, the atomic hydrogen formed in the dissociative charge exchange and recombination step Eqs. (8) is reactive with silane although at a lower rate than for the silicon radicals formed. If the electron density becomes too low the dissociative recombination reaction becomes slow [Eq. (8b)] and the reaction of silane molecular ions with silane takes over. This occurs at an electron density of approximately $10^{16} - 10^{17} \text{ m}^{-3}$.

As can be observed from Fig. 3 the silane depletion for pure argon is approximately 80% which corresponds to an absolute silane depletion of 8 sccs at 45 A. From Fig. 2 we observe that the ion fluence is lower than 8 sccs. In Fig. 4 we have plotted the absolute silane depletion (depletion times silane flow injected) versus silane flow for three different arc

FIG. 4. Absolute silane depletion vs SiH_4 flow injected in the ring downstream for three arc currents. Plasma conditions are argon flow 55 sccs, no hydrogen flow and chamber pressure 20 Pa. Dashed lines indicate saturation values of absolute depletion.

currents. The absolute depletion first increases linearly with silane flow after which it saturates. For the highest arc current no saturation is yet observed. The saturation value for different arc currents is indicated by a dashed line (for the highest current we estimated the saturation value). This saturation is expected since the initial reactivity (the ion-electron fluence) is limited. In Fig. 5 the saturation value of the absolute depletion is given as a function of the ion fluence for the different arc currents. The slope of the dashed line is around 2, indicating that approximately two silane molecules are consumed for every ion-electron pair entering the chamber.

B. Atomic hydrogen dominated region

The right part of Fig. 3 is dominated by hydrogen abstraction reactions since for relatively large hydrogen admixtures in the arc mainly hydrogen atoms are available in the region where silane is injected (cf. Fig. 2).^{31,34,48}

FIG. 5. Saturated absolute depletion values of SiH_4 vs the ion fluence for three arc currents. Plasma conditions are argon flow 55 sccs and chamber pressure 20 Pa. The slope of the line gives the amount of silane molecules consumed per ion-electron pair injected downstream into the vacuum chamber.

FIG. 6. Silane depletion vs H_2 flow injected in the arc for different arc currents as determined by the quadrupole mass spectrometer for $M/Z=30$. Plasma conditions are argon flow 55 sccs, silane flow 10 sccs and chamber pressure 20 Pa.

The rate for this reaction has a small activation energy of around 1250 K and a prefactor of around $2.8 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$, as confirmed by several experiments.⁴⁸

Although the atomic hydrogen fluence at 20% of hydrogen admixed (using an estimated dissociation degree of 60%–80%) is much larger than the fluence of ions emanating from the arc for a pure argon plasma, the depletion of silane is higher for a pure argon plasma. The interaction length L_{int} for hydrogen abstraction under similar conditions as given in Table II is around 0.1–1 m, depending critically on the temperature. This is in agreement with the lower reaction rate for hydrogen abstraction Eq. (10) in comparison with the dissociative charge exchange [the rate limiting step in Eqs. (8)], even if we correct for the consecutive reactions of $\text{SiH}_x^{r,v}$ ($x < 3$) formed in the dissociative recombination step or SiH_x^+ ($x < 4$) formed in the charge exchange step.

In the region where atomic hydrogen induced dissociation of silane is dominant also consecutive reactions between H and SiH_3 or between two SiH_3 radicals can occur leading in both cases to SiH_2 .^{31,34,48}

Both rates are relatively large in comparison with the hydrogen abstraction of SiH_4 , 2×10^{-17} and $7.9 \times 10^{-17} \text{ m}^3 \text{ s}^{-1}$, respectively. In these reactions SiH_2 is formed which can again react with silane to form higher silane radicals if stabilized by a third body. It is of course easy to understand that increasing the growth rate, which is achieved by increasing, e.g., the SiH_3 flux, leads to relatively more reactions of the Eqs. (11) type. This has possible consequences for the contribution of SiH_2 and/or higher silanes to the growth of $a\text{-Si:H}$ and thus for the quality of $a\text{-Si:H}$ deposited utilizing an expanding thermal arc as discussed below. Note that at low growth rates and low power during rf plasma deposition, thus low SiH_3 flux towards the substrate, reactions Eqs. (11) are quadratically less important.³⁰

In Fig. 6 the silane depletion (only as determined from mass 30 is shown) is given as function of the hydrogen admixed in the arc for different arc currents. In view of the discussion given above, the results of Fig. 6 can be explained

as follows. Increasing the arc current leads first of all to more ions emanating from the arc. Second, the ion composition will change towards dominantly H^+ instead of Ar^+ as function of increasing H_2 flow. It is known that H^+ has a larger reaction rate with silane than Ar^+ . Third, the dissociation degree of H_2 in the arc will be higher especially for the highest arc current. These three reasons lead to an overall higher depletion of silane for higher arc currents, as can be observed in Fig. 6. Furthermore, the minimum in the depletion as function of the hydrogen admixture shifts towards a higher hydrogen admixture because the influence of the ion induced dissociation remains relatively more important than the atomic hydrogen induced dissociation.

It is straightforward to deduce the possible significance of ion-electron induced dissociation when hydrogen is admixed in the arc. At approx 20% H_2 flow admixture (10 sccs H_2 in 55 sccs Ar) the ion flux emanating from the arc has decreased by at least two orders of magnitude, or is smaller than 0.06 sccs (cf. Fig. 2). Important is that also the identity of the ion has changed: at 20% H_2 admixture the dominant ion is H^+ . Because we are dealing with a remote plasma, the maximum amount of SiH_4 consumed by these ions in the first instance is 0.06 sccs for this particular condition. From Fig. 5 it then follows that subsequent reactions of the radicals and ions formed with silane lead to a factor of 2 higher consumption. The latter is only true if we assume that the radicals and ions formed are similar to those formed in case argon ions perform the first dissociating step.^{31,34,40,41} So the absolute silane depletion due to ions for 20% hydrogen admixture (=10 sccs) and 10 sccs of silane injected is at maximum $2 \times 0.06 \approx 0.12$ sccs. In this condition we measured an absolute silane depletion of around 2 sccs (cf. Fig. 3), meaning that ions contribute about 6% to the total SiH_4 consumption.

The particular condition discussed, i.e., H_2 -flow admixture of 10 sccs was chosen to demonstrate the ion contribution to the growth of $a\text{-Si:H}$ because under this condition we deposited our optimal properties of $a\text{-Si:H}$.^{6,8,19} As demonstrated, good optoelectronic properties in terms of light/dark conductivity, photoresponse, hydrogen content and optical band gap of $a\text{-Si:H}$ are achieved at a substrate temperature of 450 °C. The deposition rate achieved is around 11 nm/s, a rate which is approximately two orders of magnitude larger than the deposition rate obtained using, e.g., rf capacitively coupled plasma.⁴⁹ At hydrogen admixtures above approximately 10 sccs large fluences of SiH_3 are formed by hydrogen abstraction of silane. It is known that SiH_3 is less reactive with silane and thus is capable of reaching the substrate relatively easy.^{42–44,49} Therefore numerous authors have claimed that SiH_3 is probably the dominant precursor for growth of high quality $a\text{-Si:H}$. The nonreactivity of the silyl radical with Si-H bonds is thought to be the key issue in reaching near unity saturation on the growth surface leading to a small probability for the incorporation of surface dangling bonds into the film.^{9,13,15,42–44,49–53} This is in line with our observation that good quality $a\text{-Si:H}$ is grown under high admixtures of H_2 in the arc for which the conditions are such that SiH_3 is dominant,^{6,8,18,19} although it needs to be said that we need a higher substrate temperature to achieve

FIG. 7. The produced equivalent H_2 flow measured at $M/Z=2$ vs absolute silane depletion for different hydrogen flows (in sccs) injected into the arc. Plasma conditions are argon flow 55 sccs, silane flow 10 sccs, arc current 45 A and chamber pressure 20 Pa. The dotted line indicates one produced H_2 per consumed SiH_4 .

the good film properties. The higher temperature is probably needed because we have a higher growth rate. The latter is very similar to the growth of *a*-Si:H by hot wire CVD.⁵⁴

C. Other observations: H_2 and Si_2H_6 production

In Fig. 7 the produced equivalent H_2 flow as function of the absolute silane depletion is shown. The equivalent H_2 flow is defined as the imaginary flow which gives rise to the H_2 partial pressure measured given that the residence time does not differ to much with plasma on and off. The fact that we utilize a large argon flow and that the produced H_2 flow approximately equals the consumed SiH_4 flow justifies the latter assumption. From Fig. 7 we conclude that for a variety of conditions, with vastly different ion electrons and atomic hydrogen fluences and thus different plasma chemistry, about one hydrogen molecule is produced per silane molecule consumed.

The main sources of H_2 production are the different gas phase and wall reactions. For example, some of the reactions give atomic hydrogen which could again abstract silane and form H_2 or go to the wall, either passivate a dangling bond or recombine with an adsorbed H to form H_2 and return back into the gas phase.⁵⁵ Another possible source of H_2 is the network reconstruction of *a*-Si:H on the walls.^{19,49,50,56} From the observed production of about one H_2 per consumed silane we conclude that, if we neglect the small production of disilane and trisilane, the stoichiometry of *a*-Si:H deposited on the cold walls is that of polysilane with Si:H=1:2. This conclusion is corroborated by hydrogen incorporation studies¹⁹ which reveal that *a*-Si:H contains about 66% hydrogen below 100 °C.

The production of H_2 is also observed in other type of plasmas, specifically rf capacitively coupled plasma. In hot wall PECVD reactors the production of H_2 could be larger than one molecule per silane molecule consumed as thoroughly discussed by Perrin.³⁰ Longeway *et al.*⁵⁷ determined the hydrogen production and found a smaller H_2 production due to significant Si_2H_6 and higher silane formation, more or less in agreement with what others have found.^{30,58} On the other hand, the results of Jasinski on a remote He/ SiH_4

FIG. 8. The produced equivalent Si_2H_6 flow measured $M/Z=60$ vs the remaining equivalent silane flow for three different currents and varying silane flows injected into the ring. Plasma conditions are argon flow 55 sccs, hydrogen flow 15 sccs and chamber pressure 20 Pa.

plasma are very similar to ours with an approximate production of one H_2 per consumed silane molecule.¹² Also in that case most of the walls were cold. Comparison between experiments on a PECVD system and a kinetic model by Nienhuis *et al.*⁵⁹ revealed a similar trend as we observe: about one H_2 is produced per silane molecule.

Figure 8 shows the produced equivalent disilane flow measured as function of the remaining equivalent silane flow for three different arc currents. The first observation is that the disilane produced is less than the values reported in literature for rf and dc generated plasmas, in which cases the disilane partial pressure is a significant fraction of the total pressure. Longeway *et al.*⁵⁷ report that disilane production equals about 0.39 of the consumed silane in agreement with results obtained on similar systems.^{30,58} Doyle *et al.*⁶⁰ conclude from their data that disilane produced in the discharge, and which is again dissociated and ionized by electron impact, contributes significantly to the growth of *a*-Si:H. Veprek *et al.* have argued that disilane produced through SiH_2 insertion in SiH_4 is the precursor for growth of high quality *a*-Si:H.⁶¹ These results were based on mass spectrometric analysis of the disilane signal. Others have argued that these conclusions are incorrect.^{52,60} Parsons *et al.* and Tsu *et al.*¹⁴ report no significant disilane production in their remote He/ SiH_4 plasma more or less in agreement with the modeling of He/ SiH_4 discharges by Kushner.¹⁵ On the other hand, the modeling of remote Ar/ SiH_4 plasma by Kushner¹⁵ predicts high production levels of disilane and higher silanes. In our case we see a significant Si_2H_6 production of around 7.5% of the consumed silane more or less in contrast with results obtained by Jasinski.¹²

A clear observation is that disilane production depends mainly on the remaining silane density, i.e., the more silane remains, or if the consumption of silane is low, the more disilane is produced. Because of the dependence of the disilane production on the remaining silane flow we propose that disilane is most likely produced by reaction Eq. (9a). Note that the total particle density of the downstream plasma is around a factor of 3–10 lower than for, e.g., for rf PECVD plasmas at similar pressure because the gas temperature is around 1000–3000 K. The dependence depicted in Fig. 8 therefore indicates that the critical reaction of forming disi-

lane is the insertion reaction of SiH_2 in SiH_4 and that the third body needed to stabilize the excited Si_2H_6 is most likely silane. The latter is related to the fact that v - v exchange between a silane molecule and a disilane molecule is more effective than collisions with argon or molecular hydrogen.³⁴ We do not rule out that disilane is produced by surface reactions as others have argued.⁶² However, because of our observation Fig. 8 we think that the dominant process to form disilane is gas phase reactions.

In our experiments we also observe trisilane. The density of this molecule is again a factor of 10 lower than for disilane. Although we did not study the dependence of the partial pressure of trisilane on process parameters, we expect that trisilane is formed by means of higher silane radicals (e.g., Si_2H_4) inserted in silane similar to reaction Eq. (9a).

IV. CONCLUSIONS

Depletion measurements of silane admixed in the downstream plasma show that the dissociation can be directly linked to the reactive particles emanating the arc: it is demonstrated that the dissociation of silane is by a charge exchange reaction with a thermal ion and a consecutive dissociative recombination of the molecular ion formed, or hydrogen atom abstraction of silane by atomic hydrogen. In the latter case the dominant radical is most probably the silyl radical. In the ion-electron dominated regime it is shown that approximately two silane molecules are consumed per argon ion-electron pair, indicating that consecutive reactions of silane with silane radicals formed play a role too. We believe that part of these reactions lead to the production of disilane and trisilane in the gas phase. The consumption of silane is largest for pure argon plasma, due to the efficient charge exchange reaction and the reactivity of the silane radicals SiH_x ($x < 3$) and atomic hydrogen formed. When silane is admixed about one hydrogen molecule is produced per consumed silane irrespective of the specific plasma condition. This means that the stoichiometry of the α -Si:H deposited is on the average that of polysilane (Si:H = 1:2), except for the substrate region when hydrogen is effectively eliminated by the high substrate temperature.

The hydrogen abstraction dominated plasma condition corresponds to the condition under which the best quality α -Si:H is produced. This corroborates the general opinion that good quality α -Si:H is deposited when the deposition of α -Si:H is silyl radical dominated.

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