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Plasma diagnostic study of silicon nitride film growth in a remote Ar–H₂–N₂–SiH₄ plasma: Role of N and SiH_n radicals

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A remote expanding thermal plasma operated on an Ar–H₂–N₂–SiH₄ mixture has been studied by several plasma diagnostics to obtain insight into the plasma processes and the hydrogenated amorphous silicon nitride (*a*-SiN_x:H) growth mechanism from the N₂–SiH₄ reactant mixture. From Langmuir probe measurements, ion mass spectrometry, and threshold ionization mass spectrometry, it is revealed that the Ar–H₂–N₂ operated plasma source leads mainly to N and H radicals in the downstream region. The H radicals react with the SiH₄ admixed downstream creating a high SiH₃ density as revealed by cavity ringdown spectroscopy. By cavity ringdown measurements, it is also shown that Si and SiH have a much lower density in the downstream plasma and that these radicals are of minor importance for the *a*-SiN_x:H growth process. The ground-state N radicals from the plasma source do not react with the SiH₄ injected downstream leading to a high N density under the *a*-SiN_x:H deposition conditions as revealed by threshold ionization mass spectrometry. From these results, it is concluded that N and SiH₃ radicals dominate the *a*-SiN_x:H growth process and the earlier proposed growth mechanism of *a*-SiN_x:H from the N₂–SiH₄ mixture [D. L. Smith *et al.*, J. Vac. Sci. Technol. B **8**, 551 (1990)] can be refined: During deposition, an *a*-Si:H-like surface layer is created by the SiH₃ radicals and at the same time this *a*-Si:H-like surface layer is nitridated by the N radicals leading to *a*-SiN_x:H formation. This growth mechanism is further supported by the correlation between the SiH₃ and N plasma density and the incorporation flux of Si and N atoms into the *a*-SiN_x:H films as deposited under various conditions. © 2004 American Vacuum Society. [DOI: 10.1116/1.1631294]

I. INTRODUCTION

The deposition process of silicon nitride deposited by plasma-enhanced chemical vapor deposition has been widely investigated as silicon nitride films have numerous applications in the microelectronics industry.¹ However, applications of silicon nitride films keep emerging and this brings forth different demands on the properties and process conditions of the film. For example, plasma deposited silicon nitride films are currently emerging as multifunctional antireflection coatings on the next-generation crystalline silicon solar cells.² Besides antireflection performance, the silicon nitride films induce bulk passivation of defect states in the lower-quality silicon stock material that is currently used to reduce the price of photovoltaic electricity. Moreover, silicon nitride can also induce surface passivation of the cells which increases the efficiency of a cell. In the photovoltaics industry, it is, however, essential to obtain a sufficiently high production throughput while keeping the investments in equipment relatively low. The deposition rate of silicon nitride is, therefore, a critical parameter for this industry. Another example of an emerging application of silicon nitride films is as encapsulation layers for protection of devices from moisture. Although this application itself is not new, a class of organic material-based devices is at stake and this requires high-

quality encapsulation layers deposited at low temperatures (below ~100 °C). Important examples are polymer- and organic-based light emitting devices for flexible displays.³ Another issue for these nonsemiconductor industries, is the use of precursor gases other than NH₃ and SiH₄. Although so far usually the best film properties (for the microelectronics industry) are obtained from these precursor gases, they require extensive investments with respect to safety and environmental aspects that would rather be avoided.

These demands on the properties and production process of the film, together with the fact that the deposition process of silicon nitride has not yet been completely unraveled despite the significant progress in the last decade, make continued research of the deposition process of the material necessary. In this article, silicon nitride film growth will be studied for the expanding thermal plasma (ETP) using N₂ and SiH₄ as precursor gases. This remote plasma has shown to be able to deposit different materials at very high deposition rates while maintaining good film properties.^{4,5} Recently, it has been shown that the ETP can produce hydrogenated amorphous silicon nitride (*a*-SiN_x:H) films at deposition rates up to 20 nm/s and that these films are very well suited as bulk passivating antireflection coatings for multicrystalline silicon solar cells.⁶ This result has been obtained for both NH₃–SiH₄ and N₂–SiH₄ mixtures.⁷

Although the deposition process of silicon nitride has mostly been studied for silicon nitride deposited from

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$\text{NH}_3\text{-SiH}_4$ plasmas, some studies have carried out on $\text{N}_2\text{-SiH}_4$ plasmas. Specifically, the seminal work of Smith and co-workers^{8–10} has led to considerable insight into the deposition mechanism of $a\text{-SiN}_x\text{:H}$ films. From mass spectrometry and film studies, Smith and co-workers¹⁰ pointed out that the formation of $a\text{-SiN}_x\text{:H}$ is not governed by Si–N precursor species from the plasma when using N_2 . Instead, they proposed that the deposition process proceeds by the reaction of silane radicals (SiH_n) and nitrogen radicals (N) at the surface. This mechanism has been concluded from measurements of N radicals in the plasma by threshold ionization mass spectrometry (TIMS). Silane radicals SiH_n were not experimentally observed in their study but their role in the deposition process was inferred from the deposition process of hydrogenated amorphous silicon ($a\text{-Si:H}$) from SiH_4 plasmas. Other research groups have focused on the surface reactions and the evolution of the film properties during film growth, e.g., by *in situ* infrared spectroscopy on the film.^{11,12} Although these studies reveal important information on the (sub)surface reactions, there is usually no direct information on the plasma species present. Therefore, in these studies, one can only speculate on the nature of the radicals and ions arriving at the substrate during film deposition.

In this article, we will focus on the determination of the N radical and SiH_n radical densities in the $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ operated ETP. The N radicals have been investigated by TIMS while the densities of the silane radicals Si, SiH, and SiH_3 have been determined from cavity ringdown spectroscopy (CRDS). The SiH_2 radicals have not been investigated by cavity ringdown in the ETP setup so far, however the information on the Si, SiH, and SiH_3 densities provide a sufficient basis to draw conclusions about the SiH_n radical chemistry in the plasma and the corresponding $a\text{-SiN}_x\text{:H}$ growth mechanism. The results obtained by the plasma diagnostics will be compared to the film properties obtained under various plasma conditions as have been reported in Ref. 6. As mentioned earlier, the deposition rates associated with these ETP conditions are very high, i.e., in the range of 4–35 nm/s. Finally, we will show that our results are in line with the results obtained by Smith and co-workers^{8–10} in a conventional rf plasma and from the SiH_n radical densities found, we will refine the proposed growth mechanism of $a\text{-SiN}_x\text{:H}$.

In Sec. II, the ETP setup and the plasma diagnostic techniques used will briefly be described. The detection of N radicals by TIMS will be addressed in more detail (Sec. II C). In Sec. III, the results of the investigations will be presented and discussed. First, the reactive species emanating from the plasma source of the ETP will briefly be addressed (Sec. III A) as these species induce the dissociation of the downstream injected SiH_4 . Section III B contains the results on the N radical and the SiH_n radical density in the downstream plasma. Some aspects of the growth mechanism of $a\text{-SiN}_x\text{:H}$ will be discussed in Sec. IV on the basis of results reported in this study as well as on the basis of data reported in literature. In Sec. V, the main conclusions of this article will be summarized.

FIG. 1. ETP setup with plasma diagnostics.

II. EXPERIMENT

A. Expanding thermal plasma deposition setup

A diagram of the ETP with the plasma diagnostics is given in Fig. 1. The ETP setup has been described extensively in previous publications^{4,6} and, therefore, we will only briefly address the main characteristics for $a\text{-SiN}_x\text{:H}$ deposition.

In a dc operated cascaded arc plasma source, a plasma is created in an $\text{Ar-H}_2\text{-N}_2$ gas mixture. This plasma creation takes place at subatmospheric pressure (typically 300 Torr) and at the exit of the plasma source, the plasma expands into a low-pressure deposition chamber. The reactive species in the plasma can subsequently react with the SiH_4 gas that is injected into the downstream plasma by an injection ring. The plasma operating conditions have been chosen equal to those used in Ref. 6, which reports about the $a\text{-SiN}_x\text{:H}$ film properties obtained by the $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ operated ETP. Briefly, the gas flows used are 55 standard cubic cm³/s (sccs) Ar for all conditions, 0–5 sccs H_2 , 0–10 sccs N_2 , and 0–15 sccs SiH_4 . The pressure in the downstream region is in the range of 130–150 mTorr and the cascaded arc is typically operated at a current-controlled arc current of 45 A and a voltage of 230 V. For convenience, the deposition rate and Si/N atomic ratio obtained for various SiH_4 flows are reproduced in Fig. 2 from Ref. 6.

The $a\text{-SiN}_x\text{:H}$ films have been deposited at samples positioned at a substrate holder but, for the present study, the substrate holder has been replaced by a mass spectrometer with a similar geometry. The reactor is pumped by a stack of two roots blowers and a forepump with a high pumping capacity (2600 m³/h). Overnight, the reactor is pumped by means of a turbopump reaching a base pressure of 10^{-6} Torr.

B. Probe measurements and ion mass spectrometry

The density of ions and electrons, as well as the electron temperature for the nondepositing $\text{Ar-H}_2\text{-N}_2$ plasma emanating from the plasma source, has been measured by single Langmuir probe measurements. The probe configuration and analysis procedure are described in detail in Ref. 13. The Langmuir probe measurements have been carried out at a

FIG. 2. Deposition rate and Si/N atomic ratio of the α -SiN_x:H films as a function of the SiH₄ flow. The data (taken from Ref. 6) are obtained for these plasma conditions: 55 sccs Ar, 10 sccs N₂, 5 sccs H₂, 45 A arc current, and 150 mTorr. The error bars for the N/Si ratio are an upper limit.

distance of 6 cm from the cascaded arc nozzle, i.e., approximately at the position where the SiH₄ gas is injected under α -SiN_x:H deposition conditions.

Information on the ions present in the plasma has been obtained by ion mass spectrometry as described in Ref. 13. The mass spectrometer used is a Hidden Analytical EPIC 300 (Hidden Analytical Ltd., 420 Europa Blvd., Warrington WA5 7UN, UK). The ions in the plasma are extracted effusively into the mass spectrometer by a knife-edged extraction orifice with a diameter and thickness of 50 μ m. By means of a turbopump with a pumping capacity S of 56 l/s, the pressure in the mass spectrometer is kept below 10^{-6} Torr during plasma operation (at ~ 150 mTorr). The ions are separated by their mass-over-charge ratio [expressed in atomic mass units (amu)] in a triple-stage mass filter and detected by a channeltron (DeTech 415). The mass range of the mass filter is 300 amu. Ion mass spectrometry is applied for the nondepositing Ar–H₂–N₂ plasma as well as for one condition of the depositing Ar–H₂–N₂–SiH₄ plasma. In the latter case, the measurement time (integration time per step in amu) taken is very short to avoid the influence of clogging of the extraction orifice by film deposition. However, this reduces the signal-to-noise ratio of the measurement.

C. Threshold ionization mass spectrometry

The presence and density of ground-state N radicals in the plasma have been investigated by mass spectrometry, using the so-called TIMS or appearance potential technique. This technique has also been applied by Smith and co-workers^{8–10} in their studies of the α -SiN_x:H deposition mechanism. In the present study, a Hidden Analytical EPIC 300 mass spectrometer [with “plasma sampling mass spectrometer (PSM) upgrade” for TIMS]¹⁴ has been installed at the position of the substrate holder. This enables the detection of the radical species contributing to film growth.

The gas extraction takes place through the same orifice as described in Sec. II B, as are the pumping capacity and pressure in the mass spectrometer. Under operation in the TIMS mode, gas species are ionized by electrons emitted by a thoriated iridium filament located in the ionizer region of the

FIG. 3. Electron energy scan at a mass-over-charge ratio of 14 amu for the determination of the N radical density. The plasma on condition clearly shows the signal created by N radicals at low energies. The signal at high energies is lower for the plasma on condition than for the plasma off condition due to the depletion of N₂ by the plasma. The electron energy scale has been recalibrated using the threshold energy for ionization of Ar and other noble gases (see Ref. 14).

mass spectrometer. This ionizer region is situated “line of sight” at a distance of 24 mm from the extraction orifice. The electron emission current I_e is controlled at a relatively low current (2–20 μ A) to avoid space-charge buildup and to keep the filament temperature low. The low temperature will minimize thermal decomposition of plasma species, such as N₂ at the filament. From the ionizer, the ionized species are led through a Bessel box type of energy filter followed by the triple-stage mass filter and the channeltron detector.

The ionization of the ground-state N radicals ($N + e \rightarrow N^+ + 2e$, $E_i = 15.2$ eV) is distinguished from the dissociative ionization of N₂ molecules ($N_2 + e \rightarrow N^+ + N + 2e$, $E_a = 25.3$ eV) in the ionizer by scanning the electron energy E of the electrons emitted by the filament. The electrons are monoenergetic with a spread of less than 0.5 eV. Figure 3 shows a typical electron energy scan at a mass-over-charge ratio of 14 amu for N radicals. The “plasma on” condition shows a clear hump at energies above the threshold energy E_i for the ionization of N radicals. For the “plasma off” condition, a large signal appears for energies above the threshold energy E_a for dissociative ionization of N₂ into N⁺. The small signal at lower electron energies can be attributed to the ionization of N radicals that are created by the aforementioned thermal decomposition of N₂ at the hot filament in the mass spectrometer. Furthermore, Fig. 3 gives no indication for dissociative ionization of excited nitrogen molecules in the mass spectrometer, which would be observed by an additional hump in the signal for the plasma on condition in the electron energy region of 15–25 eV.

The density n of N radicals is derived from the signal of the mass spectrometer (corrected for the small contribution to the signal by thermal decomposition) by

$$I(E) = \alpha I_e \sigma(E) n \quad \text{with} \quad E_i < E < E_a, \quad (1)$$

in which $\sigma(E)$ is the cross section for ionization and α is the geometry and mass dependent proportionality constant. The determination of the unknown constant α is avoided by linking the signal due to N radicals to a signal due to other

species with a known number density in the plasma. For this, we have taken the Ar signal during the plasma off condition, following the procedure proposed by Singh *et al.*¹⁵ Singh *et al.*¹⁵ pointed out that it is necessary to use the signal created by ionization of a monoatomic species in this procedure. The application of a signal created by dissociative ionization (e.g., N₂) will introduce considerable error because dissociatively ionized species have a different extraction efficiency in the mass filter.

In the procedure of quantifying the N atom radical density by using the known density of Ar atoms in the plasma off condition, differences in the ionization cross sections (taken from Refs. 16, 17, and 18), as well in mass filter transmittance and channeltron detector efficiency, are taken into account. The product of mass filter transmittance and channeltron detector efficiency has a m^{-1} dependence on the mass m of the analyzed species.^{13,15} Furthermore, the difference in surface reactivity for Ar and N atoms needs to be taken into account. Both Ar and N atoms enter the ionizer of the mass spectrometer by the effusively extracted beam. Ar species can however have wall collisions inside the ionizer without being lost at the walls and, therefore, Ar can build up a background density in the ionizer. N radicals are more reactive than Ar, and the N radicals can possibly react at the ionizer walls. Depending on the surface reactivity of N, expressed by the surface loss probability γ_N , the N radicals can only build up a smaller background density or even no background density in the mass spectrometer. For example, in the case that $\gamma_N=1$, the N radicals will have no background density component $n_{\text{ion,back}}$ in the ionizer but only a density component in the effusive beam $n_{\text{ion,beam}}$. As described in Ref. 14, in this specific case of $\gamma_N=1$, the N radical density derived from the comparison with the Ar density needs to be corrected by the correction factor C :

$$C = \frac{n_{\text{ion,beam}} + n_{\text{ion,back}}}{n_{\text{ion,beam}}} \quad (2)$$

For the particular mass spectrometer used, this factor $C = \sim 35$.¹⁴ When the surface loss probability γ_N of N radicals in the ionizer is smaller than unity, Eq. (2) no longer holds and the factor C is smaller. The lower limit is $C=1$, in this case, the N radicals are as unreactive with the wall as the Ar atoms. To determine the correction factor C for our measurements, information about γ_N on stainless steel is needed. The surface loss probability of N radicals on stainless steel has been reported in Refs. 19 and 20 for different pressures. These values are shown in Fig. 4. Although γ_N is only a few percent at typical plasma operating pressures, it is clear that γ_N increases for decreasing pressures. On the basis of this trend, we assume, therefore, that $\gamma_N=1$ in the ionizer considering the fact that the pressure in the ionizer is 10^{-6} Torr. This assumption is also in line with the fact that N reacts easily at stainless steel unless the stainless steel is covered with a “protective” N₂ layer formed over the saturated N layer adsorbed at the stainless steel. This N₂ layer has a greater fractional surface coverage at higher pressures.¹⁹ In conclusion, we can assume that $C = \sim 35$. We need to men-

Fig. 4. Surface loss probability γ_N of N radicals on stainless steel as a function of the partial pressure of N₂ as reported by Adams and Miller (see Ref. 19) and Singh *et al.* (see Ref. 20.)

tion that this assumption is rather crude and leads to a large systematical uncertainty in the N radical density in the plasma as determined by TIMS. However, as pointed out in Ref. 21, the N radical density determined by TIMS using this assumption is in good agreement with the ground-state N(⁴S) density determined by the two-photon absorption laser-induced fluorescence (TALIF) method applied under similar conditions.²²

D. Cavity ringdown spectroscopy

Silane radicals SiH_n have been measured by CRDS, which is a very sensitive and relatively easy-to-apply absorption spectroscopy technique.²³ The high sensitivity is obtained because the technique is based on multipassing and due to the fact that the change in absolute light intensity is not measured like in traditional absorption spectroscopy. Instead, the decay rate of a short laser light pulse trapped inside a high-quality optical cavity, created by two highly reflective mirrors, is measured. For an “empty” cavity, the decay rate depends on the reflectivity of the mirrors as well as on their distance. When an absorbing medium is created inside the cavity, e.g., by plasma ignition such that plasma radicals are generated, the decay rate of the laser light (with a wavelength corresponding to the absorption spectrum of the radical) in the cavity will be enhanced. Comparison of the two decay rates directly yields the magnitude of absorption due to the radicals. From this absorption value, information on the density of the radicals can be extracted.

For the present work, the radicals Si, SiH, and SiH₃ have been measured at a distance of 3.5 cm from the substrate holder. The experimental details and procedures have been described in detail in Refs. 24 and 25 for *a*-Si:H deposition conditions and, therefore, only the basics will be described here. The Si radicals have been detected by scanning the laser over the Si(4s ³P₁ ← 3p² ³P₁) transition at 251.9 nm. The Si absorption peak in this wavelength region is superimposed on the broadband SiH₃ absorption spectrum as discussed below. The total ground-state Si density has been determined by assuming thermal equilibrium for a gas temperature of 1500 K.²⁵ Special attention has been given to

FIG. 5. Parts of the normalized SiH_3 absorption spectrum as measured by CRDS in an $\alpha\text{-SiN}_x\text{:H}$ and $\alpha\text{-Si:H}$ depositing plasma. The absorption spectrum reported by Lightfoot *et al.* (see Ref. 26) is given for comparison and is in arbitrary units. The inset shows the correlation between the absorption values measured at 217 nm and 251.8 nm as obtained under various $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ plasma conditions.

the laser pulse energy used in order to avoid optical saturation of the transition. SiH radicals have been measured on the $A^2\Delta \leftarrow X^2\Pi$ electronic transition around 414 nm. The laser has been scanned over the $Q_1(11.5)$ rotational line at 413.46 nm and the total SiH density has been determined by using a rotational SiH temperature of 1500 K. This rotational temperature has been estimated from the relative distribution of the $Q_1(14.5)$ and $R_2(1.5)$ rotational lines of SiH which was determined for some characteristic conditions of the $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ plasma.²⁵ The SiH_3 radicals have been measured by the $\tilde{A}^2A_1 \leftarrow \tilde{X}^2A_1$ electronic transition. The corresponding absorption band is featureless and ranges from ~ 200 to ~ 260 nm (due to the predissociative nature of the excited state) with a maximum around 215 nm.²⁶ The SiH_3 radicals in the $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ plasma have been measured around 217 nm and 250 nm and the absorption values at these wavelengths measured are shown in Fig. 5, together with the SiH_3 absorption spectrum reported by Lightfoot *et al.*²⁶ The absorption values for the $\alpha\text{-SiN}_x\text{:H}$ depositing plasma fit well to the SiH_3 spectrum, just as is the case of the $\text{Ar-H}_2\text{-SiH}_4$ plasma for $\alpha\text{-Si:H}$ growth. This strengthens the conclusion that, indeed, SiH_3 is measured in absorption and that the measurement is not significantly disturbed by the presence of clusters or particles. As discussed in Refs. 24 and 25, absorption and light scattering by clusters/particles could, in principle, lead to an apparent “broadband absorption”. It would, however, be expected that the scattering behavior is significantly different for Si clusters/particles than for Si-N clusters/particles.

III. RESULTS AND DISCUSSION

A. Plasma source: Downstream $\text{Ar-H}_2\text{-N}_2$ plasma

Understanding of the downstream plasma processes with SiH_4 requires information on the $\text{Ar-N}_2\text{-H}_2$ plasma emanating from the cascaded arc plasma source. The reactive species emanating from this source will initiate the dissociation and ionization reactions of the injected SiH_4 . These reactive

FIG. 6. Electron temperature T_e , electron density n_e and ion density n_i , and the relative abundance of the different ions in (a) the Ar-N_2 and (b) the $\text{Ar-N}_2\text{-H}_2$ plasma as determined by Langmuir probe measurements and ion mass spectrometry. The data in the ion spectra have been corrected for the m^{-1} dependence of the mass spectrometer for the ion mass m . The N_2 flow is 10 sccs and the H_2 flow for the $\text{Ar-N}_2\text{-H}_2$ plasma is 5 sccs.

species have already been extensively addressed for Ar and Ar-H_2 plasmas^{13,27} and here we will consider the species for Ar-N_2 and $\text{Ar-N}_2\text{-H}_2$ plasmas.

First, we concentrate on the electrons and ionic species which have been investigated by Langmuir probe measurements and ion mass spectrometry. Figure 6 gives information on the electron temperature T_e , electron density n_e and ion density n_i , and the relative abundances of the different ions in an Ar-N_2 and $\text{Ar-N}_2\text{-H}_2$ plasma. The Ar-N_2 plasma is generated with an Ar flow of 55 sccs and a N_2 flow of 10 sccs while the $\text{Ar-N}_2\text{-H}_2$ plasma is obtained by adding 5 sccs H_2 to these conditions. The electron temperature obtained from the Langmuir probe measurements is relatively low for both plasmas, as is generally found for downstream plasmas in the ETP technique.¹³ This low T_e is caused by the fact that no power is coupled to the plasma electrons anymore in the downstream region. An important consequence of the low T_e is that electron-induced ionization and dissociation processes of precursor gases are very improbable in the downstream region. The electron temperature for the $\text{Ar-N}_2\text{-H}_2$ plasma is somewhat lower than for the Ar-N_2 plasma (for which T_e is slightly higher than for a pure Ar

plasma).¹³ Such a decrease in T_e when H_2 is admixed has also been observed in previous work.¹³

The electron and ion densities n_e and n_i in the Ar- N_2 plasma are very high and only slightly lower than for a pure Ar plasma.¹³ It is, therefore, expected that ion-induced dissociation of SiH_4 will be very important in an Ar- N_2 - SiH_4 plasma. This expectation is based on the equivalent case of an Ar- SiH_4 plasma for deposition of a -Si:H.^{13,14} In the Ar- SiH_4 plasma, ion-induced SiH_4 dissociation reactions are predominant and this leads generally to relatively poor a -Si:H material properties. High-quality a -Si:H is only obtained when n_e and n_i are significantly reduced by adding H_2 to the Ar in the cascaded arc plasma source. A drastic reduction in n_e and n_i is also observed in Fig. 6: When H_2 is added to the Ar- N_2 plasma in the cascaded arc, the ion density is reduced roughly by a factor 10. The value for n_e and n_i in the Ar- N_2 - H_2 plasma is, furthermore, about equal to the value for n_e and n_i in the Ar- H_2 plasma as obtained at a distance of ~ 6 cm from the plasma source. Moreover, also for a - SiN_x :H films, an improvement in film quality has been observed when admixing H_2 in the cascaded arc plasma source (i.e., an Ar- N_2 - H_2 plasma) compared to working with only an Ar- N_2 plasma.⁶

Figure 6 shows the relative abundance of the ions present in the plasmas as measured by ion mass spectrometry. These measurements are performed at a distance of ~ 37 cm from the plasma source and, therefore, the data do not necessarily represent the relative abundance of ions at the position of the injection ring. The “composition” of the ions in the plasma is expected to change when the ions flow from the plasma source to the mass spectrometer due to gas phase reactions in the plasma. In the Ar- N_2 plasma and at the position of the mass spectrometer/substrate holder, argon ions, Ar^+ , have the highest density followed by atomic nitrogen ions, N^+ , and molecular nitrogen ions, N_2^+ [Fig. 6(a)]. Furthermore, hydrogenated nitrogen ions (NH_x^+ and $N_2H_x^+$) are observed in which the hydrogen atoms are expected to originate from residual H_2 in the reactor. Residual H_2 is present because measurements with H_2 have been carried out throughout the ion mass spectrometer experiments and no special procedure for pumping down the reactor has been applied in between the measurements. Furthermore, some signal due to atomic hydrogen ions H^+ is observed for the Ar- N_2 plasma.

When a H_2 flow of 5 sccs is admixed to the Ar- N_2 plasma [Fig. 6(b)], the ion composition in the plasma (again in front of the mass spectrometer) changes drastically. The signal due to Ar^+ disappears similar to what happens when going from a pure Ar plasma to a Ar- H_2 plasma.¹³ One type of ion, NH_4^+ , is predominantly present in the plasma while there is also a small signal due to $N_2H_2^+$ ions. These ions may be created by ion-molecule reactions of N^+ and N_2^+ ions emanating from the plasma source and moving through the H_2 background density in the reactor. Consequently, Fig. 6(b) does not exclude the possibility that N^+ is mainly present in the Ar- N_2 - H_2 plasma at the position of the SiH_4 injection ring. Very remarkable, however, is that the signal due to H^+ has completely disappeared despite the fact that,

FIG. 7. Density of N radicals in the Ar- H_2 - N_2 plasma in front of the substrate holder (mass spectrometer) as determined by TIMS. The H_2 flow is 5 sccs. For comparison, also the density of N radicals for an Ar- N_2 plasma is given for a N_2 flow of 10 sccs. The indicated error bars are standard deviations (1σ intervals) as determined from multiple data points. Systematic errors, mainly arising from the used correction factor C [Eq. (2)], are not taken into account.

in this case, H_2 is actively admixed to the plasma source. For comparison, H^+ ions are the dominant ions in an Ar- H_2 plasma used for the deposition of a -Si:H.

As explained in Sec. III C, the N radical density in the plasma has been measured by TIMS. The N density is given in Fig. 7 as a function of N_2 flow for the Ar- N_2 - H_2 plasma while one data point is given for the Ar- N_2 plasma (for a N_2 flow of 10 sccs). We concentrate on the Ar- N_2 - H_2 plasma because this leads to lower electron and ion density as well as to better material properties as addressed above. Figure 7 shows that the N radical density increases with increasing N_2 flow. The highest N density is reached at 10 sccs N_2 and is equal to $\sim 15 \times 10^{12} \text{ cm}^{-3}$. This high density shows that the cascaded arc plasma source is an efficient N radical source, even when it is operated with an Ar- N_2 - H_2 mixture. When operated with Ar- N_2 , the N density is higher, but the difference with the Ar- N_2 - H_2 plasma is less than a factor of 2. Considering the much lower ion density for the Ar- N_2 - H_2 plasma, the ratio of N radical density to ion density is much higher for the Ar- N_2 - H_2 plasma and, therefore, the Ar- N_2 - H_2 plasma is preferred for a - SiN_x :H deposition.⁶

Atomic H radicals are other species that emanate from the Ar- N_2 - H_2 operated plasma source and these are possibly very important for the downstream plasma processes. For an Ar- H_2 operated plasma source, it is even found that the plasma source operates mainly as an atomic H source.^{14,28} As a matter of fact, this fact is exploited for depositing high-quality a -Si:H films because the reactions between H radicals and SiH_4 radicals lead to film growth that is dominated by SiH_3 radicals.²⁹ Although we have no experimental data on H radical density for the Ar- N_2 - H_2 plasma, we also expect a considerable flux of H radicals from the source in this case, and reactions between H and SiH_4 are believed to be relatively important in the downstream Ar- N_2 - H_2 plasma. We expect that the high flux of atomic H, in combination with the high ratio of the N density and the ion density, is the reason for the higher-quality a - SiN_x :H that is

FIG. 8. Density of N radicals in the Ar-H₂-N₂-SiH₄ plasma as a function of the SiH₄ flow. The N₂ flow is 10 sccs and the H₂ flow is 5 sccs. The indicated error bars are standard deviations (1 σ intervals) as determined from multiple data points.

obtained for Ar-N₂-H₂-SiH₄ plasmas than for Ar-N₂-SiH₄.

B. Silicon nitride deposition: Ar-H₂-N₂-SiH₄ plasma

From Sec. III A, it can be concluded that the Ar-H₂-N₂ operated cascaded arc operates mainly as a source of N and H radicals and that the influence of ions and electrons in the downstream dissociation reactions is limited under these conditions. In line with literature,^{8,9,31} it is, therefore, expected that *a*-SiN_x:H film growth is dominated by radical species and not by ionic species. Accordingly, first the density of N radicals and SiH_n radicals will be addressed and subsequently the ionic species in the Ar-H₂-N₂-SiH₄ plasma will briefly be considered.

The N radical density has been investigated by TIMS at the position of the substrate holder and in Fig. 8, it is given as a function of the SiH₄ flow. The N density shows a very particular behavior because the N density first increases when SiH₄ is admixed and decreases again for higher SiH₄ flows. This behavior will be addressed in more detail later (Sec. IV) but first, the relatively high density of N radicals in the SiH₄ plasma itself will be discussed. This high density, as well as the fact that the N density increases initially when SiH₄ is admixed, suggests that ground-state N radicals are unreactive with SiH₄. This has also been pointed out by Piper *et al.*³⁰ who found an upper limit for the reaction rate between ground-state N and SiH₄ of $<8 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. This extremely low reactivity of the N radicals with SiH₄ is related to the fact that the abstraction reaction of H from SiH₄ by N radicals is endothermic by $\sim 0.45 \text{ eV}$ (compare this with the abstraction reaction of H from SiH₄ by H which is exothermic by $\sim 0.54 \text{ eV}$).^{30,31} The fact that the N radicals are unreactive with SiH₄ furthermore implies that N radicals in the expanding plasma survive at least up to the point where they reach the substrate holder. Therefore, surface reactions between N radicals and the depositing *a*-SiN_x:H film need to be considered. The extremely low reactivity of the N radicals with SiH₄ furthermore indicates that the N radicals do not significantly contribute to the generation of neutral Si-N species in the plasma, which will be addressed below.

FIG. 9. Density of Si, SiH, and SiH₃ radicals in the Ar-H₂-N₂-SiH₄ plasma as a function of the SiH₄ flow for the same conditions as in Fig. 8. The error bars represent the 1 σ interval.

The SiH_n radicals, Si, SiH, and SiH₃, have been detected by CRDS at a position of 3.5 cm from the substrate holder. Their densities are given in Fig. 9 as a function of the SiH₄ flow. Figure 9 reveals that the density of SiH₃ (ranging from 10^{12} – 10^{13} cm^{-3}) is much higher than the density of SiH (ranging from 10^{10} – 10^{11} cm^{-3}) and Si (about 10^{10} cm^{-3}). Both SiH₃ and SiH show a clear increase with increasing SiH₄ flow but the increase levels off at higher flows. The Si density shows no clear trend with SiH₄ flow. Although not all possible silicon-containing radicals have been considered yet for this plasma, these observations indicate that SiH₃ radicals are very important for *a*-SiN_x:H film growth. Assuming a reasonably high sticking probability of SiH₃ radicals on the *a*-SiN_x:H surface (of roughly the same magnitude as for SiH₃ on *a*-Si:H),³² the high SiH₃ density indicates that the Si atoms incorporated into the film are for a large part brought to the surface by SiH₃ radicals. The radicals, Si and SiH, have a much smaller contribution to *a*-SiN_x:H film growth: Even if their sticking probability is equal to one (which is about the case for SiH as has been revealed experimentally³³ and which is generally assumed for Si),³² their density is, by far, too low to explain the *a*-SiN_x:H growth rate. Furthermore, both the SiH₃ density and the *a*-SiN_x:H deposition rate increase with increasing SiH₄ flow. This fact, which will be considered in more detail in Sec. IV, also indicates that SiH₃ dominates *a*-SiN_x:H formation. These observations are similar to those for *a*-Si:H. For high-quality *a*-Si:H films, there is clear evidence that SiH₃ dominates film growth to a very large extent and that Si and SiH have only a minor contribution.^{14,24,25,29} For the present plasma conditions, it is expected that the SiH₃ radicals are mainly created by H abstraction reactions from SiH₄ by the H radicals emanating from the plasma source:

It is, however, not excluded that vibrationally excited and metastable N₂ and N atoms also contribute to the production of SiH₃ to some extent.³⁰ The Si and SiH radicals can be created by several pathways, e.g., by reactions initiated by ions and by sequential H abstraction reactions.²⁵ Si and SiH can also possibly be created by H abstraction from SiH_n

FIG. 10. Ion mass spectrum (i.e., with ionizer off) for the Ar-H₂-N₂-SiH₄ plasma with a SiH₄ flow of 8 sccs SiH₄. The N₂ flow is 10 sccs and the H₂ flow is 5 sccs. The data in the spectrum have not been corrected for the m^{-1} dependence of the mass spectrometer for the ion mass m .

radicals by N radicals because these reactions are exothermic (abstraction of H by N from SiH₃ and SiH₂ are exothermic by ~ 0.28 eV and ~ 0.19 eV, respectively).³⁰ The latter reactions can contribute to the fact that both the Si and SiH densities are higher for the Ar-H₂-N₂-SiH₄ plasma than for the Ar-H₂-SiH₄ plasma under similar plasma conditions.²⁵

On the basis of these results, we postulate at the moment that Si atoms are mainly brought to the α -SiN_x:H film by SiH₃ radicals while N atoms are brought to the film by N radicals. The ions in the plasma have been studied for the condition with 8 sccs SiH₄ by ion mass spectrometry. In Fig. 10, the ion mass spectrum is given. The signal-to-noise ratio is relatively poor because a very short integration time is used in order to keep the orifice of the mass spectrometer from clogging under this condition with a very high deposition rate (~ 20 nm/s). Figure 10 shows that although the ion flux from the cascaded arc is relatively low, these ions lead to the production of Si_nN_mH_x⁺ ions by ion-molecule reactions. This is similar to the observation of Si_nH_m⁺ ions in Ar-H₂-SiH₄ plasmas in the ETP setup used to deposit α -Si:H.¹³ By comparing the ion mass spectrum to spectra obtained for Ar-H₂-SiH₄ plasmas, the presence of N atoms in the ions is clearly revealed from the ion spectrum in Fig. 10. However, the exact assignment of the peaks in the spectrum is complicated by the fact that Si atoms have exactly twice the mass of N atoms. A possible assignment, based on the observations in the Ar-H₂-SiH₄ plasma, is given in Fig. 10. Furthermore, H⁺ and NH₄⁺ ions are observed in the spectrum. In summary, Fig. 10 indicates that the Si_nN_mH_x⁺ ions have a relatively low contribution to α -SiN_x:H film growth, similar to the case of α -Si:H film growth by the ETP.

Apart from these Si_nN_mH_x⁺ ions, it needs to be mentioned that no neutral Si-N precursor species with a significant density have been observed in the Ar-N₂-H₂-SiH₄ plasma. Similar to the results of Smith *et al.*,^{8,9} mass spectrometry on the stable gas molecules in the plasma has revealed only N-related peaks (mainly N₂ and a very small signal due to NH₃) and Si-related peaks (mainly SiH₄ and a very small signal due to Si₂H₆) as well as peaks due to Ar and H₂. This

is different from the observations for NH₃-SiH₄ plasmas where neutral Si-N species are found to dominate α -SiN_x:H film growth.^{8,10} It has to be mentioned that the mass spectrometry measurements on the stable gas molecules (i.e., not in the TIMS mode) in the Ar-N₂-H₂-SiH₄ plasma are not very sensitive and will not reveal the presence of low-density Si-N precursor radicals. A low density of SiN radicals in the plasma might, for example, be indicated by observation of a small “ghost” peak in the SiH spectrum around 414 nm.³⁴ This has, however, first to be investigated in more detail before conclusions can be drawn.

IV. DISCUSSION ON THE α -SiN_x:H GROWTH MECHANISM

On the basis of the results presented in Sec. III B, we postulate that the Si atoms in the α -SiN_x:H film are mainly brought to the substrate by SiH₃ radicals, while the N atoms in the film originate from N radicals in the plasma. This is in line with the growth mechanism for α -SiN_x:H as proposed by Smith *et al.*^{8,9} who proposed that SiH_n radicals and N radicals react at the surface to produce α -SiN_x:H in a rf plasma. This present study extends the insight into this growth mechanism because we have evidence that mainly SiH₃ is responsible for the Si atoms in the film and that ions and other radicals (such as Si and SiH) play only a very minor role. Our results are also in agreement with a similar reaction mechanism proposed by Hanyaloglu and Aydil,¹² apart from the fact that they concluded that excited molecular nitrogen (N₂^{*}) species, and not N radicals, cause the nitridation of the surface Si-Si bonds. Because they observed no optical emission from N radicals, they inferred that the N radical concentration is too low to cause the nitridation reaction. Therefore, they suggested that it is more likely that N₂^{*} species cause the nitridation because it is very well known that N₂-based plasmas contain various (relatively long-lived) electronically excited N₂ species.³⁵ Furthermore, Piper *et al.*³⁰ have shown that vibrationally excited N₂ can cause decomposition of silane. Plasma and surface reactions by excited N₂ (either electronically or vibrationally excited but represented in a general way as N₂^{*}) should, therefore, not be underestimated. On the other hand, N₂^{*} species might not survive up to the point where they reach the substrate when they are very reactive with species, such as SiH₄.

Although we cannot exclude a possible influence of N₂^{*} species in the α -SiN_x:H growth mechanism, we will provide more evidence for the growth mechanism based on N and SiH₃ radicals as schematically illustrated in Fig. 11: The creation of an α -Si:H-like surface layer on the α -SiN_x:H by SiH₃ radicals which, at the same moment, is nitridated by N radicals. To do so, the SiH₃ and N densities will be correlated with the α -SiN_x:H film properties, such as deposition rate and N/Si ratio in the film. These film properties, given in Fig. 2, as a function of the SiH₄ flow for a constant N₂ flow, are taken from a previous study using the same plasma conditions.⁶ Figure 2 shows that the deposition rate increases with increasing SiH₄ flow while the N/Si ratio decreases. As mentioned earlier, the increase in the deposition rate corre-

FIG. 11. Schematic ball-and-stick model of the proposed $a\text{-SiN}_x\text{:H}$ growth mechanism from a N_2/SiH_4 plasma. This model is based on the work by Smith *et al.* (see Refs. 8, 9, and 12) and in this article.

sponds with the increase in SiH_3 density for increasing SiH_4 flow (Fig. 9). This can be considered in more detail by using the information on the Si atomic density in the film for the different conditions.⁶ From the Si atomic density of the film (in cm^{-3}) and the deposition rate (in nm/s), the Si incorporation flux (in $\text{cm}^{-2}\text{s}^{-1}$) can be calculated and correlated to the SiH_3 density in the plasma. This is done in Fig. 12(a). It is clear from this Fig. 12(a) that the Si incorporation flux increases linearly with increasing SiH_3 density. This is also

FIG. 12. (a) Incorporation flux of Si atoms into the $a\text{-SiN}_x\text{:H}$ film vs the SiH_3 density in the plasma and (b) incorporation flux of N atoms into the $a\text{-SiN}_x\text{:H}$ film vs the N density in the plasma. The incorporation fluxes of Si and N have been calculated from the data in Fig. 2 (and as presented in Ref. 6).

expected when SiH_3 radicals are almost solely responsible for the Si atoms incorporated into the $a\text{-SiN}_x\text{:H}$ film. This can be inferred from:^{25,29,36}

$$\text{Si incorporation flux} = N_{\text{Si}} R_{\text{dep}} = \frac{1}{4} n \nu \frac{s}{1 - \beta/2} \bigg|_{\text{SiH}_3}, \quad (4)$$

with N_{Si} as the Si atomic density in the film, R_{dep} as the deposition rate, n as the SiH_3 density, ν as its thermal velocity, and s and β as the SiH_3 sticking and surface loss probability, respectively (with $s \leq \beta$). Moreover, using Eq. (4), it is possible to check whether the numbers for the Si incorporation flux are compatible with the absolute numbers of the SiH_3 density. Assuming a thermal velocity of 1000 m/s for SiH_3 (corresponding with a gas temperature of 1500 K),²⁵ the slope of the fit in Fig. 12(a) is perfectly compatible with values of $s=0.15$ and $\beta=0.30$. In principle, no information about s and β is available for $a\text{-SiN}_x\text{:H}$, but the values mentioned are very close to those usually reported for $a\text{-Si:H}$. For $a\text{-Si:H}$, the reported values of β usually range between 0.25 and 0.30, while it is generally assumed that $s = 1/2\beta$.^{32,37} Although the s and β values might differ to some extent for $a\text{-SiN}_x\text{:H}$, the agreement strongly indicates that the SiH_3 density and Si incorporation flux are compatible. It provides further evidence that the Si atoms in the $a\text{-SiN}_x\text{:H}$ originate from SiH_3 radicals from the plasma. Moreover, this assessment clearly shows that a very high density of radicals in the plasma is necessary to account for the high deposition rate of the $a\text{-SiN}_x\text{:H}$ in the ETP.

For the N atoms, a similar comparison between the N radical density in the plasma and the N incorporation flux can be made. However, unlike the SiH_3 radicals whose production increases for higher SiH_4 flows, the production rate of N radicals is unaffected by the SiH_4 flow. In the present case, the N density can only be affected by a change in the N loss rate, either by gas phase or surface reactions. In Fig. 12(b), the N incorporation rate (calculated from the N atomic density in the film and the deposition rate)⁶ is given as a function of the N density in the plasma. Figure 12(b) shows that the N incorporation flux is higher for low N densities. This behavior can be understood fairly easily: As the N density is given by the balance between production (which is constant in the present case) and loss, a higher N incorporation flux leads to more surface loss and, therefore, to a lower N density. In other words, this means that the N density in the plasma is governed by the surface loss of N radicals in the plasma and, consequently, by reactions that incorporate N atoms into the $a\text{-SiN}_x\text{:H}$ film. It should be noted in this respect that the N incorporation flux has an upper limit given by the stoichiometric limit of the $a\text{-SiN}_x\text{:H}$ ($x = \text{N/Si ratio} \approx 4/3$). This consideration sheds also more light on the particular behavior of the N radical density as a function of SiH_4 flow in Fig. 8. When more SiH_4 is admixed, more N atoms are incorporated into the $a\text{-SiN}_x\text{:H}$ film and this leads, therefore, to a lower N radical density in the plasma. This implies that the surface loss probability γ_{N} (in principle, we can distinguish for these depositing conditions also a sticking and surface loss probability for the N radicals)

changes with SiH_4 flow. When assuming for simplicity that all N radicals that are lost at the surface stick at the surface, we can calculate the corresponding value of γ_N for the different N radical densities/plasma conditions. For example, for a N density of $\sim 60 \times 10^{12} \text{ cm}^{-3}$ (corresponding with N incorporation flux of $\sim 6 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$), we find $\gamma_N = \sim 0.04$ while for a N density of $\sim 120 \times 10^{12} \text{ cm}^{-3}$ (corresponding with N incorporation flux of $\sim 2 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$), $\gamma_N = \sim 0.007$. Although γ_N is not known for N radicals during $a\text{-SiN}_x\text{:H}$ growth, these calculated values are realistic. Moreover, Fig. 4 indicates that these calculated values are approximately equal or smaller than the surface loss probability γ_N of N radicals at stainless steel for a partial N_2 pressure of ~ 20 mTorr. A decrease of the surface loss probability of the N radicals when SiH_4 is admixed to the plasma, therefore, also explains the initial increase of the N density when SiH_4 is admixed in Fig. 8 and when the stainless steel reactor walls become coated with $a\text{-SiN}_x\text{:H}$ (see Sec. III B).

In conclusion, the results on the densities of the plasma species and, in particular, the correlation between the SiH_3 and N radical density and the Si and N incorporation flux, provide strong evidence for the proposed growth mechanism of $a\text{-SiN}_x\text{:H}$ from a N_2/SiH_4 plasma as illustrated in Fig. 11. Furthermore, this correlation yields reasonable values of the surface loss probability of SiH_3 and N radicals and leads to a consistent explanation of the remarkable behavior of the N density as a function of the SiH_4 flow (Fig. 8). However, we cannot totally exclude a significant role of other reactions and plasma species. Not all silane radicals have been studied, while also possible Si–N precursor species have not been investigated with highly sensitive diagnostics. Future studies of radicals, such as SiH_2 , NH , and NH_2 (all detectable with CRDS) can provide more information on the reactions in the plasma and the $a\text{-SiN}_x\text{:H}$ growth mechanism. The hypothesized role of nitridation reactions by N_2^* can be clarified by studying the density of excited N_2 molecules and relating their density to the N incorporation flux. It should be noted here that importance of N_2^* was hypothesized by Hanyaloglu and Aydil on the basis of optical emission experiments.¹² Their conclusion is, therefore, only indirect and much more a subject of debate than the more direct evidence on the N radical density presented in this article.

Another way to test the proposed growth mechanism is to investigate the surface reactions of radicals, for example, by determining the surface loss probability of the radicals. The present study reveals that SiH_3 on $a\text{-SiN}_x\text{:H}$ has a surface loss probability which is of a similar magnitude as for $a\text{-Si:H}$. This is not unlikely in the case that the SiH_3 leads to an $a\text{-Si:H}$ -like surface layer. For the N radicals, we find a surface loss probability on $a\text{-SiN}_x\text{:H}$ which is slightly lower than for stainless steel. This is fully compatible with the observations in Fig. 8 but experimental data on γ_N for $a\text{-SiN}_x\text{:H}$ would resolve the matter. Furthermore, these studies can be coupled to *in situ* film diagnostic studies of $a\text{-SiN}_x\text{:H}$ growth. One particular interesting issue that can be addressed by these studies is the fact that the $a\text{-SiN}_x\text{:H}$ films deposited from N_2 and SiH_4 are generally relatively

rough and have a poor step coverage.⁹ Smith *et al.*⁹ attributed this to high sticking probabilities of both the N and SiH_n radicals, however, this work has indicated that the N radicals have a relatively low surface reactivity. In future studies, we will address this apparent discrepancy and other interesting issues by *in situ* infrared reflection spectroscopy and spectroscopic ellipsometry (combined with *ex situ* atomic force microscopy) studies.

V. CONCLUSIONS

Silicon nitride film growth by the remote $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ ETP has been studied by several plasma diagnostics revealing direct information about the densities of species in the plasma, as well as insight into the plasma processes and the growth mechanism of the $a\text{-SiN}_x\text{:H}$ films. The conclusions can be summarized as follows:

- (1) The different plasma diagnostics have been applied. Special attention has been given to the detection of N radicals by TIMS. The determination of the absolute N radical density is complicated by the fact that N radicals can be lost at the inner walls of the mass spectrometer. Therefore, only an estimate of the absolute value of the N radical density is possible, but the value obtained shows good agreement with TALIF measurements. Furthermore, the detection of SiH_3 radicals in the $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ plasma by CRDS has clearly been established by probing the broadband $\text{SiH}_3 \tilde{A}_1 \leftarrow \tilde{X}^2A_1$ transition at two well-separated wavelengths.
- (2) The cascaded arc plasma source operated on $\text{Ar-H}_2\text{-N}_2$ that creates reactive species for SiH_4 dissociation, leads mainly to N and H radicals in the downstream region. For an $\text{Ar-H}_2\text{-N}_2$ plasma, the ratio between N radical density and ion density is very high, while the electron temperature is too low for SiH_4 dissociation by electrons. The fact that under these conditions also a large H flux emanates from the plasma source is inferred from experiments on an Ar-H_2 plasma under comparable conditions. Furthermore, comparison of the Ar-N_2 plasma to the $\text{Ar-N}_2\text{-H}_2$ plasma has revealed a much higher ion density in the Ar-N_2 case which is in agreement with the fact that the properties of the $a\text{-SiN}_x\text{:H}$ films deposited from $\text{Ar-N}_2\text{-SiH}_4$ plasmas are inferior.
- (3) The N and SiH_3 radicals have a very high density in the downstream $\text{Ar-H}_2\text{-N}_2\text{-SiH}_4$ plasma, while the Si and SiH density is relatively low. The latter two species are, therefore, not expected to contribute significantly to $a\text{-SiN}_x\text{:H}$ growth. The SiH_3 radicals are believed to be generated by abstraction reactions by the H atoms emanating from the plasma source. The N radicals in the SiH_4 plasma, originating directly from the plasma source, do not react with SiH_4 . No Si–N species have been observed apart from $\text{Si}_n\text{N}_m\text{H}_x^+$ ions which are created by ion–molecule reactions and which have only a small contribution to $a\text{-SiN}_x\text{:H}$ growth.
- (4) The N and SiH_3 radical densities have been correlated to the film properties obtained under various conditions. It

has been observed that the Si incorporation flux is linear in the SiH_3 density providing evidence that most Si atoms are brought to the film by the SiH_3 radicals. The corresponding value of the surface loss probability of SiH_3 shows good agreement with the reported values for $\alpha\text{-Si:H}$ growth and lies, therefore, well in the expected range for $\alpha\text{-SiN}_x\text{:H}$. The N density on the other hand decreases with increasing N incorporation flux when the SiH_4 flow is increased. This can be understood from the fact that the production of N radicals is unaffected by the SiH_4 flow, whereas the loss of the N radicals increases when more N atoms are incorporated into the film (i.e., when the N surface loss probability increases). The corresponding values of the surface loss probability are compatible with the proposed values for stainless steel and they provide a straightforward explanation for the remarkable behavior of the N density as a function of the SiH_4 flow.

- (5) The presented experimental observations provide more support for the $\alpha\text{-SiN}_x\text{:H}$ growth mechanism from N_2/SiH_4 plasmas as presented in literature. The formation of the $\alpha\text{-SiN}_x\text{:H}$ takes place by the formation of an $\alpha\text{-Si:H}$ -like surface layer by SiH_n radicals and, at the same time, this surface layer is converted into $\alpha\text{-SiN}_x\text{:H}$ by nitridation reactions by N radicals. Furthermore, the insight into this growth mechanism is extended by the present study. First of all, there is more support that the nitridation takes place by the N radicals. Second, there is clear evidence that the formation of the $\alpha\text{-Si:H}$ -like top layer is dominated by SiH_3 radicals and not by radicals such as Si and SiH .

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