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N, NH, and NH$_2$ radical densities in a remote Ar–NH$_3$–SiH$_4$ plasma and their role in silicon nitride deposition

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The densities of N, NH, and NH$_2$ radicals in a remote Ar–NH$_3$–SiH$_4$ plasma used for high-rate silicon nitride deposition were investigated for different gas mixtures and plasma settings using cavity ringdown absorption spectroscopy and threshold ionization mass spectrometry. For typical deposition conditions, the N, NH, and NH$_2$ radical densities are on the order of 10$^{12}$ cm$^{-3}$ and the trends with NH$_3$ flow, SiH$_4$ flow, and plasma source current are reported. We present a feasible reaction pathway for the production and loss of the NH$_4$ radicals that is consistent with the experimental results. Furthermore, mass spectrometry revealed that the consumption of NH$_3$ was typically 40%, while it was over 80% for SiH$_4$. On the basis of the measured N densities we deduced the recombination and sticking coefficient for N radicals on a silicon nitride film. Using this sticking coefficient and reported surface reaction probabilities of NH and NH$_2$ radicals, we conclude that N and NH$_2$ radicals are mainly responsible for the N incorporation in the silicon nitride film, while Si atoms are most likely brought to the surface in the form of SiH$_x$ radicals. © 2006 American Institute of Physics. [DOI: 10.1063/1.2358330]

I. INTRODUCTION

Plasma deposited amorphous silicon nitride ($a$-SiN$_x$:H) thin films have been studied extensively because of their electrical and optical properties that make them very suitable for many applications in microelectronics device fabrication (e.g., as gate dielectric or passivation layer).$^{1-3}$ Other applications can be found in the encapsulation of devices such as organic light emitting devices$^4$ and in the photovoltaic industry, where $a$-SiN$_x$:H is used as an antireflection coating on c-Si solar cells that also serves as a surface and bulk passivation layer to improve the carrier lifetime in silicon.$^{5-6}$ Most silicon nitride deposition processes use mixtures of SiH$_4$ and NH$_3$ or N$_2$, but also liquid precursors such as hexamethyldisilazane (HMDS), tris(diethylamino)chlorosilane (TDEACS), and bis(dimethylamino)-dimethylsilane (BD-MADMS) have been used with varying success.$^7-9$

Because of their numerous applications, silicon nitride films deposited by plasma enhanced chemical vapor deposition (PECVD) have been widely investigated and the dependence of the film properties on the plasma gas composition and deposition conditions was established in various types of plasma reactors.$^{10-13}$ However, due to the complexity of chemical reactions both in the gas phase and at the surface, the mechanisms underlying silicon nitride deposition are not yet fully understood and further knowledge of the processes taking place in the plasma is still required. For N$_2$–SiH$_4$ plasmas several studies of the silicon nitride growth mechanism were reported. In 1990 Smith et al. found that N radicals are probably directly incorporated in the $a$-SiN$_x$:H film,$^{14}$ while Hanyaloglu and Aydil (1998) suggested on the basis of optical emission spectroscopy that excited N$_2^+$ molecules are most likely responsible for the N incorporation in the $a$-SiN$_x$:H films.$^{15}$ Recently, more support for the incorporation of N radicals in the $a$-SiN$_x$:H film was found in a remote Ar–N$_2$–H$_2$–SiH$_4$ plasma and a refined growth mechanism was proposed. In this refined growth mechanism an $a$-Si:H-like surface layer formed by predominantly SiH$_x$ radicals is converted into $a$-SiN$_x$:H by nitridation reactions with impinging N radicals.$^{16,17}$

On the other hand, Smith et al.$^{11,18}$ identified the aminosilane radical as the most important precursor for silicon nitride deposition in a NH$_3$–SiH$_4$ radio frequency plasma using mass spectrometry. This result was supported by Beach and Jasinski (1990) who proposed a reaction mechanism for the formation of amino-silane radicals involving NH$_2$ radicals.$^{19}$ In 1995, Murley et al. showed that the amount of aminosilanes formed is dependent on the gas residence time inside the reactor chamber.$^{20}$ Long residence times typically lead to high amino-silane concentrations, whereas short residence times result in no amino-silanes at all, which suggests the existence of a complementary growth mechanism most likely based on SiH$_x$ and NH$_x$ radicals under short-residence-time conditions.

For $a$-SiN$_x$:H growth based on NH$_3$–SiH$_4$ gas mixtures, the role and densities of N, NH, and NH$_2$ radicals were not yet investigated in great detail. The results of Theil et al. (1992) suggest that SiH$_4$ and NH$_x$ radicals are more important for silicon nitride growth than the amino-silane radicals,$^{21}$ although they did not measure these radicals directly. More recently Umemoto et al. measured NH, NH$_2$, and SiH$_x$ radicals in a hot wire chemical vapor deposition (CVD) process and they found that SiH$_3$ and NH$_2$ are most
likely responsible for the Si and N incorporations in the film. The density and role of N radicals in NH$_3$–SiH$_4$ based plasmas, however, are not well known as limited studies into this subject have been reported.

Further insight into the silicon nitride growth mechanism can be inferred from the interaction of the various NH radicals with the surface, which was studied by several research groups. Fisher and co-workers measured the surface interaction of NH and NH$_2$ radicals for different types of surfaces using laser induced fluorescence combined with a molecular beam setup. For N radicals on stainless steel and silicon nitride surfaces, the surface reactivity has been summarized and extended by Kessels et al.17 based on the experimental results of Adams and Miller.26 and Singh et al.27

In this paper, we report the densities of the NH radicals in a remote Ar–NH$_3$–SiH$_4$ plasma and we focus on the role of these radicals in the deposition process of silicon nitride. In Sec. II, the expanding thermal plasma (ETP) technique operated on an Ar–NH$_3$ gas mixture28 is briefly described. This technique was recently introduced in industry and is capable of depositing good quality silicon nitride at nominal deposition rates ranging from 4 to 7 nm/s, which is faster than most conventional processes (<1 nm/s). The diagnostic techniques, such as cavity ringdown absorption spectroscopy (CRDS) for the detection of NH and NH$_2$ radicals and threshold ionization mass spectrometry (TIMS) for the N radical measurements, are described briefly in Sec. III. In Sec. IV, we present the NH, NH$_2$ radicals as function of several plasma parameters such as NH$_3$ flow, SiH$_4$ flow, and plasma source current (Secs. IV A–IV C) and discuss the most important plasma reactions that can explain the observed trends. Furthermore, the NH$_2$ and SiH$_4$ consumptions and the production of molecules from the dissociated molecules (Sec. IV D) are addressed for different plasma settings. Subsequently, Sec. V summarizes the plasma chemistry and discusses the surface reaction probability of the NH$_2$ radicals and the implications of our measurements on the silicon nitride growth mechanism. Finally, the conclusions are given in Sec. VI.

II. THE EXPANDING THERMAL PLASMA ON AR–NH$_3$

Figure 1 shows a schematic overview of the deposition setup including the laser setup used for the measurements of the NH and NH$_2$ densities and the mass spectrometry setup for the determination of the N density. Both diagnostic techniques will be discussed in greater detail in Sec. III.

An extensive description of the plasma source and the ETP technique can be found elsewhere28,31,32 and here a brief summary of the ETP plasma operated on an Ar–NH$_3$ mixture will be given. The ETP technique consists of a cascaded arc plasma source that operates at subatmospheric pressures (~200 Torr) and a low pressure processing chamber. A dc current of typically 45 A is used to efficiently ionize argon atoms in a narrow plasma channel with flowing argon gas. NH$_3$ gas is introduced through a slit in the nozzle at the outlet of the plasma source (see Fig. 1) and the resulting Ar–NH$_3$ plasma expands into the low pressure chamber (~0.15 Torr). The electron temperature is low (0.2–0.3 eV) in the expansion and as a consequence, electron impact induced chemistry and ion bombardment due the plasma self-bias potential are not important. The most important reactive species emanating from the plasma source are Ar$^+$ ions that transfer their charge to NH$_3$ molecules in the course of the expansion, creating mainly NH$_3^+$ molecular ions. These molecular ions recombine dissociatively with electrons into mainly N and NH radicals.29 The charge transfer reaction as well as the dissociative recombination reaction are very fast and the N and NH densities both saturate at a level of 3 $\times$ 10$^{12}$ cm$^{-3}$ for NH$_3$ flows above 3 SCCS (standard cubic centimeter per second) due to the limited amount of Ar$^+$ ions available. Langmuir probe measurements carried out at 36 cm from the plasma source revealed an exponential decrease of the ion density by three orders of magnitude until 3 SCCS NH$_3$ was injected in the plasma.28 which is in line with the constant N and NH densities above 3 SCCS NH$_3$. The saturation also implies that gas phase loss with NH$_3$ can be neglected for these radicals. NH$_2$ radicals, on the other hand, are most likely produced differently via reactions of NH$_3^+$ with NH$_3$ or via NH$_3$ dissociation reactions by H abstraction, resulting in a linear increase of the NH$_2$ density as a function of the NH$_3$ flow. The NH$_2$ density reached for 15 SCCS injected NH$_3$ flow is approximately 4.0 $\times$ 10$^{12}$ cm$^{-3}$. More information on the reaction mechanism responsible for the creation of NH and NH$_2$ in the Ar–NH$_3$ plasma can be found in Ref. 33.

When the plasma is used for silicon nitride deposition SiH$_4$ gas is injected through a ring situated at a distance of approximately 7 cm from the nozzle. The reactive fragments (NH$_x$, H, etc.) created in the initial part of the expansion are used to dissociate the injected SiH$_4$ leading to silicon containing reactive species that deposit an a-SiN$_x$:H film on a downstream situated substrate. The standard experimental conditions and the parameter range used in this study are given in Table I.

III. PLASMA DIAGNOSTICS

A. Cavity ringdown absorption spectroscopy

The cavity ringdown setup is shown schematically in Fig. 1. Laser pulses generated by a dye laser pumped by the
second harmonic radiation of a Nd:YAG (yttrium aluminum garnet) laser were injected into a high finesse optical cavity formed by two planoconcave high reflectivity mirrors (M). The mirrors, protected from reactive plasma species by a small argon flow, were placed 112 cm apart on flexible bellows at a distance of 36 cm from the plasma source, which is 3 cm before the substrate holder. Before injection into the cavity, the laser pulse energy was attenuated to below 100 μJ per pulse to avoid optical saturation of the used transitions. The light intensity leaking out of the cavity was detected through an interference bandpass filter (F) by a photomultiplier tube (PMT). For every single laser pulse, the decay rate was sampled by a 100 MHz, 12 bit data acquisition system (TU/eDACS (Ref. 34)]. All observed decay rates were single exponential and were analyzed by a weighted least squares fit of the logarithmic of the transient data, while an average of 900 single decays was used to improve the signal to noise ratio. More details on the cavity ringdown setup can be found elsewhere.33

The NH radical was detected on the $^1\Pi \rightarrow X^3\Sigma^-$ transition around ~340 nm and the NH$_2$ radical on the (0,0)-(0,0) band of the $^1\Delta \rightarrow X^1\Sigma^-$ transition at ~597 nm. For NH, the isolated $P_{3,3}(3)$ absorption line at 339.624 nm (29 444.3 cm$^{-1}$) was used, while the “isolated” $\Sigma^P Q_{1,1}$ absorption line at 597.375 nm (17 739.9 cm$^{-1}$) was used for NH$_2$. The actual density information was determined by scanning the laser over the particular absorption line and using the integrated absorption cross sections derived in Ref. 33.

First, the spectra of NH and NH$_2$ were recorded for the Ar–NH$_3$–SiH$_4$ plasma to establish the measurement procedure. We found that the addition of SiH$_4$ to the plasma introduced a broadband absorption in addition to the NH and NH$_2$ spectral features. The origin of this broadband absorption has not been identified, but it did not change the distinct spectral features of the NH and NH$_2$ radicals. The largest uncertainty in the absolute values of the densities reported is generated by the assumption about the absorption path length for the radicals in the plasma, which is estimated to be 30 cm.35 This systematic error can be as large as a factor of 3 for the local absolute densities.

B. (Threshold ionization) mass spectrometry

The triple stage differentially pumped quadrupole mass spectrometer (QMS) used in this study was modified from the version that was used to measure N radicals in an Ar–N$_2$–SiH$_4$ plasma.16 The apparatus used in this study is based on the design by Agarwal et al.36 and was described extensively elsewhere.28,37 Briefly, the plasma is sampled by effusive extraction through a 0.8 mm orifice that is situated approximately 56 cm from the plasma source and 4.5 cm off the reactor axis. The extraction creates a molecular beam that passes two consecutive orifices separating the pumping stages in the housing of the mass spectrometer. The quadrupole mass spectrometer (Hiden Analytical Epic 300, PSM upgrade) is placed in the third stage, in line of sight with the three orifices. Typical pressures in the second and third stages during measurements are 10$^{-6}$ and 10$^{-7}$ Torr, respectively, while the third stage base pressure is below 10$^{-9}$ Torr. Due to the finite pressure in the third stage, the mass spectrometer signal will not only consist of a beam component but also of a background component due to surface scattered molecules.

Ground state N radicals were detected using the so-called threshold ionization or appearance potential technique.14,28 In general, electron impact ionization of radicals has a lower threshold than dissociative ionization of parent molecules leading to the same ion. Table II shows the different electron impact ionization processes that lead to the detection of an ion with a mass-over-charge ($m/e$) ratio equal to 14. By scanning the electron energy used for ionization, we can distinguish different ionization processes. To obtain absolute densities of N radicals, we used a calibration method for the N radicals similar to the one described by Singh et al.27 The absolute N densities were obtained by correlating the measured signal of N radicals to the direct ionization signal of NH$_3$ reference gas with a known number density. The details of the calibration procedure can be found in Ref. 28.

The mass spectrometer was also used to determine the densities of stable species such as NH$_3$, SiH$_4$, H$_2$, and N$_2$ in the plasma beam. The calibration procedure to obtain the absolute densities of these molecules was carried out prior to each measurement run using different reference gas mixtures in argon (e.g. NH$_3$ in Ar, SiH$_4$ in Ar, etc.) to mimic the actual measurement conditions. From these measurements the relative consumption or depletion of a species can be calculated.

For the Ar–NH$_3$–SiH$_4$ plasma, all signals were corrected for clogging of the sampling orifice by normalizing all signals to the Ar signal in the “plasma off” case. This correction was not necessary for non-depositing plasmas.

### Table I. The range of plasma parameters used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard value</th>
<th>Range studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow</td>
<td>55 SCCS</td>
<td>...</td>
</tr>
<tr>
<td>NH$_3$ flow</td>
<td>17 SCCS</td>
<td>0–17 SCCS</td>
</tr>
<tr>
<td>SiH$_4$ flow</td>
<td>2.5 SCCS</td>
<td>0–5 SCCS</td>
</tr>
<tr>
<td>Arc current</td>
<td>45 A</td>
<td>30–70 A</td>
</tr>
<tr>
<td>Arc voltage</td>
<td>42 V</td>
<td>...</td>
</tr>
<tr>
<td>Arc pressure</td>
<td>210 Torr</td>
<td>...</td>
</tr>
<tr>
<td>Downstream pressure</td>
<td>0.15 Torr</td>
<td>...</td>
</tr>
</tbody>
</table>

### Table II. Various reactions leading to N$^+$ ions in the mass spectrometer’s ionizer by electron impact ionization. The corresponding appearance potentials are also given.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Appearance potential (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>N$^+$ + e $\rightarrow$ N$^+$ + 2e</td>
<td>15.3</td>
</tr>
<tr>
<td>B</td>
<td>NH$_3$ + e $\rightarrow$ N$^+$ + H$_2$ + H$^+$ + 2e</td>
<td>22.6</td>
</tr>
<tr>
<td>C</td>
<td>N$_2$ + e $\rightarrow$ N$^+$ + N + 2e</td>
<td>24.3</td>
</tr>
</tbody>
</table>

$^a$Reference 46.

$^b$Reference 47.
The observed density changes can be qualitatively understood by looking at the production rate \( P \) and and loss time \( \tau \) of species in a steady state situation,

\[
\frac{\partial n}{\partial t} = P - \frac{n}{\tau} = 0,
\]

with \( n \) the density of the species. In this case, the observed gradual increase of the N and NH densities can be explained by a decrease in the production rate of these radicals due to SiH\(_4\) injection. Competition between charge transfer reactions of Ar\(^+\) ions with NH\(_3\), responsible for the creation of N and NH radicals, and with SiH\(_4\) results in a lower production rate for N and NH. This effect is especially important when the NH\(_3\) flow is comparable to or smaller than the SiH\(_4\) flow, as is also observed in Figs. 2(a) and 2(b). For high NH\(_3\) flows the influence of the charge transfer reaction of Ar\(^+\) with SiH\(_4\) is of minor importance and the observed N and NH densities are similar to the values obtained in the situation without SiH\(_4\). The final N radical density seems to be somewhat higher in the presence of SiH\(_4\), which is predominantly caused by a change in the loss time of the N radical [e.g., a different surface reaction probability (see Sec. V B)].

The absence of NH\(_2\) radicals in the Ar–NH\(_3\)–SiH\(_4\) plasma for flows below 4 SCCS NH\(_3\) is another indication that the production and/or loss mechanism of NH\(_2\) is different than that of N and NH. Additional measurements showed that the NH\(_3\) flow threshold for NH\(_2\) detection depends linearly on the SiH\(_4\) flow. This behavior is not completely understood yet, but a few mechanisms changing the production or the loss time of NH\(_2\) radicals can be suggested. A first possibility is the abstraction reaction between atomic H and SiH\(_2\).

This reaction is much faster at 1750 K (Ref. 33) [reaction rate of \( \sim 8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) (Ref. 38)] than the equivalent reaction with NH\(_3\) [with a rate of \( \sim 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) (Ref. 33)] such that the NH\(_2\) production might be suppressed. Another reaction that can play a role is a fast gas phase loss reaction of the produced NH\(_2\) with SiH\(_4\) or its dissociation products. Likely candidates for this reaction are the amino-silane creation reactions as proposed by Beach and Jasinski. Finally, NH\(_2\) radicals might be preferentially incorporated in the α-SiN\(_x\):H film leading to the low NH\(_2\) density in the plasma.

This argument is supported by values of the NH\(_2\) surface loss probability as discussed in Sec. V B.

### IV. RESULTS

#### A. NH\(_x\) radical densities versus NH\(_3\) flow

Figures 2(a)–2(d) show the absolute densities of N, NH, and NH\(_2\) radicals and NH\(_3\) molecules in the expanding Ar–NH\(_3\)–SiH\(_4\) plasma as a function of the NH\(_3\) flow for a SiH\(_4\) flow of 2.5 SCCS (circles). The observed trends for a pure Ar–NH\(_3\) plasma (described in Sec. II) are also shown for comparison (triangles). When 2.5 SCCS SiH\(_4\) is added to the Ar–NH\(_3\) plasma, the behavior of the NH\(_x\) (\( x = 0–3 \)) densities is quite similar to the situation without SiH\(_4\) as can be seen in Fig. 2. The N and NH densities increase more gradual to their final values of \( \sim 4.0 \times 10^{12} \) and \( \sim 3.0 \times 10^{12} \text{ cm}^{-3} \), respectively. Also the NH\(_2\) density shows a similar linear increase as in the case without SiH\(_4\) reaching a density of \( 2.5 \times 10^{12} \text{ cm}^{-3} \) at 15 SCCS NH\(_3\). For NH\(_3\) flows below 4 SCCS, however, no NH\(_2\) radicals could be detected in the plasma in contrast to the situation without SiH\(_4\). The NH\(_3\) density obtained for 15 SCCS NH\(_3\) flow is 7.0 \( \times 10^{14} \text{ cm}^{-3} \), which is slightly lower than in the situation without SiH\(_4\).

The final N radical density seems to be somewhat higher in the presence of SiH\(_4\), which is predominantly caused by a change in the loss time of the N radical.
The N radical density decreases from $\sim 8.0 \times 10^{12}$ to $\sim 2.0 \times 10^{12}$ cm$^{-3}$ and the NH density from $\sim 3.0 \times 10^{12}$ to $\sim 2.0 \times 10^{12}$ cm$^{-3}$. The NH$_2$ density decreases from $\sim 4.0 \times 10^{12}$ to $\sim 1.0 \times 10^{12}$ cm$^{-3}$ for a SiH$_4$ flow of 5 SCCS, while the NH$_3$ density decreases only slightly from $\sim 7.5 \times 10^{14}$ to $\sim 6.5 \times 10^{14}$ cm$^{-3}$. Figure 3 also shows the values of the NH$_x$ densities in the absence of SiH$_4$ for a clean stainless steel reactor (open triangles). Note that for small injected SiH$_4$ flows the N radical density in the depositing plasma is higher than in the situation without SiH$_4$. This particular behavior will be addressed in more detail in Sec. V B, but first the NH$_x$ radical densities will be discussed in detail.

The small decrease of the NH$_3$ density versus the SiH$_4$ flow can be explained by a decreased production rate due to the competition between the Ar$^+$ charge transfer reactions with NH$_3$ and SiH$_4$, as explained in the previous section. The N and NH$_2$ densities, however, decrease faster than the NH density upon injection of SiH$_4$, which suggests that an additional loss mechanism related to SiH$_4$ lowers the N and NH$_2$ densities. A similar decreasing trend for the N radical density versus SiH$_4$ flow was observed by Kessels et al. in an Ar–N$_2$–H$_2$–SiH$_4$ plasma. Due to the endoergic nature of the reaction of N radicals with SiH$_4$ (enthalpy = $+0.45$ eV), the corresponding reaction rate is very low at room temperature ($<8 \times 10^{-14}$ cm$^3$s$^{-1}$). At a gas temperature of 1750 K, we still expect the reaction rate to be very small due to the relatively high energy barrier for this reaction. Therefore, Kessels et al. argued that gas phase loss of N radicals can be excluded and it was established that a larger fraction of N radicals must be incorporated in the a-SiN$_x$:H film. Also for the Ar–NH$_3$–SiH$_4$ plasma N incorporation in the a-SiN$_x$:H film is most likely responsible for the observed N loss. For NH$_2$, a gas phase loss mechanism involving SiH$_4$ molecules cannot be excluded on the basis of the reaction rates reported in the literature. Two possible reactions that might explain the observed NH$_2$ loss were already proposed in Sec. IV A. The first reaction, which removes atomic H from the plasma by a reaction with SiH$_4$ suppressing the NH$_2$ production, can in principle take place. But on the basis of the small amount of injected SiH$_4$ molecules, it is unlikely that this reaction can explain the total NH$_2$ decrease. The second reaction resulting in the creation of amino silanes is not expected to be significant as we found no evidence for these fragments by mass spectrometry. Moreover, a similar decrease of the NH and NH$_2$ densities versus SiH$_4$ flow in a hot wire CVD system was attributed to a decreased decomposition efficiency of NH$_3$ on the hot wire surface and not to gas phase reactions. In our case, the faster decrease of the NH$_2$ density is presumably caused by an increased incorporation of NH$_2$ into the a-SiN$_x$:H film at higher SiH$_4$ flows, similar to the situation for N radicals (Sec. V B).

**C. NH$_x$ radical densities versus arc current**

Another important plasma parameter, besides the NH$_3$ and SiH$_4$ gas flows, is the plasma source current, which determines the amount of ions emanating from the source. Figures 4(a)–4(d) show the NH$_x$ (0–3) densities as a function of the arc current for a NH$_3$ flow of 17 SCCS and a SiH$_4$ flow of 2.5 SCCS. The N density increases linearly from $\sim 2.5 \times 10^{12}$ to $\sim 9.0 \times 10^{12}$ cm$^{-3}$ when the arc current is increased from 30 to 70 A. Also the NH density increases linearly from $\sim 2.0 \times 10^{12}$ to $\sim 4.0 \times 10^{12}$ cm$^{-3}$, while the NH$_2$ density remains almost constant at $2.0 \times 10^{12}$ cm$^{-3}$. The NH$_3$ density in the plasma decreases from $\sim 10.0 \times 10^{14}$ to $\sim 4.0 \times 10^{14}$ cm$^{-3}$ when the arc current increases from 30 to 70 A.

The linear increase of the N and NH densities versus arc current confirms that the production mechanism of these radicals is dependent on Ar$^+$ ions from the plasma source, as discussed briefly in Sec. II. The stronger increase of the N density compared to the NH density indicates that N radicals might also be produced in secondary reactions of Ar$^+$ ions.
with NH radicals or N₂ molecules, while this is not the case for NH radicals. The linear decrease in the NH₃ density is expected because the NH₃ dissociation process starts with the charge transfer reaction of Ar⁺ with NH₃. Furthermore, the constant NH₂ density corroborates the previous conclusion that NH₂ is produced by a different pathway than N and NH radicals.

D. NH₃ and SiH₄ consumption

The relative amount of gas phase consumption of a precursor, also called depletion, can give valuable insights into the deposition process. Furthermore, an effective use of the precursor gas is important from a cost perspective (e.g., high depletion values allow for more efficient use of precursor gases). The amount of NH₃ and SiH₄ consumed in the plasma can be derived from mass spectrometry measurements of the NH₃ density and SiH₄ density (see Sec. III C). In Fig. 5 we show the depletion of NH₃ (a) and SiH₄ (b) in the plasma as a function of the NH₃ flow for a SiH₄ flow of 2.5 SCCS. The depletion of NH₃ decreases from ~0.9 for small NH₃ flows to ~0.4 for high NH₃ flows. Accurate measurements of depletions near 100% for low NH₃ flows are difficult, which explains the larger error bars in Fig. 5. The behavior of the NH₃ depletion versus NH₃ flow can be understood by considering the amount of reactive species from the source compared to the injected NH₃ flow and the remote character of the ETP technique. For low NH₃ flows the amount of Ar⁺ from the plasma source is sufficient to dissociate all NH₃, but when the NH₃ flow is increased further, the amount of Ar⁺ will be deficient to dissociate all NH₃. At this point the depletion of NH₃ starts to decrease. Also the depletion of SiH₄ decreases from ~1.0 to ~0.8 when the NH₃ flow increases from 0 to ~6 SCCS, whereas it remains constant at ~0.8 for higher NH₃ flows. The decrease of the SiH₄ depletion when the NH₃ flow increases is most probably related to a decrease in the direct dissociation of SiH₄ by Ar⁺ due to competition of this process with the charge exchange reaction of NH₃ with Ar⁺ as discussed in Sec. IV A. At a NH₃ flow of 6 SCCS, most Ar⁺ ions are used to dissociate NH₃, while SiH₄ is presumably dissociated indirectly by reactive NH₄ species leading to a SiH₄ depletion of ~0.8.

Figures 6(a) and 6(b) show the NH₃ and SiH₄ depletions versus the SiH₄ flow in an Ar–NH₃–SiH₄ plasma for a NH₃ flow of 17 SCCS. The NH₃ depletion remains constant at ~0.4 over the whole range of SiH₄ flows, because the injected SiH₄ flow is relatively small compared to the NH₃ flow. Furthermore, the NH₃ flow is injected in an earlier stage of the plasma expansion than SiH₄ (see Fig. 1). There-
fore, the NH3 dissociation is not affected by the injected SiH4 flow for these large NH3 flows. The SiH4 depletion remains constant at ~0.8 for SiH4 flows between 0 and 2.5 SCCS SiH4 and subsequently decreases to ~0.5 for a SiH4 flow of 5 SCCS. This suggests that the amount of reactive species created in the NH3 dissociation process is the limiting factor for the SiH4 dissociation for SiH4 flows exceeding 2.5 SCCS.

In the expanding thermal plasma, the NH3 depletion is in the order of 40% for actual deposition conditions of silicon nitride antireflection coatings on solar cells, while the SiH4 depletion is approximately 80%. Note that the consumed NH3 flow is actually larger than the consumed SiH4 flow leading to near stoichiometric silicon nitride. These values for the NH3 and SiH4 depletions are relatively high in comparison to the results reported by Umemoto et al. They reported a NH3 depletion of 5% and a SiH4 depletion of 60% in the hot wire CVD process based on NH3 and SiH4. However, when H2 is added to the NH3/SiH4 system, a much higher NH3 decomposition efficiency can be achieved in the hot wire CVD process. Chowdhury et al. reported SiH4 depletions up to 100% for small SiH4 flows and high power density in their rf PECVD system based on N2 and SiH4. In the ETP plasma, both the NH3 and the SiH4 depletions increase when the arc current and therefore the plasma power are increased. For an injected SiH4 flow of 2.5 SCCS, NH3 flow of 17 SCCS, and an arc current of 70 A, the NH3 and SiH4 depletions are ~60% and ~100%, respectively. These high values of the depletion enable high rate deposition of a-SiN+x:H using the ETP technique.

The typical depleted NH3 density when the plasma is switched on is on the order of 10^{14} cm^{-3} while the typical NH3 densities generated are on the order of 10^{12} cm^{-3} during actual deposition conditions. The difference in magnitude of these densities cannot be explained by N or H incorporation in the film alone, which means that other species besides NH3 radicals must be generated in the plasma. For an Ar–NH3 plasma, it was already demonstrated that large densities of N2 and H2 molecules were generated. Also in the Ar–NH3–SiH4 plasma we observed that most of the depleted NH3 and SiH4 flows are converted into H2 and N2 with typical densities on the order of 10^{12} cm^{-3} (not shown). A similar observation was also reported by Umemoto et al., who measured the H2 and N2 productions in their hot wire CVD system.

V. DISCUSSION

A. Summary of the plasma chemistry

From the results presented in the current study combined with the outcome of previous studies, the following reaction pathway in the Ar–NH3–SiH4 plasma can be deduced. The cascaded arc plasma source produces primarily Ar+ ions that undergo a charge transfer reaction with NH3 molecules injected in the very first part of the plasma expansion. The NH3+ ions created recombine dissociatively into N and NH radicals, while NH2 radicals are produced via ion-molecule reactions or radical-molecule reactions with NH3 molecules. This mechanism leads to relatively high N and NH densities that saturate at a level of (3.0–4.0) × 10^{12} cm^{-3} for high NH3 flows due the limited amount of Ar+ available. The NH2 density on the other hand increases linearly with the NH3 flow and reaches a level of 2.5 × 10^{12} cm^{-3}.

When SiH4 is injected in the plasma all NH radicals decrease in density. For a part, this decrease can be explained by a lower production rate due to the competition between the charge transfer reaction of Ar+ with NH3 and the charge transfer reaction of Ar+ with SiH4. However, for the N and NH2 radicals the decrease in density is more pronounced than for the NH radical suggesting that an additional loss mechanism is present for the N and NH2 radicals, besides the reduction of their production rate. This loss mechanism is most likely an increased incorporation of these radicals in the a-SiN+x:H film, as can be concluded from the surface loss of these radicals that will be discussed in Sec. V B. In this case, the Si–N bond characteristic for a-SiN+x:H is not predominantly formed in the plasma volume, but on the surface of the growing film. When the SiH4 flow injected in the plasma is increased, the surface composition of the growing film changes due to a higher flux of impinging SiH4 radicals that create additional sites for N incorporation on the film’s surface. Therefore, the surface loss rate of N radicals will increase for higher SiH4 flows.

The amount of reactive species emanating from the plasma source can be increased by a higher current, which leads to more production of N and NH radicals and a higher NH3 consumption in the plasma. The higher flow of reactive NH3 species from the plasma source also allows for a higher degree of SiH4 dissociation. For a plasma with a NH3 flow of 17 SCCS, a SiH4 flow of 2.5 SCCS, and a plasma source current of 70 A, the dissociation degree of NH3 and SiH4 can be as high as 60% and 100%, respectively. Finally, it was
observed that significant amounts of N$_2$ and H$_2$ molecules are produced in the plasma from dissociated NH$_3$ and SiH$_4$.

B. Surface loss probabilities

The kinetics of film growth in a plasma depend on the interactions of the plasma-generated species with the growing film surface. In order to understand how the film composition and electronic properties are related to the plasma parameters, detailed information on the interaction of the plasma species with the surface is required.

Information on the surface reactivity of species can be deduced from density measurements for different wall conditions. Figure 7 shows a measurement of the N radical density versus the NH$_3$ flow in an Ar–NH$_3$ plasma for a clean stainless steel wall and a wall covered with a silicon nitride film. The observed trends for both curves are identical, but the saturation value of the N radical density is substantially higher for the case of silicon nitride covered walls. For stainless steel walls the measured N density $n_{SS}$ at high NH$_3$ flows is $\sim 3.0 \times 10^{12} \text{ cm}^{-3}$, while $n_{SiN}$ is $\sim 9.0 \times 10^{12} \text{ cm}^{-3}$ for walls covered with silicon nitride. This difference in N density was already observed in Fig. 3(a), where the N density for stainless steel walls (triangles) lies considerably lower than the N density in a depositing Ar–NH$_3$–SiH$_4$ plasma (circles). Assuming constant production rate ($P$) and no difference in gas phase loss for N radicals (corroborated by the extremely low reactivity of the N radical with SiH$_4$), the observed density difference must be caused by a changing surface loss rate [see Eq. (1)]. In general, species can be lost at the surface with a probability $\beta$, which consists of a “recombination part” with a probability $\gamma$ and of a “growth part” with a probability $s$. According to Motz and Wise the flux of species that is lost at the surface is given by

$$\Phi_{\text{loss}} = \frac{nu}{4} \frac{\beta}{1 - (\beta/2)},$$

with $\beta = \gamma + s$, $n$ the density of the species, and $u$ the thermal velocity. In a nondeposition NH$_3$ plasma, the sticking probability $s$ is zero and the flux of species lost at the surface is determined by the recombination probability $\gamma$. For our experimental conditions with a partial N$_2$ pressure on the order of 10 mTorr, the recombination probability on stainless steel $\gamma_{SS}$ can be estimated at $\sim 0.1$ on the basis of the work of Adams and Miller and Singh et al. Using this value of $\gamma_{SS}$ and the experimentally observed density ratio $n_{SiN}/n_{SS}$ of $\sim 3.0$, we obtain a recombination probability of N radicals on a silicon nitride surface $\gamma_{SiN}$ of $\sim 0.03$ via Eq. (2).

In SiH$_4$ containing plasmas the sticking probability $s$ is nonzero as N radicals can also be incorporated in the growing $a$-Si$_x$N$_{1-x}$H film. When we attribute the decrease in the N density as a function of the injected SiH$_4$ flow in Fig. 3(a) solely to N incorporation in the $a$-Si$_x$N$_{1-x}$H film, we can calculate an upper estimate for the sticking coefficient $s$, assuming a constant N recombination probability $\gamma_{SiN}$, no significant change in the N production rate due to SiH$_4$ addition, and no gas phase loss. For example, the N density is $\sim 8.0 \times 10^{12} \text{ cm}^{-3}$ for a SiH$_4$ flow of 0 SCCS, while it is $\sim 6.0 \times 10^{12} \text{ cm}^{-3}$ for a SiH$_4$ flow of 1 SCCS. In the first situation the loss will only consist of N recombination on the surface ($s=0$), while in the second case incorporation of N in the film causes an additional decrease in the N density. Using Eq. (2) we obtain a sticking coefficient $s$ that varies with SiH$_4$ flow: from $\sim 0.016$ for 1 SCCS injected SiH$_4$ to $\sim 0.034$ when the SiH$_4$ flow is 5 SCCS. A similar change in the surface reaction probability $\beta = \gamma + s$ from $\sim 0.007$ for low SiH$_4$ flows to $\sim 0.04$ for higher SiH$_4$ flows was also observed by Kessels et al. in the Ar–N$_2$–H$_2$–SiH$_4$ expanding plasma. This change in the sticking probability $s$ for higher SiH$_4$ flows is most likely caused by a higher SiH$_4$ flux to the surface creating more reactive surface sites available for N incorporation.

For NH and NH$_2$ radicals no significant difference in the surface recombination probability was observed on the basis of the measured densities in nondeposition plasmas for stainless steel walls and silicon nitride covered walls [see Figs. 3(b) and 3(c)]. The surface reactivity of NH and NH$_2$ on different materials was reported by Fisher and co-workers using laser induced fluorescence in combination with a molecular beam setup. The molecular beam was created from a rf powered plasma based on a NH$_3$ or NH$_3$–SiH$_4$ feed gas mixture by expansion into a differentially pumped reactor. A surface loss probability $\beta_{NH}=0.0\pm0.1$ for the NH radical on $a$-Si$_x$N$_{1-x}$H surfaces in NH$_3$ and NH$_3$–SiH$_4$ plasmas was observed, indicating that the NH radical is virtually not reactive with the surface during plasma deposition of $a$-Si$_x$N$_{1-x}$H ($\gamma_{NH}=0$). For the NH$_2$ radical, surface production ($\gamma_{NH_2}<0$) was found on $a$-Si$_x$N$_{1-x}$H surfaces in a NH$_3$ plasma, while a surface loss probability $\beta_{NH_2}$ of $0.13\pm0.07$ was found in a NH$_3$–SiH$_4$ plasma. This suggests that NH$_2$ is incorporated in the growing $a$-Si$_x$N$_{1-x}$H film. Assuming a similar NH$_2$ recombination probability in NH$_3$ and NH$_3$–SiH$_4$ plasmas, we deduce a sticking coefficient for NH$_2$ ($\gamma_{NH_2}$) during $a$-Si$_x$N$_{1-x}$H growth that is larger than 0.13.

C. Implications for $a$-Si$_x$N$_{1-x}$H growth mechanism

The deposition of $a$-Si$_x$N$_{1-x}$H films by plasmas is governed by reactive species (radicals) created in the plasma and their reaction kinetics on the surface (see Sec. V B). More specifically, radical species are responsible for the creation of
the Si–N network and two main options were introduced for the deposition mechanism of these films. One mechanism was proposed by Smith et al. and is based on the creation of amino-silane radicals [Si(NH$_3$)$_x$]$_z$ in the plasma phase$^{14}$ that are responsible for the $a$-SiN$_x$:H growth. On the other hand, Umemoto et al.$^{22}$ have demonstrated that NH$_2$ and SiH$_3$ radicals are the dominant growth precursors in the hot wire CVD deposition process of silicon nitride. These two mechanisms differ in the formation path of the characteristic Si–N bond, e.g., in the gas phase or on the surface of the growing film. In our analysis, we also found no evidence for the existence of amino silanes in the ETP plasma by mass spectrometry, although the presence of the broadband absorption in the cavity ringdown measurements might indicate the presence of larger species. Umemoto et al. suggested that the absence of amino silanes in the hot wire CVD process is caused by the relatively high atomic H fluxes that are created in the thermal decomposition of the injected precursors on the hot filament. In the expanding thermal plasma, the production of atomic H is also very efficient via the dissociative recombination reactions of NH$_x^+$ ions with electrons (see Sec. III A). This could explain the absence of amino silanes in the ETP plasma. Alternatively, Murley et al. provided another explanation for the absence of amino silanes, which is related to the residence time of the gas in the reactor.$^{20}$ They showed that amino silanes are primarily present for residence times higher than 2–3 s, which is larger than commonly used in the ETP plasma (typically ~0.5 s).

Based on our data of the Ar–NH$_3$–SiH$_4$ plasma, we conclude that the N incorporation in $a$-SiN$_x$:H film is most likely dominated by NH$_x$ radicals, which implies that the Si atoms are brought to the surface via SiH$_3$ radicals. This mechanism of Si incorporation by SiH$_3$ radicals is also dominant in the Ar–N$_2$–H$_2$–SiH$_4$ plasma$^{16}$ and in the deposition of $a$-Si:H from Ar–H$_2$–SiH$_4$ plasmas. In the Ar–NH$_3$–SiH$_4$ plasma, we have also observed Si, SiH and SiH$_3$ radicals by TIMS measurements. A preliminary study has shown that the densities of these radicals are all approximately ~10$^{11}$ cm$^{-3}$. From this perspective, it is expected that the role of N radicals in the Ar–NH$_3$–SiH$_4$ plasma is similar to their role in the silicon nitride growth mechanism from N$_2$–SiH$_4$ plasmas proposed by Smith et al.$^{14}$ and Kessels et al.$^{16,17}$ They showed that N radicals can insert into Si–Si backbonds of an $a$-Si:H-like layer that is created by impinging SiH$_3$ radicals. NH radicals on the other hand are not reactive with the growing film, as can be deduced from the measured surface reaction probability, while NH$_2$ radicals are reactive on the surface with a reaction probability of ~0.13. This value is much higher than the reaction probability of N radicals (<0.04), indicating a different sticking process on the surface of the growing film. NH$_2$ radicals might stick on dangling bonds on the surface or insert into (strained) Si–Si bonds. Furthermore, NH$_2$ could diffuse over the growing surface in a sort of hot precursor state, similar to the suggested mechanisms for SiH$_3$ in $a$-Si:H growth.$^{15}$

The actual contribution of the NH$_x$ radicals to the silicon nitride growth depends on the measured densities and the surface reactivity of the radicals. These two parameters determine the N incorporation flux in the $a$-SiN$_x$:H film. To consider the feasibility of N incorporation by NH$_x$ radicals, we estimate the N incorporation flux in two different ways. The first one is based on the deposition rate and the N atomic density determined from elastic recoil detection (ERD) measurements and in the second one we use the measured NH$_x$ densities, the reported surface reaction probabilities, and the estimated thermal velocity of the radicals in the plasma. For 1 SCCS injected SiH$_4$, 17 SCCS NH$_3$, and 45 A arc current, the N atomic density of the film was ~3.8 × 10$^{12}$ cm$^{-3}$ and the deposition rate ~6 nm/s, resulting in a N incorporation flux of 2.3 × 10$^{16}$ cm$^{-2}$ s$^{-1}$. For the calculation of the N incorporation flux from the radical densities on the other hand, we assume a sticking probability of ~0.02 for N radicals, ~0 for NH radicals, and ~0.13 for NH$_2$ radicals based on the discussion in Sec. V B. Now we can calculate the contribution of N, NH, and NH$_2$ radicals to the growth assuming a thermal velocity of ~1600 m/s (corresponding to a gas temperature of 1750 K (Ref. 33)), resulting in 4.9 × 10$^{15}$, 0, and 1.6 × 10$^{16}$ cm$^{-2}$ s$^{-1}$ for N, NH, and NH$_2$, respectively. Taking into account the limited experimental accuracy in the sticking probability, the two incorporation fluxes 2.3 × 10$^{16}$ and 2.1 × 10$^{16}$ cm$^{-2}$ s$^{-1}$ are in good agreement. Therefore, we conclude that the N incorporation in the $a$-SiN$_x$:H film can be explained by the NH$_x$ radical densities and their sticking probabilities. The NH$_2$ radical is the most important radical for N incorporation in the film (roughly 77%), followed by the N radical (roughly 23%). This result is similar to the growth mechanism based on SiH$_3$ and NH$_2$ radicals proposed by Umemoto et al. in a hot wire CVD process.

VI. CONCLUSIONS

The densities of N, NH, and NH$_2$ radicals in the Ar–NH$_3$–SiH$_4$ expanding thermal plasma used for silicon nitride deposition were investigated. The radicals were measured as a function of several plasma parameters such as NH$_3$ flow, SiH$_4$ flow, and arc current. For typical deposition conditions, we found densities of ~5.0 × 10$^{12}$ cm$^{-3}$ for N radicals, ~2.5 × 10$^{12}$ cm$^{-3}$ for NH radicals, and ~2.0 × 10$^{13}$ cm$^{-3}$ for NH$_2$ radicals. In the SiH$_4$ containing plasma the densities of N, NH, and NH$_2$ decrease with increasing SiH$_4$ flow, with the decrease being more prominent for N and NH$_2$. For NH, the decrease is most likely only due to a change in the production rate of the radicals, while N and NH$_2$ radicals decrease also in density as they are incorporated in the $a$-SiN$_x$:H film.

Besides the radical densities also the relative consumptions of NH$_3$ and SiH$_4$ in the plasma have been measured by mass spectrometry. For NH$_3$ we found relative consumptions in the range of 90%–40%, while the observed SiH$_4$ consumption lies between 90% and 60%. A large part of the consumed NH$_3$ is converted into H$_2$ and N$_2$ molecules, as was revealed by the large densities of these molecules (typically 10$^{14}$ cm$^{-3}$) in the plasma. Also the SiH$_4$ consumption contributes significantly to the observed H$_2$ density in the plasma.
Furthermore, we presented evidence that the recombination probability $\gamma$ of N radicals is lower on a silicon nitride covered wall than on a stainless steel reactor wall. For NH and NH$_2$ such a difference in recombination probability was not observed. The sticking probability $s$ for N radicals was also deduced from the measurements and varies with SiH$_4$ flow from $\sim0.01$ to $\sim0.04$. Comparison of the N growth flux calculated from the N atomic density in the film with the contributions of N, NH, and NH$_2$ to the growth has led to the conclusion that these radicals can account for the observed N atomic density in the film. Therefore, we expect that Si atoms are delivered to the surface via SiH$_4$ radicals creating an amorphous silicon like film that is nitrided by N and NH$_2$ radicals.

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