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# Modeling of the formation of cationic silicon clusters in a remote Ar/H<sub>2</sub>/SiH<sub>4</sub> plasma

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Cationic silicon clusters, containing up to ten silicon atoms, have been measured by mass spectrometry in an argon/hydrogen/silane expanding thermal plasma. A quasi-one-dimensional model, based on the idea that the clustering process initiated by argon or hydrogen ions depends on the path length of the plasma in the deposition chamber and on silane density, is presented. The chemistry is described by ion–molecule reactions between the formed clusters and silane and by dissociative recombination. The model is able to reproduce fairly well the experimental data for various plasma conditions. It is shown that reaction rates for the clustering process do not strongly depend on the number of silicon atoms in the cluster. This result is in contrast with rates published in the previous literature. For the conditions investigated, the consumption of silane by cationic cluster formation is not significant. The contribution of neutral clusters is investigated and recombination proves to be an important process. © 2000 American Institute of Physics. [S0021-8979(00)03808-1]

## I. INTRODUCTION

The formation of large cationic clusters in deposition plasmas is a topic of interest since their presence can modify to a large extent the characteristics of the plasma and of the deposited film. The size and shape of these ions may lead to disturbance in the film stoichiometry and to defects.<sup>1–3</sup> Therefore, they are expected to have a drastic effect on the quality of the film.<sup>4</sup> In typical plasma-enhanced chemical-vapor deposition (PECVD) reactors, large negatively charged clusters exist in the plasma because of the confinement by the electric field. The formation and growth process of negative ionic clusters is a widely studied topic,<sup>5–7</sup> and so is the formation of dust.<sup>8–14</sup> However, the formation of large positive silicon clusters is less known. In radio-frequency (rf) plasmas, their presence is not likely since they are not confined by the electric field. However, already in the early 1980s, Haller<sup>15,16</sup> reported the presence of large silicon positive ions in a rf glow discharge in silane. In a dc discharge, Weakliem<sup>17</sup> also detected positive silane ions. This observation was followed by the development of a numerical model by Kushner.<sup>18</sup> More recently, the detection of positive silicon clusters was made by Jasinski<sup>19</sup> in a remote PECVD reactor.

Recently, Kessels and co-workers<sup>2,3</sup> reported on the detection of large positive silicon clusters in fast expanding plasmas by ion mass spectrometry. Following this observation and considering the fact that, in this kind of setup, confinement is very unlikely and that the formation of large positive ions is a process that occurs along the beam axis, Kessels and co-workers<sup>2,3</sup> developed a numerical model to explain the presence of these clusters. In their calculation, the silane density was assumed to be constant and outward

diffusion was neglected. Moreover, the velocity of the beam was constant for every mixture composition. Finally, even though recombination was included in their model, the products of the recombination processes were not further considered.

This work is an extension of the work of Kessels and co-workers<sup>2,3</sup> and takes into account outward diffusion of the plasma beam. The silane density varies due to chemistry and the beam velocity depends on the mixture composition. The recombination is also treated in an improved manner and, finally, the presence of larger clusters is considered. Our aim is to check whether the proposed chemical pathway can describe the experimental results, get information about the rates of the clustering process, and study the influence of dissociative recombination on the ion abundance in the downstream plasma.

This article is organized as follows: the experimental observation and the ion chemistry in the plasma are described in Sec. II. The model, including governing equations and discretization, is discussed in the third section. Section IV is dedicated to the results. It includes a comparison of the model with the experiment, axial profiles of cluster fluences, and a study of the recombination processes in the plasma. The influence of positive silicon clusters on the total depletion of silane as well as the formation of neutral clusters are discussed.

## II. DESCRIPTION OF THE EXPERIMENT

The expanding thermal plasma setup, shown in Fig. 1, consists of a cascaded arc and a low-pressure expansion chamber. For a more extensive description of the setup and of the experiment, the reader is referred to Refs. 2, 3, and 20. In the cascaded arc, a flowing thermal Ar/H<sub>2</sub> plasma is created at a high pressure (approximately 400 mbar) and ex-

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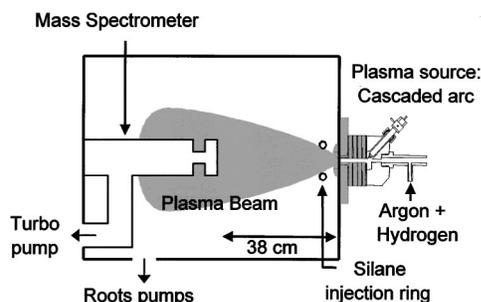
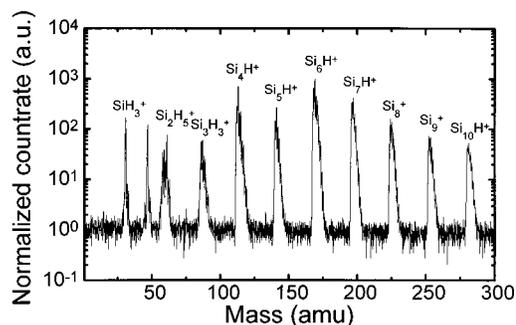


FIG. 1. Experimental setup.

pands into a low-pressure chamber ( $\approx 0.2$  mbar). A constant 55 sccs (1 sccs =  $2.5 \times 10^{17}$  particles/s) flow of argon is injected in the arc with a varying  $H_2$  flow ranging from 0 to 15 sccs. The arc, formed between three cathodes and an anode plate, dissociates and ionizes the gases. The pressure gradient between the arc and the chamber generates a supersonic expansion at the inlet of the chamber. After a stationary shock front at about 4 cm from the nozzle exit, the plasma flows at subsonic velocities. Pure silane  $SiH_4$  is injected (with flows ranging from 0 to 35 sccs) by means of a stainless-steel injection ring 6 cm after the nozzle exit. Ions and radicals emanating from the arc source dissociate the silane in radicals and ions which can deposit on an accurately temperature-controlled substrate situated at 38 cm downstream the arc exit. It has been demonstrated that using this plasma, good hydrogenated amorphous silicon (*a*-Si:H) film quality at high growth rates (around 10 nm/s) (Refs. 2, 3, and 20) can be obtained.

It is important to stress here that, due to the supersonic character of the primary expansion, the properties of the arc are determined only by the upstream conditions. The chemistry in the chamber has no effect whatsoever on the arc properties; i.e., downstream the plasma is referred to as a remote plasma.<sup>20</sup>

Recently, the study of the subsonic part of the expansion led to the observation of large positive silicon clusters.<sup>2,3</sup> These clusters are measured at the position of the substrate holder by a mass spectrometer, whose mass range is 300 amu. Clusters containing up to ten silicon atoms have been measured for various incoming gas flows of  $Ar/H_2/SiH_4$  of 55/ $x$ /10 sccs with  $x = 1, 3, 5$ , and 10, and of 55/10/ $y$  with  $y = 1, 3, 5, 10$ , and 15. Although the ion fluence emanating from the arc is strongly depending on the hydrogen fluence,<sup>3,20</sup> the cluster distribution is almost independent of the  $H_2$  flow. On the other hand, in the case of a constant  $H_2$  flow of 10 sccs, the cluster size increases with silane fluence. At low silane admission (i.e., below 3 sccs), the formed clusters have small sizes and almost no large cluster is observed. Increasing the silane flow leads to large cationic clusters.<sup>4</sup> For all operating conditions, the observed clusters were hydrogen poor. As an example, in the case 55/10/10 sccs, a typical experimental spectrum of these clusters is shown in Fig. 2 and it can be seen that the dominant cluster for each broadened peak is the one containing either none or only one hydrogen atom. The high atomic temperature (around 1000–1500 K in the subsonic part<sup>21</sup>) allows chemical elimination of  $H_2$  from the

FIG. 2. Experimental distribution of clusters at the substrate in the case of 55/10/10 sccs of  $Ar/H_2/SiH_4$ .

clusters and explains their hydrogen-poor characteristic.<sup>2,3</sup> Another feature of the distribution shown in Fig. 2 is the gap for the cluster containing five silicon atoms and the peak for the cluster containing six silicon atoms.

The conclusion that can be made from the experimental observation is that the formation of large clusters depends on the silane density in the expansion chamber. The interaction length, typically, here the distance between the silane injection ring and the substrate, is another parameter on which chemistry depends. Indeed, for a longer path length or for a higher silane density, more chemical processes can occur and larger clusters can be formed. In this respect, it should be noticed that, although the mass spectrometer cannot detect them, the presence of clusters containing more than ten silicon atoms is possible. This is especially true when the incoming silane flow is high. This point will be addressed later on.

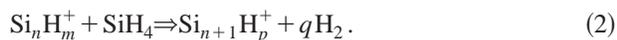
We shall now focus on the chemical reactions occurring in the plasma. As already stated by Kessels, van de Sanden, and Schram,<sup>2</sup> the ions emanating from the cascaded arc initiate the cationic clustering. In the pure argon case, the first cationic ion ( $SiH_3^+$ ) is formed by dissociative charge exchange of  $Ar^+$  with silane with a reported rate in the range of  $10^{-17}$ – $10^{-16} m^3 s^{-1}$ .<sup>20,22</sup> The radicals formed are very reactive with silane and with surfaces. This reaction is followed by dissociative recombination of the molecular-ion formed,<sup>4</sup> which is a very fast process with a rate of around  $10^{-13} m^3 s^{-1}$  at 3000 K.<sup>18</sup>

When  $H_2$  is added in the arc, argon ions are quenched by molecular hydrogen<sup>23–28</sup> with a rate of approximately  $10^{-15} m^3 s^{-1}$ .<sup>23–28</sup> This reaction is also followed by the very fast (approximately  $10^{-13} m^3 s^{-1}$ ) (Refs. 23–28) dissociative recombination of the formed  $ArH^+$ . Because of the quenching of argon ions, the main ion entering the chamber, when  $H_2$  is admixed, is  $H^+$ . This result is confirmed by the experiment of Kessels *et al.*,<sup>4</sup> who measured the effective mass of the ions as a function of the  $H_2$  flow. In the case of an  $Ar/H_2$  mixture,  $SiH_3^+$  is predominantly formed by a reaction of  $H^+$  with silane<sup>4</sup> with liberation of  $H_2$ :<sup>3</sup>

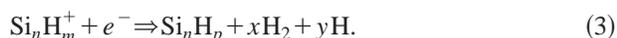


The rate for this reaction,  $5 \times 10^{-15} m^3 s^{-1}$  as given by Perin and co-workers,<sup>29,30</sup> is much higher than the rate for the pure argon case. This reaction is also followed by recombination of  $SiH_3^+$  with a similar rate as for the pure argon case.

Once a first silicon-containing ion is created, the formation of cationic clusters with more silicon atoms is simply made by addition of silane:



This process, proposed by Kessels and co-workers,<sup>2,3</sup> is based on the dependency of the cluster size with the silane flow. The reaction rates for the clustering process are still under debate and vary largely from one author to another. According to Haller and Weakliem,<sup>15-17</sup> the rates are independent of  $n$  and in the order of  $10^{-16} \text{ m}^3 \text{ s}^{-1}$ . Kushner<sup>18</sup> uses in his model rates of  $10^{-17} \text{ m}^3 \text{ s}^{-1}$  also independent of  $n$ . However, the rates for the high clustering process (i.e.,  $n \geq 5$ ) are very uncertain and, according to Mandich and Reents,<sup>31</sup> are one to several orders of magnitude lower than for the low clustering process. The formation of cationic silicon clusters could also occur via ionization of polysilanes. However, the electron temperature is very low in the chamber (0.1–0.3 eV) and, therefore, electrons are not sufficiently energetic to make this reaction very significant.<sup>26</sup> Moreover, neutral silicon clusters are not abundantly present in the plasma since, e.g., trisilane is already hardly detectable in this setup.<sup>3,4</sup> Therefore, this process is neglected. The destruction of cationic clusters is due to recombination with electrons:



This reaction has an estimated rate of  $1.7 \times 10^{-13} \text{ m}^3/\text{s}$ .<sup>18,29,32</sup> As already pointed out, this process competes with the interaction of clusters with silane [reactions (1) and (2)], depending on the ratio of electron-to-silane densities. As far as cluster recombination with electrons is concerned, only dissociative recombination [reaction (3)] is taken into account since it is a much faster process than radiative recombination.<sup>29</sup> Recombination with electrons is a very fast process compared to the formation of cationic silicon clusters and is dominant if the ratio of electrons to silane is well above 1%.<sup>4,20</sup>

The depletion of silane, defined as the percentage of silane consumed, is an important characteristic for the reactivity of the deposition setup (as a chemistry feature) and has been discussed by van de Sanden *et al.*<sup>20</sup> Depletion decreases with admixing of  $\text{H}_2$ . This feature is to be correlated to the flux of ions emanating from the arc as a function of the flow of  $\text{H}_2$ . As shown by Kessels *et al.*,<sup>4</sup> the ion fluence decreases with increasing the  $\text{H}_2$  fluence. This is due to a less efficient arc operation at high hydrogen admixtures and efficient quenching of ions downstream.<sup>23,27,33-35</sup>

### III. MODEL

The calculations concern the part of the plasma downstream of the silane injection ring, i.e., the subsonic part of the flow for which a quasi-one-dimensional model has already been used successfully by several authors.<sup>21,36</sup> Therefore, we assume a uniform velocity for the flow of around 600–1000 m/s,<sup>23,27,28</sup> depending on the initial composition of the mixture.<sup>37</sup> The initial and final (i.e., at the substrate) ion flux have been measured by Kessels *et al.*<sup>3</sup> and the velocity

in the model is fitted so that the fluence calculated at the substrate position matches these values. The flow is stationary and, according to experimental observation, the expansion is parabolic. That means that the area  $A(z)$  of the beam increases with the distance from the arc (more details are given in the appendix).

The species considered in the model are the cationic silicon clusters  $\text{Si}_n\text{H}_m^+$  ( $n=0$ , ‘‘11’’) with  $n=0$  corresponding to  $\text{H}^+$  or  $\text{Ar}^+$  without any distinction. The possibility of high silicon number clusters ( $n>10$ ) has not been examined experimentally because of the restricted features of the mass spectrometer. However, the presence of very large clusters in significant amounts could have a drastic effect on deposition. Therefore, our model includes clusters containing more than ten silicon atoms by means of the so-called cluster ‘‘11.’’ This cluster contains all clusters that possess more than ten silicon atoms. The electrons, responsible for recombination of the clusters, and silane, responsible for clustering, are the only other species considered in this model. The residence time ( $\approx 0.4$  s) in the chamber is much larger than the transit time inside the beam ( $\approx 1$  ms from the arc source to the substrate). The chamber can then be viewed as a reactor filled with silane in which an ion beam enters; the reactor is assumed to be fully mixed for silane. The consequence of this hypothesis will be discussed later. Neutral clusters are considered, but only as a product of recombination (more details will be given in Sec. IV). It should also be noticed that no attempt is made to investigate the number of H atoms present in the clusters.<sup>2</sup> This means that all clusters containing the same number of silicon atoms are treated as one species with a chemistry ruled by one and the same equation.

Consider the mass balance of any species between  $z$  and  $(z+dz)$  in a stationary case. Since the boundary of the beam is defined by a no-flux condition, the flux of this species at position  $(z+dz)$  is a function of the entering flux at  $z$  and the chemistry inside the volume  $A(z)dz$  where  $A(z)$  is the area of the beam at position  $z$ . The chemistry includes clustering reactions (1) and (2) and the recombination reaction (3). The mass conservation equation of  $\text{H}^+$  (or  $\text{Ar}^+$ ) is given by

$$\frac{\partial}{\partial z} [n_0(z)vA(z)] = -k_0 n_{\text{si}}(z)n_0(z)A(z), \quad (4)$$

where  $n_0(z)$  and  $n_{\text{si}}(z)$  are the densities of  $\text{H}^+$  (or  $\text{Ar}^+$ ) and silane, respectively, at position  $z$  and  $v$  is the velocity of the plasma beam.  $k_0$  is the reaction rate of reaction (1). Although the ions are much heavier than the electrons, the velocity of the plasma beam is assumed to be the same for every species.

The mass conservation equation for of a cluster containing  $n$  silicon atoms is given by

$$\begin{aligned} \frac{\partial}{\partial z} [n_n(z)vA(z)] = & -k_n n_{\text{si}}(z)n_n(z)A(z) \\ & + k_{n-1} n_{\text{si}}(z)n_{n-1}(z)A(z) \\ & - k_n^{\text{rec}} n_e(z)n_n(z)A(z), \end{aligned} \quad (5)$$

$n_n(z)$  is the density of  $n$ -silicon clusters,  $k_n$  and  $k_n^{\text{rec}}$  the reaction rates of reactions (2) and (3), respectively. The first and third terms refer to the destruction of the  $n$  cluster by

clustering and recombination, respectively, the second term describes the production by the clustering of a  $(n-1)$  cluster.

The mass conservation equation for silane is given by

$$\frac{\partial}{\partial z}[n_{\text{si}}(z)vA(z)] = - \sum_{n=0}^{\infty} k_n n_{\text{si}}(z)n_n(z)A(z). \quad (6)$$

Finally, the conservation equation for the electrons is

$$\frac{\partial}{\partial z}[n_e(z)vA(z)] = - \sum_{n=1}^{\infty} k_n^{\text{rec}} n_n(z)n_e(z)A(z). \quad (7)$$

The summation starts at  $n=1$  since the recombination of  $\text{H}^+$  or  $\text{Ar}^+$  is not important, and thus not included in the model.

The total domain, whose length is  $L=32$  cm is divided into  $k$  equally spaced cells of length  $\Delta z=L/k$  ( $k \approx 10^5$ ). The calculation starts in the subsonic part of the expansion at  $z_0=6$  cm and ends at  $z_{\text{sub}}=38$  cm, the position of the substrate. Since the experimental results and input data are given in terms of fluences (sccs), the set of Eqs. (4)–(7) is discretized in terms of fluences  $\Phi(z)$ :

$$\Phi_0(z+\Delta z) = \Phi_0(z) \left( 1 - \frac{k_0 n_{\text{si}}(z)}{v} \Delta z \right), \quad (8)$$

$$\begin{aligned} \Phi_n(z+\Delta z) = \Phi_n(z) \left( 1 - \frac{k_n n_{\text{si}}(z) + k_n^{\text{rec}} n_e(z)}{v} \Delta z \right) \\ + \Phi_{n-1}(z) \frac{k_{n-1} n_{\text{si}}(z)}{v} \Delta z, \end{aligned} \quad (9)$$

$$\Phi_{\text{si}}(z+\Delta z) = \Phi_{\text{si}}(z) \left( 1 - \sum_{n=0}^{\infty} \frac{k_n n_{\text{si}}(z)}{v} \Delta z \right), \quad (10)$$

$$\Phi_e(z+\Delta z) = \Phi_e(z) \left( 1 - \sum_{n=1}^{\infty} \frac{k_n^{\text{rec}} n_n(z)}{v} \Delta z \right). \quad (11)$$

The initialization of the program is straightforward. At the inlet of the domain ( $z=z_0$ ), the following parameters are given:

- (i)  $\Phi_0(z_0) = \Phi_{\text{ion}}$  is given from probe measurements. Its value is a function of  $\text{H}_2$  flow.<sup>4</sup>
- (ii)  $\Phi_n(z_0) = 0$  for every cluster.
- (iii)  $\Phi_{\text{si}}(z_0) = \Phi_{\text{si}}$  is the input silane fluence.
- (iv)  $\Phi_e(z_0) = \Phi_0(z_0)$  (no current in the plasma).

For every position  $z$ , the densities are obtained from the fluences by  $n(z) = [\Phi(z)/vA(z)]$ . However, because the reactor is supposed to be fully mixed for silane, the decrease of density is due to chemistry and not due to outward diffusion. Therefore, the beam area for silane is constant [equal to  $A(z_0)$ ] and the density is given by  $n_{\text{si}}(z) = [\Phi_{\text{si}}(z)/vA(z_0)]$ .

#### IV. RESULTS

Two sets of operating conditions corresponding to various  $\text{Ar}/\text{H}_2/\text{SiH}_4$  mixtures have been simulated. For both sets, the argon flow was kept fixed at 55 sccs. In the first set of simulations the proportion of  $\text{H}_2$  was kept constant at 10 sccs

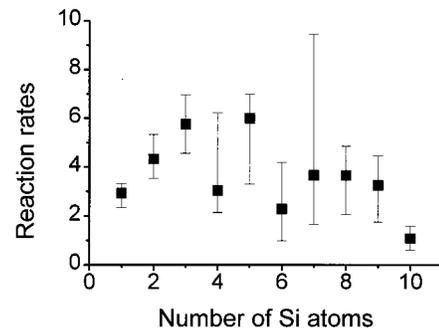


FIG. 3. Average reaction rates ( $10^{-16} \text{ m}^3/\text{s}$ ) for the clustering process.

while the inflow of silane was 1, 3, 5, 10, and 15 sccs. In the second set, the silane flow was kept fixed at 10 sccs and the  $\text{H}_2$  flow was 1, 3, 5, and 10 sccs. These two sets of simulations allow us to study separately the influence of silane and of ions on the clustering process. For each simulation, the normalized distribution of the clusters at the position of the substrate was calculated and fitted to the experimental distribution. This fitting gave us the reaction rates for the clustering process. Other important features of the plasma, such as the depletion of silane by clusters and the formation of “neutral” species were calculated. Finally, to obtain information on the influence of recombination, some simulations were performed neglecting recombination processes. The main result is that, when recombination was included, the normalized distribution at the substrate stayed the same but the absolute fluence of clusters was decreased by a factor 10. Recombination is thus an important chemical process in the plasma. Indeed, the rates for recombination are much faster than for clustering (1000 times faster) and the electron-to-silane ratio is high enough ( $>5 \times 10^{-3}$ ) to make recombination dominant in the beginning of the beam.

The reaction rates constitute a very important output of the simulation and are presented in Fig. 3 as a function of  $n$  for all the simulations performed. The rates do not depend critically on the number of silicon atoms present in the cluster as already pointed out by Kessels *et al.*<sup>3</sup> One can see that these rates have a value of around  $4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$ . This remains true for all experimental conditions simulated. The deviation from the average value is very small for almost every rate. However, it should be noted that the rates for high clustering ( $n \geq 5$ ) at low silane flows should be taken with great care. Because at low silane fluences the amount of big clusters is very small the rates become very dubious. The plot of the average rates in Fig. 3 does not include these rates. Finally, a high rate for  $n=5$  combined with a lower rate for  $n=6$  is a result of the gap for  $\text{Si}_5\text{H}_m^+$  in the experimental distributions (cf. Fig. 2). These rates are 2–4 times higher than the one obtained by Kessels *et al.*<sup>3</sup> due to the fact that diffusion was taken into account in our model. Nevertheless, both distributions are similar. On the other hand, the rates are around two times smaller than the Langevin limit.<sup>29</sup>

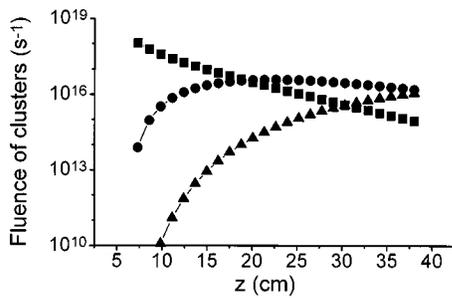


FIG. 4. Axial profile of the fluence of various cationic silicon clusters in the case of 55/10/10 sccs of Ar/H<sub>2</sub>/SiH<sub>4</sub>. ■: SiH<sub>m</sub><sup>+</sup>, ●: Si<sub>5</sub>H<sub>m</sub><sup>+</sup>, and ▲: Si<sub>10</sub>H<sub>m</sub><sup>+</sup>.

**A. Axial profiles**

The amount of clusters arriving at the substrate is determined by the chemistry upstream of the substrate. Therefore, we plotted in Fig. 4 the profiles of various clusters as a function of *z* in the 55/10/10 sccs case. Clusters containing only one silicon atom are formed by reaction of H<sup>+</sup> (or Ar<sup>+</sup>) with silane. Since H<sup>+</sup> is only present at the beginning of the beam, cluster SiH<sub>x</sub><sup>+</sup> keeps being destroyed along the beam and decreases from the injection ring to the substrate. For clusters containing five silicon atoms, the chemistry is such that at the beginning its fluence is small. Since Si<sub>5</sub>H<sub>x</sub><sup>+</sup> is the fifth step in the clustering process, it takes a certain path length before this cluster is created. That is the reason why its fluence first increases along the beam and reaches a maximum at around *z* = 22 cm. Then, production of this cluster is almost compensated by its destruction. The path length for the creation of clusters with ten silicon atoms is even longer. The fluence of this cluster increases continuously towards the substrate. It should be noted here that the fluence of clusters with ten silicon atoms starts to be significant only next to the substrate and confirms the low contribution of larger cluster ions.

**B. Depletion of silane**

As already stated, the depletion of silane is an important measure for the efficiency of the plasma deposition setup. The silane depletion is defined by the relative flow of dissociated silane and is obtained by<sup>20</sup>  $D = (I_{\text{SiH}_4,\text{off}} - I_{\text{SiH}_4,\text{on}}) / I_{\text{SiH}_4,\text{off}}$  where *I*<sub>SiH<sub>4</sub>,off</sub> and *I*<sub>SiH<sub>4</sub>,on</sub> are the channel-tron current signals of the quadrupole mass spectrometer measured with plasma off and on, respectively. In our model,

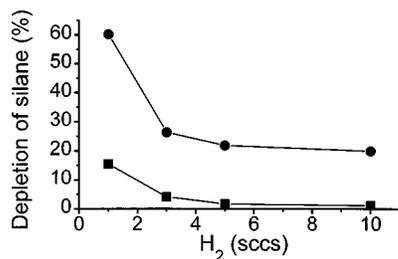


FIG. 5. Depletion of silane as a function of H<sub>2</sub> flow for 10 sccs of SiH<sub>4</sub>. Comparison experiment/modeling. ■: model (contribution of ions). ●: experiment.

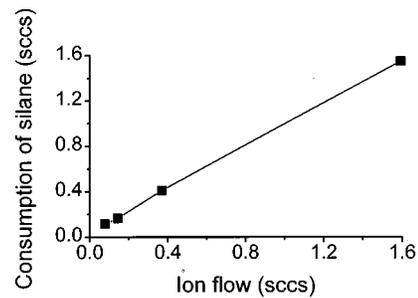


FIG. 6. Consumption of silane as a function of ion flow.

we only take into account the depletion of silane due to clustering reactions. The modeled depletion  $D_{\text{cluster}} = 1 - \Phi_{\text{si}}(L) / \Phi_{\text{si}}(0)$  is only an indication of the influence of ionic clusters on the consumption of silane. In Fig. 5, the modeled depletion of silane is compared to the experimental one as a function of H<sub>2</sub> flow. The depletion decreases with increasing H<sub>2</sub> flow. Indeed, at low H<sub>2</sub> admixtures, the flow of H<sup>+</sup> ions is maximum<sup>4,20</sup> and the clustering processes are more efficient and the consumption of silane is more important. Figure 5 also shows that the trend for the model and the experiment are the same but the values for the model are much lower. The contribution of ions to the total depletion is maximum 25% and decreases with H<sub>2</sub> flow. This demonstrates that depletion of silane molecules by ionic clustering is rather low. In Fig. 6, the absolute consumption of silane, due to the clustering process, and defined as  $\Phi_{\text{si}}(L) - \Phi_{\text{si}}(z_0)$  is plotted as a function of the ion flow for a given silane flow of 10 sccs. The linear increase, with a slope of approximately 1, indicates that each ion emanating from the are consumes about one silane molecule. This result can be compared to the results of van de Sanden *et al.*,<sup>20</sup> where the plot of the total absolute consumption of silane as a function of the ion flux indicated that one ion consumed about two silane molecules. The comparison experiment/model confirms that the experimental depletion is not due to ions only. The conclusion is that other processes contribute significantly to the depletion of silane, mainly reactions involving atomic hydrogen:<sup>18,20,29,38</sup>



In Fig. 7, the absolute consumption of silane by clusters is plotted as a function of silane flow for a H<sub>2</sub> flow of 10 sccs. The ion flow for these conditions is 0.08 sccs. The consumption increases as a function of silane. The increase in the

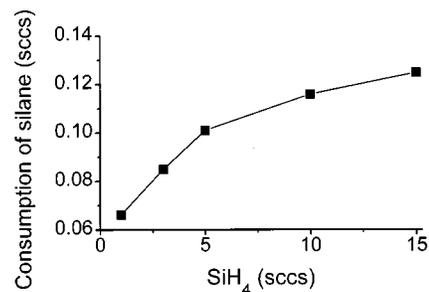


FIG. 7. Consumption of silane as a function of SiH<sub>4</sub> flow for 10 sccs of H<sub>2</sub>.

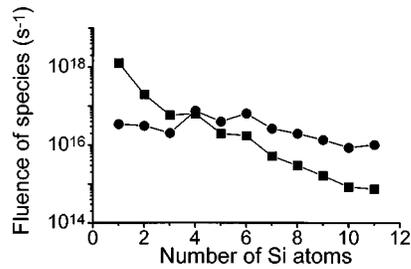


FIG. 8. Distribution at the substrate position in the case of 55/10/5 sccs of Ar/H<sub>2</sub>/SiH<sub>4</sub>. ■: number of recombination processes for a cluster containing  $n$  silicon atoms. ●: fluence of a cluster containing  $n$  silicon atoms.

consumption of silane is not very sharp since an increase of silane flow from 1 to 15 sccs only doubles the consumption of silane. The consumption tends to saturate to a value of 0.13 sccs. This indicates that one ion consumes around one and a half silane molecules. Calculations performed in the same conditions, but removing dissociative recombination, showed a consumption of three silane molecules per ion injected in the arc. The discrepancy between the model and the experiment clearly demonstrates the importance of additional chemistry. Therefore, we investigated the recombination of ions in the plasma.

### C. Neutrals

In order to get better insight into the influence of neutral species on the chemistry, the production of neutral clusters was calculated. To keep the model as simple as possible, and since we do not know which products are formed in the dissociative recombination of, e.g., Si<sub>5</sub>H<sub>4</sub><sup>+</sup>, we only made calculations of the number of recombination processes occurring in the beam. This gives valuable information on the number of neutral species present in the beam. One should keep in mind that no subsequent reaction after the recombination is taken into account. This means that, in the following,  $N_p(z)$  is the number of recombination processes (per unit time) of a cationic  $p$  cluster between positions  $z_0$  and  $z$  without any consideration of the products formed. In other words,  $N_p(z)$  is not necessarily a neutral containing  $p$ -silicon atoms, on the contrary, it originates from the cluster ion Si <sub>$p$</sub> H <sub>$x$</sub> <sup>+</sup>. In Fig. 8, the distribution of recombination processes at the substrate is plotted as a function of  $p$ . For comparison, the distribution of cationic clusters is also shown. This plot corresponds to a 55/10/5 sccs mixture of Ar/H<sub>2</sub>/SiH<sub>4</sub>. The distribution of recombination processes at the substrate decreases with increasing  $p$ . The decrease can be explained by the fact that larger clusters need a longer path length to be created. Therefore, recombination of large clusters occurs later in the beam and in lower quantity. Indeed, cationic cluster and recombination process distributions are not correlated. As an example, Si<sub>10</sub>H <sub>$x$</sub> <sup>+</sup> is formed later than other clusters and has, therefore, less time to recombine. Consequently,  $N_{10}$ , which represents the number of recombinations of Si<sub>10</sub>H <sub>$x$</sub> <sup>+</sup>, has a smaller value at the substrate. Since recombination has the same efficiency for every cluster, the decrease in the distribution is only a path-length problem. This figure, however, demonstrates the fact that the number

of recombination processes is large and, therefore, the amount of neutral clusters formed is also significant.

### V. CONCLUSIONS

The formation process of cationic silicon clusters in an expanding thermal plasma used for deposition of hydrogenated amorphous silicon  $a$ -Si:H has been studied by means of a quasi-one-dimensional model. This model proves to be satisfactory to fit experimental data. The proposed simple chemical pathway is relevant and the rates for the formation of the clusters are roughly constant around  $(4 \pm 1) \times 10^{-16}$  m<sup>3</sup>/s. The fact to take into consideration is that outward diffusion leads to rates higher than the one obtained by Kessels *et al.*<sup>3</sup> and closer to the Langevin limit. The formed clusters have a negligible influence on silane depletion and it is shown that big clusters ( $n > 10$ ) are not produced in large amounts in the plasma for every flow composition investigated due to the restricted path length. An attempt to investigate the influence of recombination processes has also been made and it is shown that this process cannot be neglected.

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### APPENDIX: ESTIMATION OF THE RADIUS OF THE BEAM

The radius of the beam is an important parameter which appears in the Eqs. (4)–(7) via the area  $A(z)$ . We present here the way it was estimated. The radius of the beam at position  $z_{\text{inj}} = 6$  cm (injection ring) is obtained from measurements. Indeed, the fluence and density of H<sup>+</sup> have been measured for various H<sub>2</sub> flows. The ratio  $\Phi(z_0)/n(z_0) = vA(z_0)$  is constant and equal to 5.31. Then, the radius  $r_{\text{inj}}$  is obtained by  $r_{\text{inj}} = \sqrt{5.31/\pi v}$ . For various silane flows, the radius of the beam at  $z_{\text{sub}} = 38$  cm (position of the substrate) was also measured, as shown in Table I. Moreover, as already mentioned in Sec. III, the expansion is parabolic. That means the radius of the beam is related to the axial position  $z$  by the following formula:

$$z = ar(z)^2 + br(z) + c.$$

At  $z = 0$ , the radius is equal to the radius of the arc. In this calculation it was, however, taken 0 for simplicity and considering that the radius of the arc is much smaller than the radius of the beam. This hypothesis implies  $c = 0$ . With the other “boundary conditions” given above, we can write

$$z_{\text{inj}} = ar_{\text{inj}}^2 + br_{\text{inj}},$$

$$z_{\text{sub}} = ar_{\text{sub}}^2 + br_{\text{sub}},$$

TABLE I. Radius of the beam as a function of silane flow.

SiH <sub>4</sub> (sccs)	1	3	5	10	15
$r_{\text{sub}}$ (cm)	15.6	13.1	12.2	11.4	10.8

which leads to

$$a = \frac{z_{\text{sub}} r_{\text{inj}} - r_{\text{sub}} z_{\text{inj}}}{r_{\text{sub}} r_{\text{inj}} (r_{\text{sub}} - r_{\text{inj}})},$$

$$b = \frac{z_{\text{inj}}}{r_{\text{inj}}} - \frac{z_{\text{sub}} r_{\text{inj}} - r_{\text{sub}} z_{\text{inj}}}{r_{\text{sub}} (r_{\text{sub}} - r_{\text{inj}})}.$$

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