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Formation of large positive silicon-cluster ions in a remote silane plasma

W. M. M. Kessels, a) C. M. Leewis, A. Leroux, M. C. M. van de Sanden, b) and D. C. Schram

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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The formation of hydrogen poor cationic silicon clusters \( \text{Si}_n \text{H}_m^+ \) with up to ten silicon atoms in an expanding argon–hydrogen–silane plasma has been studied by mass spectrometry and Langmuir probe measurements. Sequential clustering reactions with silane, initiated by silane ions, cause their size to depend on the product of silane density and geometrical path length having possible implications for \( \text{a-SiH} \) films deposited by remote plasmas. Reaction rates, estimated by a one-dimensional model, show no strong dependence on the number of silicon and hydrogen atoms present in the ions in contrast with rates determined by ion-cyclotron resonance mass spectrometry studies. Possible causes of the discrepancy are discussed as well as the hydrogen poverty of the clusters. The maximum contribution of the cationic clusters to the growth flux is about 6% for the conditions investigated. © 1999 American Vacuum Society. [S0734-2101(99)10304-X]

I. INTRODUCTION

Today's studies concerning silane plasma chemistry and deposition mechanism of hydrogenated amorphous silicon (\( \text{a-Si:H} \)) are mainly concentrated on silane radical processes. However, the chemistry of silicon containing ions and their impact on the deposition process should not be underestimated. Although their contribution to the silicon growth flux can be limited, they can for example supply a considerable amount of potential and kinetic energy to the surface as they are accelerated in the plasma sheath. Furthermore, silicon containing ions can reach a considerable size as sequential ion-molecule reactions with silane are relatively fast. This clustering can particularly be important in remote silane plasmas as it will be shown that the size of silicon containing ions depends on the product of silane density and distance between plasma source and substrate.

In this article the formation of large positive ions containing up to ten silicon atoms in an expanding argon–hydrogen–silane plasma as reported in Ref. 1 is further investigated. The plasma under consideration is a thermal plasma source created argon–hydrogen plasma to which silane is injected downstream. With this setup it is possible to deposit solar grade quality \( \text{a-Si:H} \) at a growth rate of 10 \( \text{nm/s} \) at a substrate temperature of 400 °C. Furthermore, this plasma is very well suited to study the plasma chemistry as the downstream plasma properties can be varied without influencing the source properties. In the present study, the silane flow admixed to the plasma and consequently the silane density has been varied for constant source properties and the consequences for cationic cluster formation are investigated. Results concerning the ion chemistry in the plasma are compared to fundamental ion-molecule reactions as, e.g., studied by Mandich and Reents \(^3\)–\(^6\) and the extrapolation of such results to silane plasmas is discussed. Moreover, the contribution of the cationic clusters to film growth has been determined and their impact on film quality is considered.

II. EXPERIMENT

The setup is schematically illustrated in Fig. 1. A thermal argon–hydrogen plasma is created in a cascaded arc operating at a current of 45 A, a voltage of about 180 V, and a pressure of about 400 mbar. The argon and hydrogen flow are, respectively, 55 and 10 sccs (standard cubic centimeter per second). The plasma in the arc has typically an electron density of \( 10^{22} \text{ m}^{-3} \) and an electron temperature of 1 eV. The plasma expands supersonically into the low pressure (0.2 mbar) deposition chamber, and after a stationary shock at about 4 to 5 cm from the arc exit the plasma flows subsonically (with about 1000 m/s) into the direction of the substrate holder. Silane is injected about 5 cm from the arc exit by means of an injection ring and at flows varied between 1 and 15 sccs.

The substrate holder is positioned at 38 cm from the arc exit and is replaced by a mass spectrometer (Hiden Analytical EPIC 300) with similar geometry in the present study. The setup is also equipped with a double cylindrical Langmuir probe positioned at 2 cm in front of the substrate holder or mass spectrometer and which can be scanned in radial direction. As measurements have been performed in a depositing plasma the probe characteristics obtained have been carefully checked. It turned out that the current to the probe in the depositing plasma was sufficiently low to avoid a significant voltage drop over the resistive \( \text{a-Si:H} \) film formed. Yet severe disturbances occurred in measurements at the electron current branch of single probe measurements, particularly in the saturation region. Before every measurement the probe was cleaned by drawing high currents to each of the probes separately. The probe characteristics obtained were analyzed by the method proposed by Peterson and Talbot.\(^8\) A more detailed description about the measurements

\(^{a)}\)Electronic mail: w.m.m.kessels@phys.tue.nl
\(^{b)}\)Electronic mail: m.c.m.v.d.sanden@phys.tue.nl
in the depositing plasma and the analysis can be found in Ref. 9.

III. RESULTS AND DISCUSSION

As presented in an earlier article\textsuperscript{10} the dissociation of silane is determined by ions (either Ar\textsuperscript{+} or H\textsuperscript{+}) and atomic hydrogen emanating from the arc as the electron temperature is too low (0.1–0.3 eV) for electron induced ionization. In the plasma condition described a large atomic hydrogen flux emanates from the plasma source and its interaction with silane leads to a large SiH\textsubscript{3} flux towards the substrate. The presence of both atomic hydrogen in the argon–hydrogen plasma and SiH\textsubscript{3} in the argon–hydrogen–silane plasma have been demonstrated by appearance potential mass spectrometry using the same mass spectrometer as mentioned above. Yet no quantitative information has been obtained by this technique and therefore an indirect way was used showing that SiH\textsubscript{3} is the dominant species contributing to film growth.\textsuperscript{10} Nevertheless, also a small flux of mainly atomic hydrogen ions (about a factor 100 lower than the atomic hydrogen flux) emanates from the arc creating silane ions by charge transfer with silane, most probably by:\textsuperscript{11}

\[
\text{H}^+ + \text{SiH}_3 \rightarrow \text{SiH}_2^+ + \text{H}_2.
\]

(1)

It is expected that sequential clustering reactions of these primary silane ions lead to the cationic clusters as shown by ion mass spectrometry scans in Fig. 2. This figure shows peaks due to silicon cluster ions Si\textsubscript{p}H\textsubscript{m}, containing up to 10 silicon atoms for silane flows of 10 and 15 sccs. Possible larger clusters cannot be observed due to the limited range of the mass spectrometer. Around 47 amu also silanol ions are observed most probably caused by oxygen remaining in the deposition chamber after a plasma clean with an argon–carbon tetrafluoride–oxygen mixture. The mass spectra, obtained with ionizer off, are not corrected for mass dependent transmittance and detector efficiency of the spectrometer. The background signal is caused by photons from the plasma source arriving at the mass spectrometers detector which is almost in line-of-sight with the plasma source. As can be seen in Fig. 2 the cluster size increases with silane flow and consequently silane density. This dependency on silane density confirms the proposed reaction mechanism: \textsuperscript{11,12,13}

\[
\text{Si}_n\text{H}_m^+ + \text{SiH}_3 \rightarrow \text{Si}_{n+1}\text{H}_{p+1}^+ + q\text{H}_2
\]

(2)

with \(n \geq 1\) and \(m + 4 = p + 2q\). Reactions leading to the formation of atomic hydrogen are neglected as they are endothermic.\textsuperscript{14} According to Haller,\textsuperscript{12,15} and copied by Weakliem,\textsuperscript{13} also charge transfer can occur between the cationic clusters and silane molecules. Calculations\textsuperscript{16} showed, however, that the ionization potential of bare silicon clusters \(\text{Si}_n\) with \(n \geq 2\) is at most 8 eV which is smaller than ionization potential of silane. Assuming a similar ionization potential for silicon clusters containing few hydrogen atoms makes charge transfer with silane very unlikely even when the silane is rovibrationally excited.

Another possible production mechanism of the cationic clusters is by means of ionization of polysilanes. This mechanism is very unlikely as the polysilane density is very low in the expanding plasma. The disilane density is about a factor 100 lower than the silane density,\textsuperscript{10} whereas trisilane and tetrasilane are estimated to be respectively a factor 10\textsuperscript{4} and 10\textsuperscript{6} lower. Larger polysilanes have not been observed.\textsuperscript{9}

As reported earlier, it is remarkable that the hydrogen content of the cationic clusters in Fig. 2 is distinct from the hydrogen content in positive ions and cluster ions generally observed in silane plasmas.\textsuperscript{12,13,15,17} For all clusters containing more than three silicon atoms the most abundant ion contains only one or no hydrogen atom and only ions containing up to seven hydrogen atoms, \(\text{Si}_n\text{H}_7^+\), are clearly observable. The clusters with even and odd number of hydrogen atoms appear also to be decoupled,\textsuperscript{5} which can be understood from the endothermicity of the elimination of atomic hydrogen in reaction (2). Furthermore, the distribution of hydrogen in the clusters suggests that the ion-molecule reactions of Eq. (2) occur mostly with elimination of two hydrogen molecules, i.e., \(q = 2\). Assuming the reaction pathway in Eq. (2), the release of hydrogen has been studied by a simple computer code as proposed by Hollenstein.\textsuperscript{18} The code starts at clusters containing four silicon atoms as smaller ions are more hydrogen saturated which is possibly due to side effects as charge transfer reac-
tions between the ions emanating from the arc and the small quantity of disilane and trisilane present in the plasma. A comparison between experimental and calculated results has demonstrated that the probability for elimination of two hydrogen molecules and therefore the addition of only a Si atom is larger than 95%. This is in strong contrast with cluster ions in conventional radio-frequency (rf) and direct-current (dc) silane plasmas, where the hydrogen to silicon ratio is about constant for larger cluster ions. In these plasmas the observed cationic cluster growth can satisfactorily be explained by sequential addition of SiH₂ and consequently the release of only one hydrogen molecule. For remote plasmas only little information about cationic clusters is available, apart from the observation by Theil and Powell that the degree of hydrogenation of the cluster ions decreased (leading dominantly to Si₅H₉⁺) with increasing discharge power in 13.56 MHz and 2.45 GHz generated discharges in helium. Therefore we attribute the hydrogen poverty of the cationic silicon clusters to the high gas temperature (1000–1500 K) in the expanding plasma compared to conventional silane plasmas which is due to the fact that the plasma is created in a thermal plasma source. This is in agreement with the expectation of Mandich and Reents, observing mainly SiH₂ addition in their ion-silane studies at thermal energies, and more that more hydrogen is eliminated when additional energy is present. Furthermore, Henis et al. postulated that the probability for reactions between silicon containing ions and silane leading to products requiring extensive rearrangement and bond breaking, necessary to create two hydrogen molecules, is increased at higher kinetic energies of the involved species. This corresponds also with the structure of the cluster ions as the limited hydrogen content implies very compact clusters. Such compact structure is particularly stable and is in fact the ground state geometry for dehydrogenated neutral and ionic clusters. Their hydrogenated counterparts show also a particular stability at compact structures, but at intermediate and fully hydrogen-terminated bulk-like tetrahedral coordinated structures as well. The compact structure is most probably created in the expanding plasma with relatively high gas temperature, where the other two structures are dominantly observed in conventional silane plasmas.

Quantitative information on presence of the cationic clusters has been determined from Langmuir probe measurements. In Fig. 3 the ion flux at 2 cm in front of the substrate is shown for different silane flows. The ion flux for the non-depositing argon–hydrogen plasma is given for comparison. The silane flow decreases considerably when silane is admixed due to dissociative recombination of the silicon containing ions with electrons. The reaction rate for this reaction is assumed to be $10^{-13} T_e^{-1/2}$ ($T_e$: electron temperature in eV) and to be rather independent of ion size. The electron temperature obtained is in the range of 0.2–0.3 eV. Notice that the ion flux increases with silane flow as the source properties are kept constant. Although small differences in dissociative recombination rates for the different clusters cannot be excluded, it can probably be attributed mainly to a decrease of beam width. While no beam properties are observed for the non-depositing plasma, the beam diameter decreases with increasing silane flow and consequently increasing cluster size for the depositing plasma. The beam radius scales with $1/\sqrt{M}$ ($M$: the average ion mass) showing reduced outward diffusion of the heavy ions for a more or less constant forward velocity in the beam.

From these results a simple one-dimensional model has been setup to obtain information about the reaction rates for the reactions in Eq. (2). This model, an extension of the model presented in Ref. 1, is based on sequential clustering reactions starting from an initial atomic hydrogen ion flux of 0.08 sccs including dissociative recombination of the molecular species with electrons. Different silane flows were modeled (cf. Fig. 3). It is assumed that the silane density is homogeneous throughout the deposition chamber and proportional to the silane flow. The total ion flux at the position of the substrate holder is given by the probe measurements and it fixes more or less the directed velocity of the clusters due to the fact that the magnitude of dissociative recombination depends most critically on the time it takes to travel from the silane injection point to the substrate. The obtained directed velocity is about 900 m/s which is in good agreement with other experiments on a similar setup. The relative distribution of the cationic clusters is determined from the mass spectra without distinguishing between the different numbers of hydrogen atoms present. Setting the reaction rate of the hydrogen ions with silane at $5 \times 10^{-15} \text{m}^3 \text{s}^{-1}$ the reaction rates for the sequential reactions have been estimated by matching the calculated densities to the experimental values. It has turned out that the reaction rates obtained for the different silane flows are in relative good agreement despite the very simple model. The averaged reaction rates are shown in Fig. 4 where $k_n$ denotes the reaction rate of a cluster ion containing $n$ silicon atoms with silane.

Figure 4 shows that the reaction rates are in the range of $10^{-17} – 10^{-16} \text{m}^3 \text{s}^{-1}$ and that the rates do not depend critically on the number of silicon atoms present in the clusters. These near-collisional rates are in accordance with the ones suggested by Haller, Weakliem, and Kushner and are
about a factor 5–10 smaller than the Langevin rates.\textsuperscript{11} They are, however, not in agreement with the rates proposed by Mandich and Reents.\textsuperscript{3–6} From both ion-cyclotron resonance mass spectrometry at thermal energies and theoretical considerations they derived rates which span three orders of magnitude as the rates show a strong dependence on the number of silicon and hydrogen atoms present in the cluster and on their isomeric state. Moreover, they do not observe production of clusters containing more than six silicon atoms in their ion-silane reactions,\textsuperscript{3–6} although such ions are observed in silane plasmas as shown in this article as well as in others.\textsuperscript{17–19} Possible causes of the differences between their observations and those in silane plasmas will be discussed below.

First of all, the experimental conditions between both cases are very different. In their ion-cyclotron resonance mass spectrometer the pressure is roughly six orders of magnitude lower than in silane plasmas and the only gas used is pure silane. The fact that they use mostly SiD$_4$ instead of SiH$_4$ is not expected to cause significant differences.\textsuperscript{3} In silane plasmas on the other hand also silane radicals are present which can influence the clustering reactions.\textsuperscript{21} Their lower abundance can possibly be compensated for by their higher reactivity. Furthermore, also polysilanes like disilane and trisilane are present in silane plasmas. Mandich and Reents show for example that reactions between silicon cluster ions and disilane can proceed to clusters with up to eight silicon atoms and then terminate.\textsuperscript{25} Although this can explain the observation of cationic clusters with more than six atoms it would probably cause a sharper transition in the mass spectrum between the clusters with six and seven silicon atoms as silane is much more abundant. Another aspect is the influence of small amounts of water which are always present in processing silane plasmas. Mandich and Reents observed that the growth of ions is significantly enhanced and does not terminate for ions below 400 amu in mixtures of silane containing 7\% water.\textsuperscript{25} In this mixture, however, also some large ions containing oxygen atoms were observed. In the expanding plasma such an amount of water is surely not present and the size and magnitude of cationic cluster did not change with the presence of silanol ions. The influence of water is therefore probably limited though it cannot totally be excluded.

Another aspect is the presence of higher kinetic energies and excited species in plasmas. The rates presented by Mandich and Reents apply to ground state reactions with silane at room temperature. Additional energy can possibly increase the ion-molecule reaction rates and overrule the bottle necks observed as also suggested by Kushner.\textsuperscript{24} It would for instance explain the observation of Weakliem\textit{et al.} who found that at higher gas temperatures larger cluster ions where formed.\textsuperscript{13} That additional energy can have an effect has already been concluded from the compactness and hydrogen poverty of the cationic silicon clusters in the expanding plasma. Mandich and Reents observed even intriguing effects in the reaction of hot side products, created by nonthermal energy species, with silane. Yet they expect the enhanced elimination of molecular hydrogen due to additional energy to lead finally to highly stable compact structures at limited size which are chemically unreactive with silane.\textsuperscript{5} They do not expect large differences from the presence of vibrationally excited silane as concluded from an analogy with the reactions with disilane.\textsuperscript{25} Nevertheless, a considerable influence of the presence of higher kinetic and internal energies cannot be excluded to our opinion. For example, in their case the sequential reactions terminate either at bare silicon clusters or at ions with a large number or hydrogen atoms created by association reactions with silane.\textsuperscript{25} These reactions have a strong negative temperature dependence\textsuperscript{4} and will therefore not occur in the expanding plasma. The reaction rates of the hydrogen poor clusters with silane are however not thoroughly investigated. It can therefore be concluded that the straightforward application of the reaction rates determined by techniques like ion-cyclotron resonance mass spectrometry in silane plasmas can be rather troublesome and can lead to erroneous results when any of the above mentioned aspects are neglected.

Finally, from the ion flux in Fig. 3 the contribution of the cationic clusters to the silicon growth flux has been calculated. This, as well as the total growth flux, is shown in Fig. 5. The total growth flux is determined from the growth rate and the silicon density in the film. The latter is derived from a relation between refractive index of the films and the silicon density.\textsuperscript{26} The contribution of the cationic clusters to
this growth flux is obtained by multiplying the ion flux with the average number of silicon atoms in the clusters as estimated from the mass spectra. As it is assumed that the clusters have unity sticking probability this is the maximum contribution cationic clusters can have to the growth flux.

Figure 5 shows that the maximum contribution of the ions is rather independent of the silane flow. Under the condition where device quality $\alpha$-Si:H is deposited, i.e., with 10 scs silane, the maximum contribution is about 6%. This relatively small contribution is not in contrast with the dominant contribution of SiH$_3$ to deposition. Nevertheless the cationic clusters can have a significant impact on the film quality due to the small self-bias ($\sim$2 V). The absence of this energy flux can be one of the reasons that a higher substrate temperature is necessary to obtain solar grade material with the expanding argon–hydrogen–silane plasma. Another point of interest is the dissociatively recombined ions. When a significant fraction of cationic clusters recombines with electrons possibly large polysilane radicals are created which can have a similar impact on film growth as cluster ions. These aspects considered have also some implications for other remote plasmas. Depending on silane density and distance between plasma source and substrate holder the creation of relatively large silicon cluster ions cannot be neglected, not even when the ion or metastable fluence from the plasma source is relatively low.

IV. CONCLUSION

It is shown that cationic clusters are created in silane plasmas by sequential ion-molecule reactions with silane. In a plasma these reactions proceed at near-collisional rates rather independent of the number of silicon and hydrogen atoms present in the ions and even clusters larger than expected from ion-cyclotron resonance mass spectrometry studies can be created. The hydrogen content of the clusters is probably related to the kinetic energy of the species involved in the reactions. The cationic clusters can also have a significant impact at the film quality despite the fact that their maximum contribution to the growth flux is in the order of percent.

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