Numerical study of the effect of gas temperature on the time for onset of particle nucleation in argon–silane low-pressure plasmas

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Received 25 February 2003
Published 28 May 2003
Online at stacks.iop.org/JPhysD/36/1399

Abstract

Particle nucleation in silane plasmas has attracted interest for the past decade, both due to the basic problems of plasma chemistry involved and the importance of silane plasmas for many applications. A better understanding of particle nucleation may facilitate the avoidance of undesirable particle contamination as well as enable the controlled production of nanoparticles for novel applications. While understanding of particle nucleation has significantly advanced over the past years, a number of questions have not been resolved. Among these is the delay of particle nucleation with an increasing gas temperature, which has been observed in experiments in argon–silane plasmas. We have developed a quasi-one-dimensional model to simulate particle nucleation and growth in silane containing plasmas. In this paper we present a comparative study of the various effects that have been proposed as explanations for the nucleation delay. Our results suggest that the temperature dependence of the Brownian diffusion coefficient is the most important effect, as diffusion affects both the loss rate and growth rate of particles.

1. Introduction

Particle nucleation in processing plasmas has numerous aspects. The detrimental aspect of particle formation in processing plasmas that can cause ‘killer defects’ in the manufacture of semiconductor devices has been studied for years [1–7]. More recently, the potential for using plasmas as sources for nanoparticles with various novel properties has been pointed out. For instance, nanoparticles are believed to play an important role in the improved electronic properties of nanostructured (‘polymorphous’) silicon thin films, which are believed to be formed by the deposition of 1–3 nm sized particles and even smaller clusters [8–12]. These films were recently shown to be more stable with respect to light-induced defect creation, which is the main cause for the decay in the efficiency of amorphous silicon solar cells. The ability of reactive plasmas to generate small 1–10 nm, crystalline nanoparticles at room temperature makes them an attractive source for quantum dots [13–15]. In fact, a number of electronic devices have been demonstrated based on silicon quantum dots synthesized by the use of low-pressure plasmas, such as nanocrystalline-Si based memory [16, 17], single electron transistors [18], and cold electron emitters [19]. The fact that low-pressure silane plasmas tend to form crystalline quantum dots (particles 1–10 nm in size) even at room temperature within a matter of hundreds of milliseconds [20] makes them competitive with other current methods that often require prolonged annealing of samples at temperatures up to 1100°C for times of the order of 1 h [21, 22].

For both the positive and the negative aspects of particle formation in plasmas, a better understanding of particle nucleation with the aim of being able to control this process is important. While significant progress in this direction has been made in recent years, there are still a number of unresolved questions. Among these is the observed delay of particle nucleation in argon–silane plasmas due to an increase in the gas temperature [20, 23–25], as shown in figure 1 reproduced from [23]. In this study, Boufendi et al used a method called laser
induced particle explosive evaporation (LIPEE). They used a high power UV laser ($\lambda = 308$ nm, pulse energy = 25 mJ) to evaporate the small crystallites formed in the plasma and measured the emitted radiation. The sharp rise in each curve is identified with the onset of nucleation, and is seen to be delayed significantly as the gas temperature increases. The authors argue that the observed LIPEE signal is proportional to the particle number density and the fourth power of the particle radius. (In contrast, Rayleigh scattering is proportional to the sixth power of the particle radius.) Obviously, this effect has the potential to be used to control particle formation. Various explanations for this effect have been proposed:

(a) Fridman $et$ $al$ [25] proposed the temperature dependence of the de-excitation of vibrationally excited SiH$_4$ as an essential mechanism that may delay nucleation. Their explanation is based on the assumption that the clustering pathway in silane plasmas involves chain reactions between anions and neutral SiH$_4$ [25–30], which are close to thermonutral [25, 27, 30]. Vibrationally excited SiH$_4$ with excitation energies of 0.113 and 0.271 eV relative to the ground state may help to accelerate the clustering mechanism. Fridman $et$ $al$ argue that an increase in the gas temperature will reduce the density of excited species through vibrational–rotational transitions described by a Landau–Teller expression. The decrease in the density of vibrationally excited species thus slows the clustering chain.

(b) The effect of gas temperature on electron attachment rates was proposed by Perrin $et$ $al$ [31, 32]. Electron attachment to silicon hydrides leads to the formation of anionic species ($e + $Si$_x$H$_y$$\rightarrow$ Si$_y$H$_{y-1} + H$). Some of these reactions may lead to attachment rather than dissociative attachment and may need a third body for stabilization of the anionic complex. In the absence of sufficiently fast stabilization, auto-detachment may prevail. Since the reaction rate for stabilization reactions depends on the number density of the surrounding gas, it will be inversely proportional to the gas temperature [31, 32]. Thus, the higher the gas temperature, the lower is the expected attachment rate, leading to slower formation of anions. Since anions are expected to propagate the clustering chain, a reduction in their concentration may slow the nucleation process [32].

(c) In a previous study, we investigated the effects caused by the reduced gas density with increasing temperature [33]. This could slow the nucleation mechanism at higher gas temperatures due to reduced precursor density.

However, numerical simulations [33] indicate that none of the above explanations can account for the strong effect of gas temperature seen in figure 1. In this paper, we study the role of diffusion and, in particular, that of the temperature dependence of the Brownian diffusion coefficient of particles and particle growth species. In a comparative study, we will compare the effect of temperature dependence of diffusion with that of the other above-mentioned effects.

The model used in our calculations is described in section 2, a brief description of the computational method and the procedure used to distinguish the effect of the temperature dependence of diffusion from the other effects is given in section 3, and a discussion of the results is presented in section 4.

2. Model

To study the formation and growth of particles in low-pressure silane plasmas we have developed a quasi-one-dimensional model that solves for gas-phase chemistry and particle growth. Using this model, simulations are performed to determine important reaction pathways and processes that affect particle nucleation and growth. These simulations involve an argon–silane mixture in the volume ratio 96.2 : 3.8. The conditions are identical to those found in the experiments reported by Bouchoule and Boufendi [23, 34, 35] and used in figure 1.

The chemistry model used in this study is based on the gas-phase chemistry model for silicon hydride clustering in low-pressure silane plasmas that we previously developed [27]. The present model uses additional reactions involving argon and vibrationally excited silane so that it applies to argon–silane plasmas used in [23, 34, 35]. This chemistry module is coupled to a sectional aerosol dynamics module similar to the one that was developed earlier [36]. These two modules solve for the evolution of species concentrations and particle growth in the plasma. Since the presence of various species and particles influences plasma properties, both of the above modules are coupled to a global zero-dimensional plasma model. The plasma module accounts for the evolution of ion and electron density as well as electron temperature.

The main gas-phase reactions in the chemistry module are given in [27], and the additional reactions used in these simulations are given in table 1. The additional reactions involve electronic excitation and ionization of argon atoms (reactions 1–3), neutralization of anions with Ar$^+$ (reaction 4), dissociation of silicon hydrides by collisions with excited argon (reactions 5–9), formation of vibrationally excited SiH$_4$ (reactions 10–11), the respective de-excitation reactions (reactions 12–17), elimination of vibrationally excited SiH$_4$ (reactions 18–19), and reactions between vibrationally excited SiH$_4$ and anionic and neutral silicon hydrides that propagate the clustering chain (reactions 20–24). For the de-excitation reactions, the rate constants in the table reflect the values at 293 K (20°C). The corresponding values at 500 K are given at the end of the table. To account for the temperature dependence...
of this process, proposed as an important mechanism for nucleation delay by Fridman et al we assume a similar relationship as the one given by Perrin et al [31] for the probability $P$ of de-excitation of vibrationally excited SiH$_4$ due to collisions with ground state SiH$_4$ molecules,

$$P = 0.495 \times \exp \left( -\frac{38.3}{T^{1/3}} \right).$$  \hspace{1cm} (1)

Here $T$ is given in kelvin. Perrin et al [31] also assume a similar dependence for the de-excitation rate of vibrationally excited SiH$_4$ in collisions with ground state H$_2$, Ar and He. The authors have tabulated these values for gas temperatures of 295 and 500 K. For the case of collisions with SiH$_4$, a linear interpolation of the tabulated values approximates the above formula well in the temperature range 295–500 K and we have used the same approximation for collisions with H$_2$, Ar and He. Reaction rate constants for attachment reactions to silicon hydrides are given in [27], though they are scaled inversely with gas temperature for these simulations to account for the temperature dependence of electron attachment. The rate constant $k_{att}(T)$ at temperature $T$ ($T$ in degrees kelvin) is then given simply as follows:

$$k_{att}(T) = k_{att}(300\text{ K}) \times \frac{300}{T}. \hspace{1cm} (2)$$

Silicon hydride species with up to 13 silicon atoms are considered in the model, and, as in our previous work [27], we assume that species with more than 10 silicon atoms are

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**Table 1.** Additional reactions added to mechanism in [27].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$</th>
<th>$\beta$</th>
<th>$E_a$ (cal mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron reactions with Ar and Ar$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Ar + e $\rightarrow$ Ar$^+$ + e</td>
<td>$7.04 \times 10^{15}$</td>
<td>0.0</td>
<td>275 360</td>
<td>[47]</td>
</tr>
<tr>
<td>2. Ar + e $\rightarrow$ Ar$^+$ + 2e</td>
<td>$4.25 \times 10^{13}$</td>
<td>0.6</td>
<td>371 860</td>
<td>[47]</td>
</tr>
<tr>
<td>3. Ar$^+$ + e $\rightarrow$ Ar + 2e</td>
<td>$5.0 \times 10^{16}$</td>
<td>0.1</td>
<td>120 280</td>
<td>[47]</td>
</tr>
<tr>
<td>Neutralization due to Ar$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. SiH$_4$ + Ar$^+$ $\rightarrow$ SiH$_4$ + Ar</td>
<td>$8.64 \times 10^{13}$</td>
<td>−0.5</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>Dissociation due to Ar$^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Ar$^+$ + SiH$_4$ $\rightarrow$ SiH$_4$ + 2H + Ar</td>
<td>$2.77 \times 10^{14}$</td>
<td>0.0</td>
<td>0</td>
<td>[48–50]</td>
</tr>
<tr>
<td>6. Ar$^+$ + SiH$_4$ $\rightarrow$ SiH$_4$ + H + H$_2$ + Ar</td>
<td>$1.44 \times 10^{13}$</td>
<td>0.0</td>
<td>0</td>
<td>[48–50]</td>
</tr>
<tr>
<td>7. Ar$^+$ + SiH$_3$ $\rightarrow$ SiH$_4$ + H + Ar</td>
<td>$6.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0</td>
<td>[48–50]</td>
</tr>
<tr>
<td>8. Ar$^+$ + SiH$_2$ $\rightarrow$ SiH$_4$ + H + Ar</td>
<td>$6.0 \times 10^{13}$</td>
<td>0.0</td>
<td>0</td>
<td>[48–50]</td>
</tr>
<tr>
<td>9. Ar$^+$ + H$_2$ $\rightarrow$ 2H + Ar</td>
<td>$4.2 \times 10^{13}$</td>
<td>0.0</td>
<td>0</td>
<td>[48–50]</td>
</tr>
<tr>
<td>Formation of excited SiH$_4^*$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. SiH$_4$ + e $\rightarrow$ SiH$_4^*$ (v=1, v=3) + e</td>
<td>$8.32 \times 10^{19}$</td>
<td>−0.7</td>
<td>97 200</td>
<td>[47]</td>
</tr>
<tr>
<td>11. SiH$_4$ + e $\rightarrow$ SiH$_4^*$ (v=2, v=4) + e</td>
<td>$2.72 \times 10^{21}$</td>
<td>−1.0</td>
<td>43 560</td>
<td>[47]</td>
</tr>
<tr>
<td>De-excitation of excited SiH$_4^*$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. SiH$_4^*$ (v=1, v=3) $\rightarrow$ 2SiH$_2$</td>
<td>$3.73 \times 10^{11}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>13. SiH$_4^*$ (v=1, v=3) $\rightarrow$ H$_2$ + SiH$_4$ + H$_2$</td>
<td>$1.26 \times 10^{12}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>14. SiH$_4^*$ (v=1, v=3) $\rightarrow$ Ar + SiH$_4$ + H$_2$</td>
<td>$3.49 \times 10^{10}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>15. SiH$_4^*$ (v=2, v=4) $\rightarrow$ 2SiH$_2$</td>
<td>$3.65 \times 10^{11}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>16. SiH$_4^*$ (v=2, v=4) $\rightarrow$ H$_2$ + SiH$_4$ + H$_2$</td>
<td>$1.24 \times 10^{12}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>17. SiH$_4^*$ (v=2, v=4) $\rightarrow$ Ar + SiH$_4$ + H$_2$</td>
<td>$3.42 \times 10^{10}$</td>
<td>0.0</td>
<td>0</td>
<td>[31]</td>
</tr>
<tr>
<td>Elimination of excited SiH$_4^*$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. SiH$_4^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>$7.11 \times 10^{19}$</td>
<td>0.0</td>
<td>$\Delta H_{ad}$</td>
<td>[27,51]</td>
</tr>
<tr>
<td>19. SiH$_4^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>$1.58 \times 10^{17}$</td>
<td>0.0</td>
<td>$\Delta H_{ad}$</td>
<td>[27,51]</td>
</tr>
<tr>
<td>Negative silylene with excited silane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20. Si$_2$H$_2^*$ (v=1, v=3) + SiH$_4$</td>
<td>Langevin $\times 0.1$</td>
<td>Calc.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21. Si$_2$H$_2^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>Langevin $\times 0.1$</td>
<td>Calc.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irreversible particle formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22. Si$_2$H$_2^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>1.6 $\times 10^{13}$</td>
<td>0.5</td>
<td>0</td>
<td>[51]</td>
</tr>
<tr>
<td>23. Si$_2$H$_2^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>Langevin $\times 0.1$</td>
<td>Calc.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24. Si$_2$H$_2^*$ (v=1, v=3) $\rightarrow$ Si$_2$H$_2$ + SiH$_4$</td>
<td>Langevin $\times 0.1$</td>
<td>Calc.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Forward rate constants are expressed in the form $k_f = A \exp(-E_a/RT)$. The units of $k_f$ are moles$^n$ cm$^m$ s$^{-1}$, where $n$ and $m$ are integer constants that depend on the order of the reaction. $T$ is expressed in kelvin.

$^a$ The values for reactions 12–17 are at a temperature of 293 K. The values of $A$ at a temperature of 500 K are, respectively, $1.02 \times 10^{12}, 3.6 \times 10^{12}, 9.6 \times 10^{13}, 8.36 \times 10^{11}, 3.2 \times 10^{12}$ and $8.5 \times 10^{11}$, while the values for the temperatures in between are linearly interpolated. De-excitation of SiH$_4^*$ (v=3) is assumed to have the same rate constant as the one of SiH$_4^*$ (v=2).

$^b$ These are the reactions similar to those found in the table of reaction in [27] except that the pre-exponential factor has been multiplied by a factor $\exp(E_{att}/kT)$.

$^c$ The species with suffix ‘B’ in reactions 18, 19, 20, 22 and 23 refer to silicon hydrides with an Si=Si double bond.

$^d$ Reactions 18 and 19 are written as silane elimination reactions. Since the reverse reaction, i.e. the silane insertion reactions are assumed to be barrierless, it is assumed that the elimination reactions have an activation energy equal to the enthalpy of the reaction $\Delta H_{ad}$. See [27] for more details. Since these neutral–neutral reactions are of overall minor importance for the clustering, we have evaluated $\Delta H_{ad}$ at a fixed temperature of 500 K.
formed irreversibly. The production rate of species with more than 10 silicon atoms then forms the source term (nucleation rate) for the smallest size section (see below) of the sectional growth model for particles.

Our mechanism considers a total of 350 gas-phase species including anions, neutrals (ground state and excited), positive ions and electrons. We solve the following balance equation for the gas-phase species ($X_k$ represents the molar concentration of species $k$),

$$\frac{dX_k}{dt} = \frac{X^G_k}{\Lambda^2} + \frac{D_{jk}}{\Lambda^2} X_j - L_{kp} + G_{kj},$$

(3)

where $X^G_k$ is the gain/loss term due to gas-phase reactions, and $X^L_{kl}$ is the gain/loss due to surface reactions. The third term on the right-hand side is the loss due to diffusion, the fourth term accounts for loss due to gas pumping and the fifth term accounts for gain due to gas inflow. The pumping and diffusion loss terms are applied only to the neutral species, whereas the negative species are assumed to be trapped by the ambipolar potential of the plasma. The gain term due to gas inflow applies only to silane (SiH$_4$) and argon. The positive ions are treated by different equations in the plasma module described below.

The diffusion coefficients are calculated using the Chapman–Enskog theory [37] for binary gas systems. We assume that Ar and SiH$_4$ are the most abundant gases in the system at the beginning (i.e. time $t = 0$). Thus, diffusion coefficients are calculated for all other species diffusing in a mixture of Ar and SiH$_4$. However, if the concentration of the predominant species (Ar) changes by more than 10% during the simulations we recalculate the diffusion coefficients. The binary diffusion coefficient for two species $j$ and $k$ is expressed as follows [37],

$$D_{jk} = \frac{3}{16} \left( \frac{2 \pi k_B T}{M_j M_k} \right)^{1/2} \left( \frac{1}{n \pi \sigma_{jk}^2 \Omega_D} \right),$$

(4)

where $D_{jk}$ is given in cm$^2$ s$^{-1}$, $M_j$ and $M_k$ are the molecular weights (in amu) of the two species, $n$ is the total number density of molecules in the mixture (cm$^{-3}$), $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. $\Omega_D$ is the collision integral for diffusion, and is calculated based on the temperature $T$ and the Lennard–Jones energy of the two species (see [37]). The term $\sigma_{jk}$ gives the equivalent characteristic Lennard–Jones length. It should be noted that at constant pressure $n \propto 1/T$ and hence $D_{jk} \propto T^{3/2}$.

The characteristic diffusion length $\Lambda$ (see equation (3)) is calculated for each species separately based on the assumed sticking coefficient for the species. The sticking coefficients are assumed to equal 0.26 for all the silyl species (i.e. species with one unpaired electron) and unity for the silylene species (i.e. species with two unpaired electrons) [31]. The double bonded silenes and the fully saturated silanes have a very small sticking coefficient [38] and we have assumed these coefficients to equal 10$^{-4}$.

The particle growth model is based on a sectional scheme [39, 40] in which the whole particle volume range is divided into a certain number of sections that are spaced logarithmically, i.e. the upper particle volume limit for each section is a constant factor times the lower limit. This sectional scheme facilitates the simulation of an otherwise unwieldy range in the particle volume. In this simulation, we have divided a volume range spanning six orders of magnitude into 180 sections using a logarithmic factor of 1.08. The model spans a particle diameter range from approximately 0.7 to 70 nm. The initial sections are considerably smaller than the latter ones which suits our purpose well since a greater resolution is provided for smaller particle sizes. For each section we can define an average particle radius, surface area and volume. In each section, an aerosol property $Q$ is chosen that is conserved. Based on the literature [39, 40] we have chosen this quantity to be the total volume in each section. We can now write a conservation equation for each of the sections,

$$\frac{dQ_k}{dt} = G_{nucl} + G_{coag} - L_{coag} + G_{surf} - L_{surf} - L_{\text{diff}},$$

(5)

where $Q_k$ is the total volume in section $k$. $G_{nucl}$ is the gain in $Q_k$ due to nucleation of new particles. This term applies only to the first section, where it represents the nucleation rate given by the chemistry module. $G_{coag}$ is the gain in $Q_k$ due to smaller particles coagulating and entering section $k$ (it also includes gain in $Q_k$ due to a smaller particle coagulating with a particle in section $k$ leading to a larger particle that remains in section $k$). $L_{coag}$ is the loss in $Q_k$ due to particles in section $k$ coagulating with particles in all other sections. The coagulation coefficients between any two sections are calculated by integrating the coagulation coefficient between particle sizes over the volume range of both the interacting sections [36, 39, 40]. The coagulation coefficients are also modified depending on the charge distribution for each particle size section [36].

In equation (5), $G_{surf}$ and $L_{surf}$ are, respectively, the gain and loss of $Q_k$ in section $k$ due to surface growth. $G_{surf}$ consists of two gain terms, viz, the gain in $Q_k$ due to surface growth of particles in section $k$ that remain in the same section, and the gain in $Q_k$ due to particles at the higher end of section $k$ arriving in section $k$. The loss $L_{surf}$ is due to particles at the higher end of section $k$ growing into the next section $k + 1$. The surface growth coefficients that determine the flow of particles from one section to the next are calculated using a number and volume conserving scheme described in [41]. Thus, the gain due to intra-sectional growth $B_k Q_k$ is described by the coefficient $B_k$,

$$B_k = \nu_S N_{de} \left[ \frac{3}{2} \left( \frac{2 \pi k_B T}{M_j M_k} \right)^{3/2} \left( \frac{V_{u,k}^{2/3} - V_{l,k}^{2/3}}{\ln(V_{u,k}/V_{l,k})} \right) \right],$$

(6)

where $N_{de}$ is the deposition rate of Si atoms per unit area calculated by the chemistry module and $\nu_S$ is the volume occupied by a bulk silicon atom. The remaining term in the brackets is a factor that when multiplied by $Q_k$ gives the surface area present in section $k$, and is calculated using the upper ($V_{u,k}$) and lower ($V_{l,k}$) volume limits of the section $k$. The sectional loss $L_{surf} = C_k Q_k$ is described by the loss coefficient $C_k$, as follows,

$$C_k = \frac{B_k}{V_k^{l+1} - V_k^l},$$

(7)

where $V_k$ is the average volume in section $k$.

It must be mentioned that this scheme is excellent for treating only coagulation but is prone to numerical diffusion
Apart from the balance equations for the positive ions, we also solve a power balance equation that states that the total input power $P_{\text{input}}$ is equal to the power lost in various plasma processes,

$$P_{\text{input}} = P_{\text{exc}} + P_{\text{ions}} + P_{\text{diss}} + P_{\text{mmtm}} + P_{\text{sheath}} + P_{\text{part}}.$$  \hspace{1cm} (9)

where $P_{\text{exc}}$, $P_{\text{ions}}$, $P_{\text{diss}}$ and $P_{\text{mmtm}}$ are power lost to excitation (vibrational and electronic), ionization, dissociation and momentum transfer collisions, respectively. $P_{\text{sheath}}$ accounts for the power lost due to ion acceleration across the electrode sheath. In capacitive plasmas, the ions see a time averaged voltage across each electrode sheath in the range of a couple of hundred volts. The energy gained by ion acceleration across these sheaths is lost to the electrodes and represents a significant energy loss term in capacitive plasmas. Similarly, if particles are negatively charged, the ions see an accelerating potential towards the particle and we represent the energy lost in this fashion as $P_{\text{part}}$. However, since the potentials are relatively small compared to those across the electrode sheaths, this term is not significant.

Finally, we invoke the plasma quasi-neutrality condition,

$$\sum_k n_k^+ = \sum_j n_j^- + n_e + \sum_l \left( \frac{q_l}{e} \right) n_{\text{part},l}. \hspace{1cm} (10)$$

where $n_k^+$ is the density of the $k$th cation, $n_j^-$ the density of the $j$th anion, $n_e$ the electron density, $q_l$ in the last term on the right-hand side is the average charge of the particles in section $l$ with concentration $n_{\text{part},l}$, and $e$ is the elementary charge.

This set of plasma equations is solved self-consistently along with the charge distribution equations for the particles in each section. Solving the above set of equations gives the charge distributions of the particles, the positive ion densities and the electron density as well as the electron temperature. The charge distributions are then used to modify the coagulation coefficients between particles and the species densities are coupled back into the gas-phase chemistry code.

3. Computational method

To simulate the conditions used by Bouchoule and Boufendi [23, 24, 34, 35], we consider an Ar–SiH$_4$ plasma with an initial gas composition of 96.2 : 3.8 at a pressure of 117 mTorr (15.6 Pa). Boufendi et al [24] used gas temperatures of 20°C, 50°C, 80°C, 120°C and 150°C. We study gas temperatures of 20°C, 80°C and 120°C at a power input into the plasma of 10 W. (The power mentioned in that study may not necessarily reflect the actual amount of power absorbed in the plasma.) We use inflows of 30 sccm of Ar and 1.2 sccm of SiH$_4$. In our quasi-one-dimensional model we assume a perfectly stirred reactor, i.e. the inflow is assumed to be distributed uniformly over the reactor volume, which is assumed to be bounded by two electrodes with diameter 13 cm and a separation of 3 cm. Starting with no particles or anions at $t = 0$, we calculate the positive ion densities, the electron density and the electron temperature using the plasma equations mentioned above. We then run the gas-phase chemistry code. This code solves equation (3) for all species using a modified
version of SENKIN [44]. The time integration of equation (5) is carried out in between the time steps for the gas-phase chemistry equation. The production rate of species with more than 10 silicon atoms is passed from the chemistry code as the nucleation rate to the smallest section of the aerosol code. The total surface area of the particles at any time step is passed to the chemistry code for solving the loss in gas species due to surface chemistry and for determining the rate of surface growth, which in turn is coupled back into the aerosol code for determining the particle size evolution due to surface growth. The plasma equations are solved whenever significant changes in the plasma conditions are observed (defined as a 0.5% change in particle or anion concentrations or an error of 0.1% in any of the plasma balance equations). The time integration is carried out up to $t = 10$ s for all calculations and up to $t = 100$ s for conditions exhibiting delayed particle formation.

In order to isolate the effect of the temperature dependence of the Brownian diffusion coefficient, we performed two sets of calculations. In the first set, all processes, including diffusion and the other reactions proposed as causes for the nucleation delay (see section 1) were evaluated at the given temperatures. We refer to these simulations as ‘complete’ calculations. In the second set, all reactions were evaluated at the given temperatures, with the exception that the diffusion coefficients were computed assuming a fixed temperature of 20˚C. The latter calculations are referred to as ‘fixed-D’ calculations.

Figure 2. Particle size distribution functions for ‘complete’ calculations at $t = 10$ ms, 100 ms, 1 s, 3 s and 9 s or 10 s. (a) $T_g = 20$˚C, (b) $T_g = 80$˚C and (c) $T_g = 120$˚C. Plots in (b) and (c) show the distribution function at 10 s rather than at 9 s as shown in (a). This is due to the adaptive time step algorithm used by our solver.

4. Results and discussion

The influence of the gas temperature on the particle size distributions in the ‘complete’ calculations is shown in figure 2 for the three different temperatures of 20˚C, 80˚C and 120˚C. Each plot shows the particle size distribution function at 10 ms, 100 ms, 1 s, 3 s and 9 s or 10 s. Obviously, the predicted size distributions are significantly different at these three temperatures. At any given time, significantly fewer particles are observed at higher gas temperatures.

In order to determine the contribution of temperature-dependent diffusion to this reduction in particle concentration we performed ‘fixed-D’ simulations as mentioned above. The results are plotted in figure 3. Figure 3(a) is just a reproduction of the ‘complete’ case at 20˚C since there is no difference in the ‘complete’ and ‘fixed-D’ cases at 20˚C. The ‘fixed-D’ cases for 80˚C and 120˚C are plotted in figures 3(b) and (c), respectively. The size distributions for fixed diffusion coefficients are obviously quite different from the ‘complete’ calculations in figures 2(b) and (c). In fact, only a very small reduction of the particle density with increasing gas temperature is observed in comparing figures 3(a)–(c). It should be noted again that these ‘fixed-D’ calculations otherwise contain the full set of mechanisms that were proposed previously as explanations for the nucleation delay (see section 1). This result suggests that the temperature dependence of the Brownian diffusion coefficient (equation (4)) is the main
mechanism leading to a reduced particle concentration with increasing gas temperature.

In order to study if the reduction in particle concentration seen in the ‘complete’ calculations in figure 2 correlates to the LIPEE studies shown in figure 1 we compute the fourth moment of the particle size distribution

\[ M_4 = \sum_k (N_k R_k^4), \]

where \( N_k \) is the concentration and \( R_k \) the average radius of particles in section \( k \). This fourth moment, which is proportional to the experimental LIPEE signal, is plotted in figure 4 for the three ‘complete’ calculations (full lines) and the two ‘fixed-D’ calculations. Obviously, the simulated LIPEE signal for the ‘complete’ calculations shows a similar delay with increasing temperature as observed in the experiments (figure 1) by a factor of about 50 between 20°C and 120°C. The ‘fixed-D’ calculations show much smaller delay inconsistent with the measurements. These results strongly suggest that the temperature dependence of the diffusion coefficients is indeed the main mechanism for the observed delay of nucleation.

While the qualitative agreement between experiments and simulations is excellent, the calculated LIPEE signal is delayed by a factor of \( \sim 10–20 \) compared to the measurements. However, given the various assumptions and simplifications used in the model, a perfect quantitative agreement can hardly be expected.

To understand the details of the influence of the temperature dependence of the diffusion coefficients, it is useful to study its influence on the growth and loss rates of particles. Figure 5 shows the fraction of neutral, positively and negatively charged particles. (The peaks in the plots at 10 ms are an artefact of our sectional model that do not affect the results of the calculations.) Particles of less than 1 nm
in size have a significant neutral fraction (≈30%). These small particles can hold only one or two negative charges and can easily be neutralized or even positively charged. The neutral and positive particles can escape from the plasma by diffusion or drift in the ambipolar field, respectively. Figure 5 suggests that if the particle size reaches between 2 and 3 nm, the probability of it being neutral or positive is drastically reduced (see especially figure 5(c)). In addition to the dominance of negatively charged particles at larger sizes, the Brownian diffusion coefficient also decreases as particle size increases. Hence, small particles that may be positive or neutral have a significantly higher loss rate than large particles. Our simulations suggest that if particles reach a ‘safe size’ of about 2–3 nm, they will with large probability remain confined in the plasma due to their mostly negative charge. Such a critical ‘safe size’ was also predicted by Fridman et al [25]. Choi and Kushner [3] also discuss a critical cluster size at which particle growth outpaces loss due to diffusion.

As long as particles are smaller than the ‘safe size’ they are subject to diffusion. However, the time that particles require to grow to the safe size depends critically on the particle growth rate. The surface growth rate depends significantly on the concentration of surface growth species and to a lesser degree on the temperature dependence of the molecular velocity of these species (∝T^{1/2}). Figure 6 shows the concentrations of SiH and SiH₃—the main surface growth species in our model—for the different gas temperatures. (SiH₂ has a low density in our simulations due to its heavy consumption in insertion reactions leading to Si₂H₆ and Si₃H₈ and is thus not an important surface growth radical.) In our quasi-one-dimensional model, these concentrations refer to those in the centre of the reactor. Obviously, the concentrations decrease with increasing temperature. This decrease is mainly due to increased diffusion losses with a diffusion coefficient ∝T^{3/2} at constant pressure (equation (4)). The corresponding surface growth rates for the three temperatures are plotted in figure 7. The full lines for the ‘complete’ calculations show a significant drop of the growth rate as temperature increases. The ‘fixed-D’ calculations show a much smaller temperature dependence since the growth species concentrations remain higher. It should be noted that during the entire length of our simulation, (i.e. which includes the time to grow to the ‘safe size’), surface growth is in fact the main growth mechanism as shown in figure 8 for 20°C. In this sense, the discussion here refers to the nucleation phase that precedes the rapid particle growth by coagulation. Coagulation is even less important at higher temperatures due to the fact that its rate scales with the square of the particle density, which is lower at higher gas temperature.

The significant effect of diffusion can now be understood, at least qualitatively, by the following thought experiment: consider the imaginary ‘tube reactor’ in figure 9. The ‘length’ of the tube reactor actually represents the particle size. Particles enter the tube with an initial size d₀ and concentration n₀. The exit of the tube represents the ‘safe size’ at which particles are almost completely negatively charged and confined in the reactor. While being in the tube and
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Figure 6. Temporal evolution of SiH and SiH$_3$ concentration at 20°C (—), 80°C (---) and 120°C (—). (In our quasi-one-dimensional model, these concentrations refer to those in the centre of the reactor.)

Figure 7. Surface growth rate predicted by our model at 20°C, 80°C and 120°C. The solid lines are for ‘complete’ calculations the dotted lines for ‘fixed-D’ cases.

Figure 8. Growth rates through surface reactions and coagulation for a particle with the ‘most probable size’, i.e. at the maximum of the large particle peak of the particle size distributions. Note that this size is changing throughout the growth process as the large particle peak moves towards larger sizes. The plot is for 20°C.

As discussed above, an increasing gas temperature lowers the growth rate $G$ and hence causes a longer residence time in the tube. Simultaneously, it leads to increased diffusion losses due to the $T^{3/2}$ scaling of the diffusion coefficients (at constant pressure). Since diffusion loss leads to an exponentially decreasing density, we expect the density of particles that reach the ‘safe size’ $n_{\text{safe}}$ to scale as

$$
\frac{n_{\text{safe}}}{n_0} \propto \exp \left( \frac{- (d_{\text{safe}} - d_0)}{G \tau_D} \right),
$$

(12)

where $(d_{\text{safe}} - d_0)/G$ is the residence time of particles in the tube and $\tau_D$ is an effective diffusion time. (The actual determination of $\tau_D$ would require a complicated average over the diffusion times as a function of the particle size and the charge distributions in all sections up to $d_{\text{safe}}$.) The proposed relation (equation (12)) at least qualitatively explains the strongly nonlinear decrease of the particle density with increasing gas temperature observed in the ‘complete’ calculations in figure 2 and the related delay in the fourth moment signal, figure 4.

5. Summary and conclusions

We have used a quasi-one-dimensional model that couples plasma chemistry and particle growth mechanisms to simulate particle generation in an argon–silane plasma with conditions similar to that found in experiments conducted by Boufendi et al [24]. We investigated the role of the gas temperature in the so far unresolved experimental observation [24] that particle nucleation is delayed with an increase in the temperature. We
performed a comparative study of all explanations proposed to date: the temperature dependence of the de-excitation of vibrationally excited species, the temperature dependence of the electron attachment rate, gas density effects, and the temperature dependence of the Brownian diffusion coefficient proposed in this study. Only calculations that included the correct temperature dependence of the Brownian diffusion reproduced, at least qualitatively, the experimentally observed nucleation delay. Hence, we conclude from our study that the temperature dependence of the diffusion coefficient is a strong candidate to explain the observed delay of nucleation. We also showed that the delay is a combined effect of increasing diffusion losses and reduced particle growth rate when the gas temperature increases.

Along these lines, we may speculate that other processes that affect the diffusion coefficients of particles may cause similar effects. For instance, using a lighter background gas such as He or H₂ would increase the diffusion coefficients, which are inversely proportional to the square root of the background gas mass, and should thus delay or prevent nucleation. Similarly, a larger pressure would reduce diffusion and lead to faster nucleation. These conclusions are consistent with reported experimental observations [45,46], though other effects may contribute as well. The effect of the background gas requires further studies.

Acknowledgments

This work was supported by NSF under grant ECS 9731568 and GOALI grant CTS-9909563 and by the University of Minnesota Supercomputing Institute.

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