Hybrid Simulation of Duty Cycle Influences on Pulse Modulated RF SiH\textsubscript{4}/Ar Discharge\textsuperscript{*}

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Abstract A one-dimensional fluid/Monte-Carlo (MC) hybrid model is developed to describe capacitively coupled SiH\textsubscript{4}/Ar discharge, in which the lower electrode is applied by a RF source and pulse modulated by a square-wave, to investigate the modulation effects of the pulse duty cycle on the discharge mechanism. An electron Monte Carlo simulation is used to calculate the electron energy distribution as a function of position and time phase. Rate coefficients in chemical reactions can then be obtained and transferred to the fluid model for the calculation of electron temperature and densities of different species, such as electrons, ions, and radicals. The simulation results show that, the electron energy distribution \(f(\varepsilon)\) is modulated evidently within a pulse cycle, with its tail extending to higher energies during the power-on period, while shrinking back promptly in the afterglow period. Thus, the rate coefficients could be controlled during the discharge, resulting in modulation of the species composition on the substrate compared with continuous excitation. Meanwhile, more negative ions, like SiH\textsubscript{3}\textsuperscript{−} and SiH\textsubscript{2}\textsuperscript{−}, may escape to the electrodes owing to the collapse of ambipolar electric fields, which is beneficial to films deposition. Pulse modulation is thus expected to provide additional methods to customize the plasma densities and components.

Keywords: hybrid model, EEDF, pulse modulation, SiH\textsubscript{4}/Ar mixture

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1 Introduction

Capacitively coupled plasmas (CCPs) are widely used in micro-electronic manufacture, mainly for etching and deposition of thin films, due to their advantages of high densities and large-area uniformity \cite{1-4}. In these material processings, densities and fluxes of species, which are the key plasma properties responsible for the processing qualities, are expected to be under control by inputs of plasma sources, such as source and bias power, gas pressure and temperature, gas flow rate, as well as source geometry. In recent years, electronegative plasmas are extensively adopted in the microelectronic industry. Owing to the more complicated plasma chemistry and physics, additional controlling parameters are required to optimize the plasma sources. Pulse modulation in reactive plasmas, in which the power is modulated by a square or other shape waves, has developed as promising techniques in micro-devices for more control variables, such as duty cycles, and pulsing frequencies. Advantages compared with continuous wave (CW) plasmas have been gradually realized, including improvement of etching or deposition rate, tailoring composition of chemical species on the substrate or in the plasma \cite{4-6}. Thus, deep understanding of temporal discharge mechanism in pulsed plasmas is required.

Pulsed CCPs, as popular reactors in plasma enhanced chemical vapor deposition (PECVD), have been investigated experimentally. Suyeon et al. \cite{7} used a pulsed PECVD in deposition of silicon nitride (SiN) films with bias power and duty ratio varied in the range of 30-90 W and 20-80% respectively, concluding that the ion flux rather than the ion energy itself, can play important roles in ion bombardment. Based on a neutral network model constructed to examine the relationships between the ion energy variables and the deposition rate, a relatively large deposition rate can be achieved by controlling the duty cycle and bias power \cite{8}. In a pulsed radio-frequency (RF) PECVD process with a N\textsubscript{2}/SiH\textsubscript{4} for a-SiN\textsubscript{x} films deposition, besides superior film quality, the chemical composition of the coatings can be tailored by adjusting the duty cycle \cite{9}. It is found that the optical properties, and microstructural characteristics of the coatings are also closely related with the duty cycles. Also for a-SiN\textsubscript{x} film deposition in a pulsed RF PECVD \cite{10}, the film densification and smoothening can be improved by pulse

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modulation compared with CW-RF conditions. They conclude that, though radical generation is restrained, the time of radicals extending to substrates is prolonged making the surface diffusion sufficient during RF off time. Mukherjee et al. [11] have studied the hydrogen dilution effect on the growth of a-Si:H films in a modified pulsed plasma discharge with hydrogen dilution ranging from 0\% to 80\%. It is shown that the deposition rate can attain a maximum value at a particular dilution.

Although pulsed plasmas are increasingly employed in PECVD for superior film quality, there is a lack of deep insight of the fundamental physics and chemistry in the plasma and on the substrate during deposition. It becomes desirable to have more numerical efforts on pulsed discharges with various reactive gases used in deposition. In this work, a fluid/MC hybrid model is used to investigate pulsed RF CCP in SiH$_4$/Ar mixture discharge mainly applied in silicon based films deposition. We first describe the hybrid model in detail in section 2. The results and discussions of pulsed CCP discharge with different duty cycles will be shown in section 3. Finally, in section 4 conclusions are given.

2 Theoretical model

In this work, a hybrid model coupled by fluid and Monte-Carlo (MC) models is used to investigate pulsed RF capacitively coupled discharge in silane mixture gas. As described in detail in Ref. [12], the fluid model includes continuity, momentum, energy equations for electrons, ions and neutrals, as well as Poisson’s equation, allowing self-consistent calculation of the electric field. Here, drift-diffusion approximation for flux balance is also adopted.

In order to clarify temporal discharge processes modulated by pulse variables, an electron MC model is adopted to define the electron energy distribution [13] Corresponding collisions between electron and neutrals are considered, including elastic, superelastic, ground state ionization, step-wise ionization, dissociative ionization, ground state excitation, vibrational excitation and dissociative attachment collisions. Averagely, 50000 pseudoparticles are adopted to represent bulk electrons. The collision type can be judged by the following expressions,

\[
r \leq p_{i,1}, (1\text{st collision})
\]
\[
p_{i,1} \leq r \leq p_{i,2}, (2\text{st collision})
\]
\[
p_{i,N_{\text{type}}} \leq r, (\text{Null collision})
\]

where \( r \) is the random number. The collision probability \( p_{i,j} \) of \( j \) type collision can be deduced as

\[
\nu_i = \sum_{j=1}^{N_{\text{type}}} \nu_{i,j}, \tag{2}
\]
\[
\nu_{i,j} = (2e\varepsilon_i/m_e)^{1/2}\sigma_{i,j}n_n, \tag{3}
\]
\[
p_{i,j} = (\sum_{j=1}^{N_{\text{type}}} \nu_{i,j})/\nu_m, \tag{4}
\]

where \( i = 1, 2, \ldots, N_e \), \( j = 1, 2, \ldots, N_{\text{type}} \) are the number of energy bins and collision types respectively. \( n_n \) refers to the densities of Ar, Ar*, SiH$_4$, Si$_2$H$_6$ or H$_2$. \( \nu_i \) represents the summing of all possible collision frequencies with electron energy at \( \varepsilon_i \), and \( \nu_m \) stands for the maximum value among \( \nu_i \). Besides, \( \nu_{i,j} \) and \( \sigma_{i,j} \) are the collision frequency and corresponding collision cross section between electron and neutrals with electron energy at \( \varepsilon_i \).

After the final type of collision, the energy and velocity of the electron are changed with the transformation formulas presented in Refs. [14,15]. The electron energy and location are traced for electron energy distribution calculation at the end of the MC procedure, as

\[
f(\varepsilon_i, z, t) = \frac{\Delta N_i(t)}{N\Delta\varepsilon}, \tag{5}
\]

where \( N \) is the total statistic particle number, and \( \Delta N_i(t) \) represents the particle quantity between electron energies \( \varepsilon_i \) and \( \varepsilon_i + \Delta\varepsilon \).

The rate coefficient as a function of position and time, can be derived as follows:

\[
k_j(z, t) = \int_{0}^{\infty} f(\varepsilon, z, t) \times \left( \frac{2e}{m_e} \right)^{1/2}\sigma_j(\varepsilon)d\varepsilon, \tag{6}
\]

where the corresponding cross section \( \sigma_j(\varepsilon) \) can be cited from the website [16]. Then, the spatial and temporal rate constants \( k_j(z, t) \) calculated by the MC model are transferred to the fluid model. Therefore, the creation or destruction terms in the continuity equations can be given from the rate coefficients, reflecting the pulse modulation. Finally, the fluid model is coupled with the MC method at the end of each 5 radio frequency cycles, and the spatio-temporal electric field is solved by Poisson’s equation and transferred to the MC model in turn.

3 Results and discussions

In this section, we consider a CCP reaction chamber with \( L = 3 \) cm distance between two electrodes. The upper electrode is grounded, while the lower electrode is applied by a RF source which is pulse modulated by a square-wave, in which the time dependent voltage can be formulated by

\[
v|_{x=0} = \begin{cases} 
   v_0 \sin(2\pi f_{RF}t), & 0 \leq t \leq \alpha\tau, \\
   0, & \alpha\tau \leq t \leq \tau,
\end{cases} \tag{7}
\]

with the voltage amplitude \( v_0 = 70 \) V, radio frequency \( f_{RF} = 13.56 \) MHz, pulse modulated frequency \( f_p = 30 \) kHz, pulse period \( \tau = 33.3 \) ms, and duty cycle \( \alpha = 0.25, 0.5, 0.75, 1 \). The gas SiH$_4$/Ar = 10/90 at 500 mTorr and 400 K is adopted in this calculation. Reactions and corresponding threshold energies in which the electrons are involved in the model are presented in Table 1. There are also 26 chemical reactions between ion-ion, ion-neutral, neutral-neutral reactions, considered in this model, which can be referred from Refs. [17-19]. Moreover, 10 kinds of neutral species (Ar,
Table 1. Electron involved chemical reactions of SiH$_4$/Ar discharge in the model

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Reaction type</th>
<th>Threshold (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + e$^-$ → Ar + e$^-$</td>
<td>Elastic collision</td>
<td>cal</td>
<td>[19]</td>
</tr>
<tr>
<td>Ar + e$^-$ → Ar$^+$ + 2e$^-$</td>
<td>Ground state ionization</td>
<td>15.6</td>
<td>[19]</td>
</tr>
<tr>
<td>Ar + e$^-$ → Ar$^*$ + e$^-$</td>
<td>Ground state excitation</td>
<td>11.56</td>
<td>[19]</td>
</tr>
<tr>
<td>Ar$^*$ + e$^-$ → Ar$^+$ + e$^-$</td>
<td>Step-wise ionization</td>
<td>4.14</td>
<td>[19]</td>
</tr>
<tr>
<td>Ar$^*$ + e$^-$ → Ar + e$^-$</td>
<td>Superaelastic collisions</td>
<td>−11.56</td>
<td>[19]</td>
</tr>
<tr>
<td>SiH$_4$ + e → SiH$_4$ + e</td>
<td>Elastic collision</td>
<td>cal</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_4$$^{(1-3)}$ + e$^-$</td>
<td>Vibrational excitation</td>
<td>0.11</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_4$$^{(2-4)}$ + e$^-$</td>
<td>Vibrational excitation</td>
<td>0.27</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_4^+$ + H + 2e$^-$</td>
<td>Dissociative ionization</td>
<td>11.8</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_4^+$ + H + 2e$^-$</td>
<td>Dissociative ionization</td>
<td>11.8</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_4^+$ + H + 2e$^-$</td>
<td>Dissociative ionization</td>
<td>11.7</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_4^+$ + H + 2e$^-$</td>
<td>Dissociative ionization</td>
<td>10.2</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_4^+$ + H + e$^-$</td>
<td>Dissociative</td>
<td>8.3</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_4^+$ + H + e$^-$</td>
<td>Dissociative</td>
<td>8.2</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_4^+$ + H + e$^-$</td>
<td>Dissociative</td>
<td>8.1</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_2$ + 2H + e$^-$</td>
<td>Dissociative</td>
<td>8.3</td>
<td>[17,18]</td>
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<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_2$ + 2H + e$^-$</td>
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<td>8.2</td>
<td>[17,18]</td>
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<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_2$ + 2H + e$^-$</td>
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<td>8.1</td>
<td>[17,18]</td>
</tr>
<tr>
<td>Si$_2$H$_6$ + e$^-$ → Si$_2$H$_5^+$ + 2H + 2e$^-$</td>
<td>Dissociative ionization</td>
<td>15.4</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_3$ + H + e$^-$</td>
<td>Dissociative attachment</td>
<td>5.7</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_3$ + H</td>
<td>Dissociative attachment</td>
<td>5.5</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_3$ + H</td>
<td>Dissociative attachment</td>
<td>5.6</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$ + e$^-$ → SiH$_2$ + 2H</td>
<td>Dissociative attachment</td>
<td>5.7</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{1-3}$) + e$^-$ → SiH$_2$ + 2H</td>
<td>Dissociative attachment</td>
<td>5.5</td>
<td>[17,18]</td>
</tr>
<tr>
<td>SiH$_4$($^{2-4}$) + e$^-$ → SiH$_2$ + 2H</td>
<td>Dissociative attachment</td>
<td>5.6</td>
<td>[17,18]</td>
</tr>
<tr>
<td>H$_2$ + e$^-$ → H$_2^+$ + 2e$^-$</td>
<td>Dissociative attachment</td>
<td>5.5</td>
<td>[17,18]</td>
</tr>
<tr>
<td>H$_2$ + e$^-$ → H$_2^+$ + H + e$^-$</td>
<td>Dissociative attachment</td>
<td>8.9</td>
<td>[17,18]</td>
</tr>
</tbody>
</table>

*cal: Calculated from corresponding cross section [16]*

Fig. 1 Time variation profiles of electron temperature (a) and electron density (b) at the centre of discharge, over two pulse periods for different duty cycles

Power-on period due to electric field acceleration and presentation of a dynamic distribution during power modulation. As we can observe, for each profile of $T_e$ with different duty cycles, a rise appears in the power-on period due to electric field acceleration and

Ar$^*$, SiH$_4$, SiH$_4^{(1-3)}$, SiH$_4^{(2-4)}$, Si$_2$H$_6$, SiH$_3$, SiH$_2$, H$_3$ and H), and 6 kinds of ions (Ar$^+$, SiH$_4^+$, SiH$_3^+$, SiH$_2^+$, Si$_2$H$_6^+$ and H$^+$), are considered, among which SiH$_4^{(1-3)}$, SiH$_4^{(2-4)}$ are excited states of SiH$_4$ and Si$_2$H$_6$ is produced by SiH$_4$+SiH$_4$ → Si$_2$H$_6$.

We first show the time evolution of electron temperature $T_e$ and electron density $n_e$ at the centre of a discharge over a pulse cycle with different duty cycles 0.25, 0.5 and 0.75, as well as the case applied by CW ($\alpha = 1$) in Fig. 1. Note that $T_e \approx 1.5$ eV and $n_e \approx 2.7\times10^{10}$ cm$^{-3}$ keep almost constant in the CW condition, while presenting a dynamic distribution during pulse modulation. As we can observe, for each profile of $T_e$ with different duty cycles, a rise appears in the power-on period due to electric field acceleration and
then a decline comes in the power-off period mainly caused by diffusion. Moreover, as \( \alpha = 0.25 \), higher maximum \( T_e \approx 2.0 \) eV can be obtained during the power on period, since fewer electrons could survive in the longer off time and then get higher average energy as the next power on starts with a certain power deposited. Meanwhile, \( n_e \) gradually increases mainly generated by gas ionization and dissociation during the power on period, while it decreases due to the restrain of discharge as the pulse power turns off. The maximum value of \( n_e \) increases with the increasing duty cycle since a longer power driving time, as the maximum value of \( n_e \approx 1.7 \times 10^{10} \) cm\(^{-3} \) with duty ratio 0.25, increases to \( n_e \approx 2.5 \times 10^{10} \) cm\(^{-3} \) with duty ratio 0.75.

We show the electron energy distribution \( f(\varepsilon) \) at different times over a pulse period for different duty cycles in Fig. 2. Under CW power on, the electron energy function \( f(\varepsilon) \) keeps almost unchangeable at a steady state. However, under pulse modulation, high energy tails of \( f(\varepsilon) \) present a noticeable deviation compared with the CW condition. In this case, it can be easily seen that the tail of \( f(\varepsilon) \) extends further into the high energy region in the active glow, but disappears rapidly as soon as the RF power turns off. This can well explain the time evolution of \( T_e \) and \( n_e \) at the active or after glow period in Fig. 1. The maximum value of electron energy \( \varepsilon > 25 \) eV exceeds all reaction thresholds listed in Table 1 during the power on period. This extension may lead to instantaneous sources for unexpected inelastic collision processes. In contrast, during the power off period, the tails of \( f(\varepsilon) \) cannot even extend to 10 eV, which is much less than the ionization threshold (about 15.6 eV) of the main gas Ar, favoring reactions with low or no threshold. Moreover, the lower the duty cycle is, the higher energy value can be obtained in the \( f(\varepsilon) \) tails as the power starts, as we can see with the blue one at \( t = 3.3 \) \( \mu \)s. This attributes to the electron temperature spike in the early active glow period in Fig. 1, considering that the lower electron density at the end of the afterglow is due to a longer off time.

Species densities on the substrate play a critical role in film qualities. We first show the time evolution of radical densities on the driving electrode for different duty cycles. From Fig. 3, we can see that densities of \( \text{SiH}_3 \), \( \text{SiH}_4^{(2-4)} \), and \( \text{SiH}_3^{(1-3)} \) decrease with the duty cycle decreasing since fewer bulk electrons have enough energy to be involved in corresponding reactions for a smaller duty cycle, but show almost no variations with the pulse wave. On the contrary, \( \text{SiH}_2 \) and H are more sensitive to the pulse wave and can be effectively modulated. Especially, the H density decreases over two orders of magnitude, from the maximum value about \( 10^{10} \) cm\(^{-3} \) to \( 10^8 \) cm\(^{-3} \) at duty ratio \( \alpha = 0.25 \), because in the afterglow the electron energy tails can seldom exceed 8.9 eV, which is the threshold energy of the main H generation reaction \( \text{H}_2 + e^- \rightarrow \text{H} + \text{H} + e^- \). Few hydrogen would be helpful to thin film properties, since large amounts of bonded hydrogen may cause the degradation of device characteristics. Thus, it is a good example to achieve respective control of species composition on the substrate, for the purpose of special film deposition.

Further evidence for the above discussion can be seen in Figs. 4 and 5, in which the density of ions, as well as the flux of electron and ions on the lower electrode, are presented respectively for different duty cycles. We can see that, densities of positive ions, as \( \text{H}^+ \), \( \text{SiH}_3^+ \), \( \text{Si}_2\text{H}_4^+ \), increase gradually during the power off period mainly caused by diffusion for density gradient, electrodes attachment and neutralization with negative ions. As for negative ions, they are expected to be trapped in the bulk plasma by the electrostatic field, in the active glow stage. Thus, on the lower electrodes, the densities of negative ions, like \( \text{SiH}_2^- \) and \( \text{SiH}_3^- \), decrease abruptly as the power turns on. Then during the afterglow stage, without strong confinement of the electric field, negative ions can have the chance to escape to the substrate. In Fig. 4(a), densities of negative ions on the driving electrode are close to \( 10^8 \) cm\(^{-3} \). In addition, the flux of electrons and negative ions to the
lower electrode presented in Fig. 5 increase promptly during the power off period owing to the collapse of electric fields, which might induce electronic traction for positive ions. Moreover, the flux of positive ions to electrodes decreases a lot during power off time, since the energy of positive ions decreases in the afterglow discharge, allowing a lower bombardment of substrates under pulse modulation.

To well understand the spatio-temporal evolution of negative ion density, we show in Fig. 6 the SiH$^-$ density between electrodes over a pulse period at different duty cycles. In Fig. 6(a) for duty cycle $\alpha = 0.25$, the negative ions have enough afterglow time to diffuse to the electrodes. Clear propagation of the negative ion front from bulk plasma to the sheath can be observed. The introduction of negative ions is considered to be good to film deposition since the neutralization of positive charges on the substrate.

![Fig.4](image1)

**Fig.4** Ions densities on the lower electrode over a pulse period for different duty cycles: (a) 0.25, (b) 0.5, (c) 0.75, (d) 1

![Fig.5](image2)

**Fig.5** The flux of ions and electrons on the lower electrode over a pulse period for different duty cycles: (a) 0.25, (b) 0.5, (c) 0.75, (d) 1

4 Conclusions

In summary, we have studied pulsed RF-CCP in SiH$_4$/Ar mixture discharge by using a one-dimensional fluid and MC hybrid model. Totally, 17 different species (electrons, ions, neutrals, and radicals) and 54 reactions are considered in the model. The electron energy distributions as a function of time are obtained by a self-consistent MC model. Compared with the CW discharge, $f(\varepsilon)$ could be shaped by the pulse parameters, with high energy tails or a large amount of cool electrons, giving rise to the high threshold e-impact processes or low threshold attachment, so that species composition bombarding on the substrate can be tailored. H density reduces obviously and deposition precursors spread to electrodes sufficiently owing to the longer power off time in pulse modulation with the lower duty cycle, which would make the film densify and smooth. Meanwhile, negative ions may escape to electrodes if the power off time is long enough, which will be beneficial to the neutralization of positive ions on them. Thus, the electron energy distribution and plasma composition can be customized in pulse modulation by altering the duty cycles.

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