Numerical simulation on silane plasma chemistry in pulsed plasma process to prepare a-Si : H thin films

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Abstract–We numerically calculated the effects of pulse modulation (plasma-on and -off times) on the concentra-
on changes of the chemical species (SiH₄, SiH₄, SiH₄⁺ and polymerized negative ions) and also the gro tion changes of the chemical species (SiH₄, SiH_x, SiH_x⁺ and polymerized negative ions) and also the growth rate of a-
Simulation is a state of a- Si : H thin films in the pulsed SiH_a plasmas. During the plasma-on, SiH_a is generated quickly by a fast dissociative reaction of SiH₄, but, during plasma-off, SiH₄ disappears rapidly by a reaction with hydrogen and also by the deposition onto the reactor wall. During the plasma-on, the negative ions are polymerized by the reactions with SiH₄, but, during the plasma-off, they disappear by neutralization reactions with positive ions. As the plasma-on time increases or as the plasma-off time decreases, the time-averaged concentrations of SiH, and negative ions and also the time-averaged film growth rate increase. This study shows quantitatively that polymerized negative ions, which are not considered to be preferred precursors for the high-quality thin films, can be efficiently reduced by the pulsed plasma process.

Key words: Pulse Modulation, SiH₄ Plasma Chemical Reactions, Pulsed Plasmas, Polymerization of Negative Ions, Highquality Thin Film

INTRODUCTION

Numerical simula
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2002a; Kim et al., 2003a, b; Kirimura et al., 1994; Koga et al., 2002, 2004; Madan et al., 1999; Madan and Morrison, 1998; Maemura There are several studies on the suppression of the generation and growth of particles in the SiH₄ plasma reactor for preparing a-Si : H thin films by using the pulse modulation or the thermophoretic force due to temperature gradient or by adjusting the gas flow pattern or the distance between the powered and ground electrodes [Fukuzawa et al., 1999; Itagaki et al., 2000; Kim and Kim, 2000, et al., 1999; Shiratani et al., 1999; Watanabe et al., 2002]. Watanabe and his colleagues [Fukuzawa et al., 1999; Koga et al., 2004; Shiratani et al., 1999] suggested that the growth of nanosized particles in

the plasma reactor can be suppressed efficiently by using the pulsemodulated plasma technique. They also developed the cluster-suppressed plasma method by heating the electrodes and also by removing the stagnation zone by changing the gas flow pattern inside the plasma reactor, and they successfully prepared the high-quality thin films of a-Si : H [Koga et al., 2002; Watanabe et al., 2002]. Kirimura et al. [1994] investigated the effects of the plasma parameter changes on the particle growth and on the properties of a-Si : H thin films in the pulsed plasma process, and they synthesized the a-Si : H films of high-quality at a high deposition rate by the amplitude modulated plasmas. Maemura et al. [1999] reported that the particle generation can be controlled by changing the electrode distance with heating the electrodes in the $SiH₄$ PCVD reactor, and they prepared the a-Si : H films with a good opto-electronic property even at a high deposition rate. Madan and Morrison [1998] reported that the amorphous/polycrystalline silicon thin films were synthesized at the maximum deposition rate of 1.5 nm/s in the pulse-modulated PCVD. Itagaki et al. [2000] used the pulsed electron cyclotron resonance plasmas to synthesize the a-Si : H thin films, and showed that the deposition rate and the quality of thin films could be changed by pulse modulation. The high-quality thin films then can also be grown at a deposition rate of 1.4 nm/s without substrate heating.

Economou and his colleagues [Midha and Economou, 2000; Ramamurthi and Economou, 2002' studied the evolution of chemical species in the pulsed Cl₂ PCVD process numerically by using the fluid approach method. They addressed the effects of the process variables on the spatio-temporal evolutions of chemical concentrations, and showed that the transition of the electron-dominated plasmas to the ion-ion plasmas. The modulation of negative ion concentrations during the plasma-on (t_{on}) and -off (t_{off}) times then
depends on the changes in the process variables. Meyyappan [1996] depends on the changes in the process variables. Meyyappan [1996]

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analyzed the pulse-time modulated high density Cl_2 and CF_4 plasmas for etching and deposition processes by using a spatially averaged model, and showed that the duty ratio and pulse frequency affect the plasma density in the plasmas and that the processing rate and etch selectivity can be improved by using the pulse-time modulated discharges. Ashida and Lieberman [1997] used a spatially averaged model to simulate the pulse-power modulated high density Cl₂ plasmas, and reported that the electronegativity of the plasmas is significantly affected by the recombination coefficient of the Cl atoms on the wall and that negative ions can be efficiently extracted [2005] showed the dynamics of concentrations of chemical species, which might be important for the evolution of negative ions, as a function of time during plasma-on and -off, assuming that the particles in plasma processes can be formed homogeneously from the polymerized negative ions.

In this study, we numerically investigated the effects of pulse modcluster generation in the pulsed $SiH₄$ plasmas. We analyzed the effects of the plasma chemical reactions, fluid convection, electrical migration, diffusion, and deposition on the electrodes and reactor wall in the model equations for chemical species. We showed the evolutions of several chemical species which are important for film growth and also for particle generation in the pulsed SiH₄ plasmas during t_{on} and t_{off} . We included 36 plasma chemical reactions in the pulsed SiH4 plasmas, and analyzed the evolutions of chemical species for the processing time of 1 s within a reasonable CPU time by applying a constant concentration and energy of electrons in the plasma reactor.

THEORY

The pulsed plasma reactor proposed by Watanabe and his col-

Fig. 1. Schematic of the silane pulsed plasma reactor for modeling.

leagues [Fukuzawa et al., 1999; Shiratani et al., 1999] as shown in Fig. 1 was applied for this numerical analysis. The upper and lower electrodes in the diameter of 8.5 cm were separated by a distance of 5 cm, and were assumed to have many perforations so that the input and output gas streams could pass through both electrodes. Such a design for electrodes allows us to assume one-dimensional plug flow of the gas stream inside the reactor, and to neglect the momentum balance equation in the model equations.

1. SiH₄ Chemical Reactions in the Pulsed Plasmas

There are more than 50 chemical species and 200 chemical reactions in the SiH4 plasmas for semiconductor processing [Courteille et al., 1996; Fridman et al., 1996; Howling et al., 1994, 1996; Kushner, 1988]. Howling and his colleagues [Courteille et al., 1996; Howling et al., 1994, 1996] suggested that negative ions can be polymerized homogeneously to form high-mass chemical species in the SiH4 plasmas on the basis of the experimental observations. We considered 18 chemical species and 36 chemical reactions that might be important for film growth and polymerization of negative ions.

 x^*) and negative (SiH $_x^-$) ions, ∗
∫ and vibrationally excited molecules (SiH₄(v1, 3) and SiH₄(v2, 4)) by the collision with the energetic electrons. The electron impact dissociative reactions, R_1-R_5 of SiH₄, are [Kushner, 1988]: in grown and perjinimization of rigginal collistic contract

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a There are two radicals mainly produced by the electron impact dissociative reactions with SiH_4 : SiH_3 , the precursors for a-Si: H thin films in $SiH₄$ plasmas, and $SiH₂$, the precursors for the polymerized neutral clusters. According to the theoretical study of Bhandarkar et al. [2000], the SiH₂ radical insertion can be important in the production of small clusters, Si_nH_x (n~3 or 4), even though the the production of small clusters, Si, H_z (n-3 or 4), even though the
model results were overestimated in comparison with the experi-
menst due to the large reaction rates of SiH_z insetion. In our suddy,
respectively, model results were overestimated in comparison with the experiments due to the large reaction rates of SiH_2 insertion. In our study, we solved the governing equation for SiH_2 instead of SiH_2 and SiH_3 , we solved the governing equation for SiH₁ instead of SiH₂ and SiH₃, respectively, to reduce a computational time. The reaction rate constants of SiH₄ with H and of SiH₃ recombination are smaller than tof SiH₄ respectively, to reduce a computational time. The reaction rate constants of SiH_4 with H and of SiH_3 recombination are smaller than that of SiH_4 with electrons (R_2) by the order of 100 and 10, respectively, according to Kushner $[1988]$. Thus, we did not include the reaction of SH_4 with H for SH_3 production and of SH_3 recombination with SiH_3 for SiH_2 production in our study. The vibrationally excited molecules are relaxed by the collisions with hydrogen as follows [Kushner, 1988]: SiH₄(v1, 3)+H₂→SiH₄+H₂ k₆=3.05×10⁻¹² cm³
SiH₄(v1, 3)+H₂→SiH₄+H₂ k₆=3.05×10⁻¹² cm³
SiH₄(v2, 4)+H₂→SiH₄+H₂ k₆=3.05×10⁻¹² cm³
SiH₄(v1, 3)+H₂→SiH₄+H₂ k₆=3.05×10⁻¹² cm³ the recombinationally
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 $, \qquad (R_6)$
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SiH_4(v2, 4) + H_2 \longrightarrow SiH_4 + H_2
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k_6 = 3.05 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}, \quad (R_6)
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SH_4(v2, 4) + H_2 \rightarrow SH_4 + H_2
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K_6 = 3.05 \times 10^{-12} \text{ cm}^3 \text{ s}^4,
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K_7 = 6.08 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}.
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8) SiH_x can also be formed by a recombination reaction (R₈) between
positive ions and electrons, and is consumed by electron attachment
(R₉) and hydrogen adsorption (R₁₀) reactions [Kushner, 1988].
SiH_x⁺+e→SiH_x positive ions and electrons, and is consumed by electron attachment (R_9) and hydrogen adsorption (R_{10}) reactions [Kushner, 1988]. SiH_4
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 g) and SiH_x^+ (v1, 3)+H₂→ SiH₄+H₂ k₇=6.08×10⁻¹¹ cm

an also be formed by a recombination reaction (l

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K_{10} = 1 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}.
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∕11 Positive ions disappear by a recombination reaction with electrons (R_8) and neutralization reactions with negative ions $(R_{11}-R_{23})$ [Kushner, 1988]. n_2 → Stri₄(or +ri

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ons (R₁₁-R₂₃) [Kus

, n=3, 1.4×10⁻⁷ cm³

-13, 2×10⁻⁷ cm³s⁻¹) sitive ions disappear by a recombination reaction with ele

(a) and neutralization reactions with negative ions $(R_{11}-R_{23})$ [1, 1988].

SiH_x⁺+Si_nH_x⁻→Si_{n+1}H_x⁺(H or H₂) (n=1-13) (R

($k_{(10+n)}$, n=1, 5×10

$$
SH_{x}^{+}+Si_{n}H_{x}^{-} \to Si_{n+1}H_{x}+(H \text{ or } H_{2}) \qquad (n=1-13) \qquad (R_{11}-R_{23})
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;a There are several reports on possible precursors (mainly negative ions and radicals) for the formation of high-massed cluster particles which are negatively charged in the plasma reactor [Courteille et al., 1996; Fukuzawa et al., 1999; Howling et al., 1994, 1996; Shiratani et al., 1999]. Fridman et al. [1996] proposed that the negative ions can be polymerized by the reactions with the vibrationally excited molecules (SiH₄(v1, 3) and SiH₄(v2, 4)). Howling and his colleagues [Howling et al., 1994, 1996; Shiratani et al., 1999] proposed that negative ions are polymerized to the higher mass-clusters by the polymerization reactions with SiH_4 ($R_{24}-R_{36}$) and can grow in the plasma reactor. They assumed that the polymerization reactions $(R_{24}-R_{36})$ of negative ions are pseudo-first order with respect measured the rate constants, $k_{24} - k_{36}$, for those reactions with the unit of s−1 [Howling et al., 1994, 1996; Shiratani et al., 1999]. Fractions while SIT_4 ($\text{K}_{24} \text{K}_{36}$) and can grow
They assumed that the polymerization reactive ions are pseudo-first order with respect
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to negative ions and are independent of the SiH₄ concentration, and
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- k_{36} , for those reactions with the unit
of s⁻¹ [Howling et al., 1994, 1996; Shiratani et al., 1999].
Si_nH_x⁻+SiH₄ \rightarrow Si_{n+1}H_x⁻+(H or H₂) (n=1-13) (R₂₄-R₃₆)
 $(k_{(23+n)}, n=1, 10^4 \text{ s}^{-1}, n=2, 2.5\times10^3 \text{ s}^{-1}, n=3, 2.8\times10^3 \text{ s}^{-1}, n=4, 3.2\times10^3 \text{ s}^{-1},$
n=5, 3.6×10³ s⁻¹, n=6-13, 4×10³ s⁻¹).

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⊥ 1 and are charged negatively by the electron attachment during the discharge [Fridman et al., 1996; Nomura et al., 1996]. Recently, ∗
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|C during the discharge can play a role to produce SiH_{r} . We neglected rate constants of R_{24} - R_{36} for the growth of negative ions are the em-
pirical data including the electron attachment reactions to Si_nH_s . In this study, the SiH_4 concentration changes according to the reactor length with time. The reaction rates of $R_{24} - R_{36}$ were modified as the second order reactions with respect to negative ions and SiH₄ to account for the changes in SiH₄ concentration in the reactor.
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SiH₁+e-→SiH₄ k₁=1×10⁻¹ cm³

SiH₁+1+1-→SiH₄(or +H) k₁=1×10⁻¹ cm³

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1938], and neutralization reactions with neg SiHx $+H_2 \rightarrow$
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and are charged regarively by the electron attachment during the
discharge [Fridman et al., 1996; Nomura et al., 1996]. Recently,
Gallagher et al. [2002] Gallagher et al. [2002] reported that the electron attachment to Si₂H_n, whis electron attachment reactions to to produce SiH₁. We neglected that electron attachment reactions to Si₃H₁ on ur study because the rap during the discharge can play a role to produce SiH₃th electron attachment reactions to Si₂H₃^t in our stu rate constants of R₂₄-R₃₆ for the growth of negative i pircical data including the electron attachmen the electron attachment reactions to Si_xH_x in our study because the
rate constants of R_{3x}-R_{Ns} for the growth of negative ions are the em-
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th} pirical data including the electron attachment reactions to Si_nH_x. In
this study, the SiH_n concentration changes according to the reactor
length with time. The reaction rates of $R_{24}R_{36}$ were modified as
the sec Just after t_{up} , the electrons disappear rapidly by ambipolar diffu-
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1996]; th x^* and a recombination on the wall, or the electron attachment to the neutrals within 10's µs [Ashida and Lieberman, 1997; Courteille et al., 1996; Fridman et al., 1996; Howling et al., 1994, 1996; Kushner, 1988; Meyyappan, 1996; Midha and Economou, 2000; Ramamurthi and Economou, 2002]. The reactions involved with the electrons are considered only during t_{*m*}, while the reactions involved with the molecules and radicals are considered during both t_m and t_{nf} . There will be several reaction paths for the polymeriza reactions involved with the molecules and radicals are considered during both t_{on} and t_{off} . There will be several reaction paths for the poly-
merization of negative ions in the SiH₄ plasmas, but the rate
constants of the polymerization reactions $(R_{24} - R_{36})$ were obtained
empir merization of negative ions in the $SiH₄$ plasmas, but the rate constants of the polymerization reactions $(R_{24}-R_{36})$ were obtained empirically for the continuous-wave plasma discharge by assuming that the polymerization reactions of negative ions $(Si_nH_xSiH_4$ are dominant [Courteille et al., 1996; Howling et al., 1996]; therefore, we considered those polymerization reaction January, 2007 √
n ing that the polymerization reactions of negative ions $(Si_nH_n⁻)$ with SiH4 are dominant [Courteille et al., 1996; Howling et al., 1994, 1996]; therefore, we considered those polymerization reactions only

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2. Governing Equations for Chemical Species in the Pulsed Plasmas

In the plasma reactor, the electron concentration depends on the position and time, and we should use kinetic approaches on the basis of the particle-in-cell/Monte Carlo simulation or the hybrid Monte Carlo/fluid model to predict the exact electron concentration [Graves, 1987; Graves and Jensen, 1986; Kushner, 1988; Midha and Economou, 2000; Ramamurthi and Economou, 2002; Sato and Tagashira, 1991]. But we did not solve the governing equation for electrons to reduce the computational time, and had assumed that the were uniform inside the reactor. We used the time-averaged electric field strength in the plasma reactor, which changed as a function of position but not as a function of time [Kim and Ikegawa, 1996; Kim and Kim, 1997, 2000; Sato and Tagashira, 1991]. The fluid approach method is known to be numerically effective in terms of the CPU time and we developed the model equations for chemical species to analyze the plasma chemistry in the $SiH₄$ pulsed plasma processes on the basis of the fluid approach.

The number concentration (N_i) for chemical species, i, is balanced with the effects of plasma chemical reactions, convection, diffusion, electrical migration and deposition onto the electrodes and reactor wall, and the governing equations for N ,'s in the pulsed plasma reactor are expressed as follows [Kim and Ikegawa, 1996; Kim and Kim, 1997, 2000]: The electrodes
 $\sqrt{3}$ in the pulsed

Ikegawa, 1996;
 $\sqrt[n]{(\frac{2}{R})}$

$$
\frac{\partial N_i}{\partial t} = \sum_{j=1}^{36} \alpha_j (RXN)_j - \nabla(u_sN_i - D_i\nabla N_i - \delta_i\mu_i EN_i) - J_w \left(\frac{2}{R}\right)
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ma reactor was constant and
tions on the gas flow rate be
ered in thi In Eq. (1), t, α_{ii} and (RXN), are the time, stoichiometric coefficient for i species in the *j*th reaction and rate of the *j*th reaction. u, is the gas velocity inside the reactor and is sexuend to be uniform due to genue the perforated electrodes. The diffusion coefficients (D.) for chemic gas velocity inside the reactor and is assumed to be uniform due to the perforated electrodes. The diffusion coefficients (D_/
cal species were calculated by the Chapman and Ensk
(Reid et al., 1977]. We assumed that the reactor pressure
ma reactor was constant and neglected the effect of the perforated electrodes. The diffusion coefficients (D_i) for chemical species were calculated by the Chapman and Enskog equation [Reid et al., 1977]. We assumed that the reactor pressure in the plasma reactor was constant and neglected the effect of chemical reactions on the gas flow rate because the chemical species we considered in this model were in low concentration. δ ,
ions, -1 for negative ions and 0 for neutrals. The
coefficient, μ_s was calculated according to the Ein
[Chen, 1984]. E is the time-averaged electric field
position in ered in this model were in low concentration. δ_i is 1 for positive ions, −1 for negative ions and 0 for neutrals. The electric migration coefficient, μ ₁ (Chen, 1984) position insider and Kim, 199
and Kim, 199
in the bulk planet planet and Ikegawa,
and Ikegawa,
 $E = E_{max}$
 $E = 0$
 $E = E_{min}$
 $1 -$
In Eqs. (2)-(4
averaged elec coefficient, μ , was calculated according to the Einstein relationship [Chen, 1984]. E is the time-averaged electric field as a function of position inside the plasma reactor [Kim and Ikegawa, 1996; Kim and Kim, 1997, 2000; Sato and Tagashira, 1991]. During t_{av} , the E
in the bulk plasma region $(x_{\text{p.v.}} \le x \le x_{\text{av}})$ is zero, and the E in the sheath
regions $(0 \le x \le x_{\text{post}} x_{\text{avg}} \le x \le x_{\text{out}})$ can be expressed by in the bulk plasma region ($x_{pox} \le x \le x_{mag}$) is zero, and the E in the sheath
regions ($0 \le x \le x_{pox}$, $x_{mg} \le x \le x_{md}$) can be expressed by the Child-Lang-
muir equation by assuming a collisionless plasma as follows [Kim
a regions (0≤x≤x_{pos}, x_{neg}≤x≤x_{ond}) can be expressed by the Child-Lang-
muir equation by assuming a collisionless plasma as follows [Kim
and Ikegawa, 1996; Kim and Kim, 1997, 2000:
 $E = E_{ma} \left[1 - \left(\frac{x}{x_{pa}}\right)^{1/3} \right]$ fo muir equation by assuming a collisionless plasma as follows [Kim and Ikegawa, 1996; Kim and Kim, 1997, 2000: ira, 1991]. During t_{on}, the E
s zero, and the E in the sheath
xyressed by the Child-Lang-
less plasma as follows [Kim
97, 2000:
for 0≤x≤x_{pos}, (2)
for x_{pos}≤x≤x_{pos}, (3)
for x_{pos}≤x≤x_{pos}, (4)
ximum and minimum tim gions ($0 \le x \le x_{p_{\text{max}}}$, $x_{\text{avg}} \le x \le x_{\text{end}}$) can be expressed by the Child-Lang-

ir equation by assuming a collisionless plasma as follows [Kim

d Ikegawa, 1996; Kim and Kim, 1997, 2000:
 $E = E_{max} \left[1 - \left(\frac{x}{x_{\text{prod}}} \$ $\frac{\partial N_i}{\partial t}$ and $\frac{\partial N_i}{\partial t}$ and $\frac{\partial N_i}{\partial t}$ are performed in the space of α is a space of α is α is a space of eed with the effects of plasma chemical reaction

distinsion, electrical migration and deposition onto

It reactor vall, and the governing equations for N_i;

sma reactor are expressed as follows [Kim and II

n and Kim), it is existent as all or the hine of the hine of $\frac{98}{10}$ and $\frac{1}{10}$ and \frac E = E_{max} 1− ($\frac{1}{x}$ E = E_{max} 1− ($\frac{x}{x_p}$ = E= E_{max} 1− ($\frac{x}{x_p}$ = E= E_{max} 1− ($\frac{x}{x_p}$ E = E_{max} 1− ($\frac{x}{x_p}$ E = E_{max} 1− ($\frac{x}{x_p}$ E = C $\frac{28}{100}$, $\frac{1}{2}$
 $\frac{1}{2$ and Kim, 1997, 2000; Sato and Tagashira, 1991]. During t_{on} , the E

$$
E = E_{m\alpha} \left[1 - \left(\frac{x}{x_{\rho\alpha}} \right)^{1/3} \right]
$$
 for $0 \le x \le x_{\rho\alpha s}$, (2)

$$
E=0 \t\t for xpos \le x \le xneg
$$
 (3)

E=E_mω₁ [1-(
$$
\frac{x}{x_{\text{post}}}-\frac{x}{x_{\text{post}}}
$$
)]¹³ for 0≤x≤x_{pos}, (2)
\nE=E_mω₁ [1-($\frac{x}{x_{\text{post}}}-\frac{x}{x_{\text{post}}}$)]¹³ for 0≤x≤x_{pos}, (3)
\nE=E_mω₁ [1-($\frac{x_{\text{end}}-x_{\text{neg}}}$)]¹³ for x_{neg}≤x≤x_{end}, (4)
\nEqs. (2)-(4), E_{max} and E_{min} are the maximum and minimum time-
\neraged electric fields at the powered and the grounded electrodes,

In Eqs. (2)-(4), E_{max} and E_{min} are the maximum and minimum time-
averaged electric fields at the powered and the grounded electrodes, averaged electric fields at the powered and the grounded electrodes,

positions where the time-averaged electric field becomes zero near the sheath regions are formed near two electrodes by the differences between the concentrations of positively and negatively charged are assumed to be 0.3 cm in this analysis [Sato and Tagashira, 1991]. can be set for zero, because the sheath regions disappear quickly within 10's µsec after the plasma discharge stops [Anders, 2004]. It is assumed that the transport phenomena for ionized species for tration profiles of positive and negative ions in the plasma reactor. The electric fields in the sheath regions follow Eqs. (2)-(4) during species onto the reactor wall and we considered the deposition of

at the reactor inlet and outlet [Danckwerts, 1953]. The ions move fast under the electric field in the plasmas. For positive and negative ions, we used the flux boundary conditions at the reactor inlet condition by Graves et al. [Graves, 1987; Graves and Jensen, 1986], positive and negative ions can diffuse quickly to the electrodes; therefore, we used 0.15 as the sticking coefficients for both ions at the tani et al., 1999]. The governing equations for the 18 chemical species (Eqs. (1)-(4)) were solved numerically by using the subroutine VODPK to calculate the concentration profiles for chemical species in the pulsed plasma reactor.

RESULTS AND DISCUSSION

temperature inside the reactor are 5 cm, 20 sccm, 0.1Torr and 300 K, respectively, and they are the same as the experimental conditions as in Fukuzawa et al. [1999]. The electron concentrations were measured from 4×10^9 to 7×10^9 #/cm³ in the pulsed SiH₄ plasmas by Fukuzawa et al. [1999]. The electron concentration was assumed to be 5×10^9 #/cm³ during t_{on}, but zero during t_{off}. E_{max} and E_{min} are 100 and −100 V/cm for the actual electric fields in the industrial PCVD reactor [Graves, 1987; Graves and Jensen, 1986; Kim and t_{off} in the range from 10^{-5} to 1.0 s, and the standard conditions for study.

Fig. 2 shows the evolution of SiH₄ concentration profiles along the axial distance during (a) t_{on} and (b) t_{off} . The SiH₄ concentration at the outlet is lower than at the inlet by the effect of chemical reacelectrons (R_1-R_5) , and its concentration decreases with time, but does not reach a steady state condition for the continuous-wave plasmas electrons disappear quickly and the $SiH₄$ disappearance reactions (R_1-R_5) by the electron collisions become zero, and its concentration increases with time toward the initial SiH_4 concentration. In Figs. 3(a, b), the evolution of the SiH_4 concentration profiles is illustration in the plasma reactor increases with time and reaches the

Fig. 2. (a) Evolution of SiH₄ concentration profiles along the axial distance for various times during t_{on} ($t_{on}=0.01$ s and $t_{off}=0.02$ s). (b) Evolution of SiH₄ concentration profiles along the axial distance for various times during t_{of} ($t_{on}=0.01$ s and $t_{of}=0.02$ s).

Fig. 3. (a) Evolution of SiH_x concentration profiles along the axial distance for various times during t_{on} (t_{on}=0.01 s and t_{off}=0.02 s). (b) Evolution of SiH_x concentration profiles along the axial distance for various times during t_{of} ($t_{on}=0.01$ s and $t_{of}=0.02$ s).

concentration decreases with time due to faster disappearance rates

is generated any further by the plasma reactions because the electron with time by the hydrogen adsorption reaction, R_{10} and by the ef-

Fig. 4. (a) Evolution of SiH_x⁺ concentration profiles along the axial distance for various times during t_{on} (t_{on} =0.01 s and t_{off} =0.02 s). (b) Evolution of SiH ^+_x concentration profiles along the axial distance for various times during ${\sf t}_{\it off}$ (${\sf t}_{\it on}$ =0.01 s and ${\sf t}_{\it off}$ =0.02 s).

fects of diffusion and fluid convection.

In Figs. 4(a, b), the conventration profiles of SiH_x
In Figs. 4(a, b), the concentration profiles of the concentration profiles of the start of the plasma discharge, the SiH₁, concentration profiles the start of the p + are shown along the mind battance for various times during t_{1, an} d_{ista}, respectively.
At the start of the plasma dischange, the SHI, concentration increases
eachles by a fast dissolution increases cheme and the one of χ -mind χ At the start of the plasma discharge, the SiH₁
quickly by a fast dissociative ionization real
decreases because of faster disappearance necesses because of faster disappearance necesses because of faster disappearance n + concentration increases quickly by a fast dissociative ionization reaction (R_3) of SiH₄ and reaches the maximum at $t=0.002$ s, after which its concentration decreases because of faster disappearance reactions (R_8 and R_{11}) of $\mathrm{SiH}^\mathrm{r}_\mathrm{s}$ high mas sheat in the e sum of the sum of 10° s and diffusion and diffusion and diffusion of 0 . after Fi H $\mathrm{Si}_7\mathrm{H}$ tions $_{x}^{+}$. The SiH $_{x}^{+}$ concentration for the pulsed plasmas at t=0.01 s is . The SiH_x

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he SiH_x⁺ c o higher than that at the steady state for the continuous-wave plasmas by 3%. During t_{ur}, the SiH_x
mas have sharp peaks on the orchead the gions become lovo on the orchead the gions become lovo on the decertical migration. Just after
in the sheafth regions moves quiched the electrica + concentrations in the bulk plasmas have sharp peaks on the order of 10^9 #/cm³, and those in the sheath regions become low on the order of 10^6 #/cm³ because SiH_x⁺ because SiH_{x}^{1}
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ing coef in the sheath regions moves quickly toward the electrodes due to the electrical migration. Just after I_{m} must of the electrons are con-
simulation on the wall, or the electron stachment to the neutrals within
the significant of the electron attachment to the neutrals within
the $\frac{1}{x}$ and the recombination on the wall, or the electron attachment to the neutrals within 10's µs [Ashida and Lieberman, 1997; Courteille et al., 1996; Fridman et al., 1996; Howling et al., 1994, 1996; Kushner, 1988; Meyyappan, 1996; Midha and Economou, 2000; Ramamurthi and Econ-+ concentration decreases with time mainly by the neutralization reactions $(R_{11}-R_{23})$ with negative ions (Si_nH_x and the Sil
diffuses from the Sil
diffuses from the Sil
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of 0.15 durater t \geq 0.0
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Fig. 5 sl
distance durations of ne
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∈ ions (Si_nH_n , $n\geq 1$). There is no electric field between the electrodes, , concentrations in the sheath regions increase as SiH, $\frac{1}{x}$ is assumed to be deposited at the electrodes with a sticking coefficient + concentration at the electrode wall after t≥0.011 s is a little lower than that at the reactor center.

∗
T Fig. 5 shows the concentration profiles of $Si₁H_r⁻$ along the axial $\mathrm{Si}_7\mathrm{H}_{x}$ tions − $Si₁H_r$ increases with time as a result of the polymerization reactions of negative ions. The negative ions are being pushed toward

the bulk plasma region from the sheath regions by an electrostatic repulsion and the Si₁H_x
sheath regions and the nations in concentration
drops in concentration
drops in concentration
concentration profiles by
this study are not self-congequation for electric field is zero
ing equat ∗
∈ repulsion and the $Si₁H_r⁻$ concentration becomes nearly zero in the sheath regions and the negative ion concentration profiles show sharp drops in concentration at the sheath boundaries. The negative ion concentration profiles become flat in the bulk plasma region, where the electric field is zero. The model equations for negative ions in this study are not self-consistent because we neglected the governing equation for electrons and the ambipolar diffusion does not affect the evolution of concentration profiles of negative ions. The $Si₇H_x$ the uratio stead; concerned with and d and v and contract Si ∗
|]
)] Si_iH_v concentration at the downstream becomes higher than that at the upstream by the effect of fluid convection. The Si¹¹H_X exacts that the upstream by the effect of this content
train at $t = 0.01$ s of the pulsed plasmas is about 65% of flexed y state for the continuous-wave plasm ×
−
1 the upstream by the effect of fluid convection. The $Si₂H_z$ concentration at t=0.01 s of the pulsed plasmas is about 65% of that at the steady state for the continuous-wave plasmas. During t_{eff} , the Si₇H_{t} stead fract fract continuous-wave plasmas. During t_a, the SiHx of the Continuous-wave plasmas. During the continuous-
top-contentration decreases with time due to a disappearance reaction
with SiHI, and due to the effec ∗
1
|concentration decreases with time due to a disappearance reaction + and due to the effects of diffusion and fluid convection. ×
}
} and the $Si₁H_z$ in the bulk plasmas diffuses toward the sheath regions ∗
∩ and we can see that some $Si₂H_z⁻$ can stay in the sheath regions. Fig. ∗
h 6 illustrates the concentration profiles of $Si₀H_x⁻$ along the axial dis-∗
1¦ ∗
⊄ files of $Si₁₃H_z$ show the same pattern as $Si₂H_z$ in Figs. 5(a, b). The ∙
∈ $Si₁₃H_r$ concentration at t=0.01 s of the pulsed plasma discharge is lower than that at the steady state for the continuous plasma discharge by about 99%. By using the pulsed plasmas, the growth of polymerized negative ions can be retarded dramatically.

In Fig. 7, the time-averaged SiH₄ concentrations at the reactor center are shown as a function of t_{eff} for various t_{on} 's. During t_{off} , the $SiH₄$ disappearance reactions do not take place and the $SiH₄$ concentration becomes high and the time-averaged SiH₄ concentration
for one cycle of t_{on} and t_{off} increases, as t_{off} increases. During t_{on} , SiH₄ is consumed by the collision with the energetic electrons and the

Fig. 5. (a) Evolution of concentration profiles of Si₇H_x along the axial distance for various times during t_{on} (t_{on}=0.01 s and t_{op}=0.02 s). (b)
Evolution of concentration and flux of Si H₃ along the axial dist ×
1 Evolution of concentration profiles of Si₇H_x along the axial distance for various times during t_{off} (t_{on}=0.01 s and t_{off}=0.02 s). −

Fig. 6. (a) Evolution of concentration profiles of $Si_3H_x^-$ along the axial distance for various times during t_{on} ($t_{on}=0.01$ s and $t_{off}=0.02$ s). (b) ×
a Evolution of concentration profiles of $\rm Si_{13}H_{x}^-$ along the axial distance for various times during t $_{\rm eff}$ (t $_{\rm on}$ =0.01 s and t $_{\rm off}$ =0.02 s).

Fig. 7. Time-averaged SiH₄ concentrations at the reactor center as a function of t_{off} for various t_{on} 's.

resulting time-averaged SiH₄ concentration decreases with the in-
crease of t_m . As t_{gf} becomes zero, the time-averaged SiH₄ concencrease of $t_{\alpha r}$. As $t_{\alpha ff}$ becomes zero, the time-averaged SiH₄ concen-
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Fig. 8. Time-averaged SiH_x concentrations at the reactor center as a function of t_{off} for various t_{on} 's.

tration approaches the SiH₄ concentration at the steady state for the continuous-wave plasmas. The shorter the t_m is, the faster the timecontinuous-wave plasmas. The shorter the t_{on} is, the faster the time-

Fig. 9. Time-averaged SiH_x^+ concentrations at the reactor center as a function of t_{off} for various t_{off} 's.

Fig. 10. Time-averaged concentrations of negative ions at the reactor center as a function of t_{eff} for various t_{on} 's.

averaged SiH₄ concentration reaches the initial SiH₄ concentration with the decrease of t_{eff} . Also, as t_{eff} becomes infinite, the time-averaged SiH₄ concentration approaches the initial condition of SiH₄ concentration. Fig. 8 illustrates the time-averaged SiH_{$_x$} concentra-

+ concentrations at the reac-+ concentration for the pulsed plasmas decreases because the SiH⁺ concentration decreases quickly during t_{eff} . Dur-+ concentration decreases quickly and becomes zero by fast $_{x}^{+}$ concentration increases. In Fig. 10, the time-∗
⊓
; ∫
⊂ averaged total concentrations of negative ions $(Si_2H_x \sim Si_{13}H_x)$ at

Fig. 11. Time-averaged deposition rates of a-Si : H thin film on the substrate in electrode as a function of t_{off} for various t_{on} 's.

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zero, the time-averaged concentration of negative ions approaches the steady state value of the continuous-wave plasmas.

Howling and his colleagues [Howling et al., 1994, 1996] measured the intensities of the radicals and charged species by using the mass spectrometric method and the particles by using the light scattering method in the pulsed plasmas, changing the pulse frequencies (Fig. 3 [Howling et al., 1994, 1996]) and showed that the et al., 1999; Shiratani et al., 1999] also observed a decrease in particle contamination as the pulse frequency increases (Fig. 9 [Fukuzawa et al., 1999; Shiratani et al., 1999]). Even though we made several assumptions in our modeling, the tendency predicted by the model was in accordance with that observed in the experiments.

In Fig. 11, the time-averaged deposition rates of the a-Si: H thin centration in the reactor increases as shown in Fig. 8 and the growth rate of a-Si : H thin films also increases because of the increase of reported that the deposition rate of the a-Si : H thin films ranges from 0.064 to 0.12 nm/s in the pure SiH_4 plasma reactor without pulse modulation. In this calculation, the film growth rate in the

Fig. 12. Concentrations of (a) clusters in the size below 1 nm in experiments [Fukuzawa et al., 1999] and (b) negative ion clusters in this calculation as a function of t_{off} for various t_m 's.

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about 0.06 nm/s for the same process conditions as in Fukuzawa et al. [1999].

continuous-wave plasmas by the SiHx radicals is calculated to be
the median of the SiHx radical contents of the SiHx radical contents of
the sympersized clusters in the plasma process are considered to
the he precarastr fo The nanosized clusters in the plasma process are considered to be the precursors for the nucleation of particles, and their generation and growth must be suppressed to prepare high-quality thin films [Ashida and Lieberman, 1997; Courteille et al., 1996; Fukuzawa et al., 1999; Howling et al., 1994, 1996; Koga et al., 2002, 2004; Meyyappan, 1996; Shiratani et al., 1999; Watanabe et al., 2002]. Fig. 12 shows (a) the experimental data for the cluster concentrations in the size below 1 nm by Fukuzawa et al. [1999] and (b) the total concentrations of the negative ion clusters (Si_kH_X concentrations of the neactor center in this calculation for the same priors. Both results are in good agreement qualitative ions. Both results are in good agre ∗
∈ total concentrations of the negative ion clusters $(Si_nH_n, 2 \le n \le 13)$ at the reactor center in this calculation for the same process conditions. Both results are in good agreement qualitatively when the summation of t_o, is exactly 0.1 s for various t_u's. In Figs. 12(a, b), is exactly ones to the energy onestant for verious to it is exactly contractly constant for verious to it is because the clusters are not removed the cluster concentration for t_s shorter than 0.0001 s is shown to be ensire and the cluster concentration for the small of the continuous wave plasma. In both ensires are an enterative during a short t_s - Mad those re nearly constant for various t₅. ¹S checause the clusters are not removed this calculation, the cluster construction decreases with the continuous-wave plasmas. In both results of the experiments of the continuous-wave easily during a short t_o. And those results are almost the same as a
the continuous-wave plasmas. In both results of the experiments
and this calculation, the cluster concentration decreases with the
increase in t_o bec the continuous-wave plasmas. In both results of the experiments and this calculation, the cluster concentration decreases with the increase in t_w because the clusters can be removed during t_y larger particular the content and conto s at the cluster concentration at the comes zero at the end of t_w and the cluster concentration at the end or of e than 0.0001 s. If $t_{\rm sf}$ is larger than 0.1 s, the cluster concentration be-
conces zero at the end of $t_{\rm sf}$ and the cluster concentration at the end
of each $t_{\rm sf}$ becomes almost the same as the change of $t_{\rm sf}$ comes zero at the end of t_w and the cluster concentration at the end of teat t_w becomes simples the same as the clause of t_w , note clusters and the large of the the care and the cluster concentration is. We used the of each t_u, becomes almost the same as the change of t_u, More clusters
are generated with the increase of t_u, and the larger the t_u, is, the
stigger the cluster concentration is. We used the electron collision
rat are generated with the increase of t_{un}, and the larger the t_u, is, the higher the cluster concentration is. We used the electron colitsion hight particle constants proposed by Kushner which might be different from the higher the cluster concentration is. We used the electron collision rate constants proposed by Kushner which might be different from the experimental conditions [Kushner, 1988]. Also, Fukuzawa et al. [1999] measured the cluster concentration in the size range below 1 nm (which is equivalent to the Si number of about 24), but our model results are for negative ion clusters of Si₂H₃
might be the reason that our model results of negate
are less than the experimental results in Fukuzwava
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! model results are for negative ion clusters of $Si_2H_r^- \sim Si_1H_r^$, which might be the reason that our model results of negative ion clusters are less than the experimental results in Fukuzawa et al. [1999]. The negatively charged clusters are hard to arrive at the deposition films during the plasma-on, but some of them can deposit on the films during the plasma-off because there is no electric field between the electrodes. Also, by the neutralization reactions, the negatively charged clusters can become neutral clusters which can be easily deposited onto the thin films even during the plasma-on. Fig. 12 shows that the pulsed plasma process can be an efficient method to suppress the generation and growth of negative ion clusters and that highquality thin films can be successfully prepared by the pulse plasma technique.

CONCLUSIONS

The concentration profiles for several chemical species that might be important for the film growth and particle generation in the SiH₄ plasmas were analyzed theoretically for various t_m 's and t_m 's in the plasmas were analyzed theoretically for various t_{on} 's and t_{off} 's in the pulsed plasmas. The effects of plasma chemical reactions, fluid convection, electrical migration, diffusion, and deposition on the electrodes an pulsed plasmas. The effects of plasma chemical reactions, fluid convection, electrical migration, diffusion, and deposition on the electrodes and reactor wall were included in the model equations for chemical species. The evolution of chemical species was investigated for a processing time of 1 s within a reasonable CPU time by including 36 plasma chemical reactions in the pulsed SiH_4 plasmas and by applying a constant concentration and energy of electrons in the plasma reactor.

During t_{1,} die SiH4, concentration decreases with time by the elec-
name in impact dissociation matrician of SH4, and daring \downarrow a increases
canceare energetic electrons in the plasma dissociation reaching to
concentr tron impact dissociation reactions of SH1, and the impact of SH1, and the increase energetic electrons in the plasma disappear. During t_o the concentrations of SH1, and SH1; increase outdet) because of the solicit and S because neergetic electrons in the plasmas disappear. During $t_{\rm A}$, the space of the plasmas disappear. During the discretion reactions of SHI, and SHI, decrease mainly due to the exact
of the disappears of SHI, and SH the concentrations of SiH_x and SiH_x
discocialon reactions of SiH_x Durasdiction reactions of SiH_x During
and SiH_x Durasdic mections with negative ions,
concentrations of regative ions increases
meinly due to the * increase quickly because of dissociation reactions of SiH₄. During t₁, be concentrations of SiH₄. The concentration reaction reaction of the equivalent product and the equivalent of the equivalent product of the equivalent concentrations of re and SiH_x
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ization reconcentr
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manged times are subseq $_{x}^{+}$ decrease mainly due to the reaction with H_2 and the neutralconcentrations of negative ions increase with time due to the poly- \cdot In + concentration becomes low + , and the concentrations of negative ions become almost zero due to an electrostatic + concentration in the sheath regions + diffusion from the bulk plasmas to the sheath regions where some negative ions can penetrate.

ization reactions with tregulate ions, respectively. During t_n , the constrained in the constrained by the constrained by the merization reactions of negative ions, but, during t_n , they decreases lower
for the shear of negative relations of negative ions, they decreases low
as a result of first education relations of negative ions of negative with time mainly due to the neutralization reaction series and estables in SiHx, and the solar seal of fast electrical migration of SiH₁, and the concernent season of negative ions sea continues to the neutralization in the sheath region, during t_m , the SiH_x
as a result of fast electrical injeation
tions of negative ions become almos
repulsion. During t_w , the SiH_x⁺ concernes
becomes high because of the SiH_x⁺ direct to the s as a result of fast electrical migration of SiH_x
tions of negative ions become almost zero denotes the detail
repulsion. During L_{ge} the SiH_x¹ concentration ibcomes high because of the SiH_x¹ concentration is
t repulsion. During t_{uff}, the SiH_x
becomes high because of the S
to the sheath regions where some to the S
decentration decreases or as t_{uf} decentration decreases and the tis
and negative ions increase. As
time-averag becomes high because of the SiH_x

to the sheath regions where some as α station decreases or as t_x decreases or the time-

centration decreases and the time-

centration decreases and the time-

time-averaged SiH_x As t_y increases or as t_x decreases, the time-averaged SH₁, con-
Artaion decreases and the time-averaged concentrations of SH₁¹
In again exponent of the s-Si : increases or as t_y decreases, the
averaged SH1, co centration decreases and the time-averaged concentrations of SiH;
time-averaged SiH, concentration in the plasmas increases and the time-averaged SiH, concentration in the plasmas increases and the time-averaged SiH, conc centration decreases and the time-averaged concentrations of SiH^* and negative ions increase. As t_o increases or as t_y decreases, the subsequent growth rate of the a-Si: H films averaged during t_y and
subsequent growth rate of the a-Si: H films averaged during t_y and
subsequent time-averaged SiHx, concentration in the plasmas increases and the plasmas increases and the Ly also increases. Our theoretical analysis shows that the pulse-modulated plasma technique can be an efficient method to reduce subsequent growth rate of the a-Si : H flims averaged during t_{1,} and
subsequent growth rate of the a-Si : H flims averaged during t_{1,} and
ulated plasma technique can be an efficient method to reduce the
previncing the t_{of} also increases. Our theoretical analysis shows that the pulse-mod-
ulated plasma rechnique can be an efficient method to reduce the
holymerized negative ions of higher mass, which are not preferred
precursors for hi ulated plasma technique can be an efficient method to reduce the polymerized negative ions of higher mass, which are not preferred precursors for high-quality thin films and can also be the sources of particle contamination.

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