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Nanoparticles and plasmas*

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Abstract: Nanoparticles can form via chemical nucleation from gas-phase species during plasma processing of silicon films. Nanoparticle-plasma interactions are studied by simulating finite-rate charging and transport of particle nuclei in a low-pressure processing plasma. Results show little change in electron temperature and concentration during the early stages of particle nucleation. However, the ion density profile changes drastically as ions accumulate near the reactor center. Increased ion concentration corresponds to the growing concentration of negatively charged particles, which are shown to have the highest production rate in the reactor center where they are trapped. A significant number of neutral particles are deposited on reactor walls or onto a deposition substrate by diffusion. Positively charged particles impact the substrate at low concentrations but with high energies, which may affect film morphology during plasma-enhanced chemical vapor deposition (PECVD).

Keywords: nanoparticle charging; plasma-enhanced chemical vapor deposition; chemical nucleation; nanoparticle transport; silicon thin films.

INTRODUCTION

Silicon thin films can be deposited by plasma-enhanced chemical vapor deposition (PECVD) using a silane or diluted silane plasma. Under a range of processing conditions, silicon hydride clusters grow to large sizes through chemical reactions, and particle nucleation occurs in the gas phase. Particles may then grow and move throughout the reactor, altering the behavior of the plasma. The deposition of particles and their inclusion in a growing film are undesirable if high concentrations of large particles (tens of nm) are deposited, causing material defects. However, silicon thin films have been found in some cases to benefit from the inclusion of nanocrystallites in the 2–4 nm range, showing increased efficiency in solar cell applications [1]. Controlling the size and concentration of deposited nanoparticles is essential for processing nanostructured materials. Thus, the formation, growth, and transport mechanisms of particles in a plasma environment must be understood to accurately predict particle behavior and produce films of desired composition. A numerical model is used here to simulate a plasma-particle system during PECVD.

Fully modeling a plasma-particle system requires the consideration of chemical nucleation, particle surface growth and coagulation, particle charging, species transport, and plasma reactions. Owing to the complexity of the system, previous modeling work has combined subsets of the above mechanisms as more complete models are created. Bhandarkar et al. coupled a silane plasma chemistry mechanism with particle growth and steady-state charging models in 0D, simulating the temporal evolution of a PECVD system [2]. The extensive chemistry mechanism predicted particle nucleation and surface

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growth rates, representing system behavior in the reactor center, and particle size and charge distributions were presented for growth to about 10 nm. De Bleecker et al. predicted the spatial variation in nucleation rate using a 1D silane plasma chemistry model [3]. This was combined with a particle transport model to explore mechanisms such as ion drag on particles in the 10- to 100-nm-diameter range [4]. In the present study, a 1D model is used to investigate interactions between nanoparticles and a plasma in the early stages of particle formation, before the onset of significant particle growth. The focus of this work is the transport and charging of nuclei (less than 1 nm in diameter) in a PECVD environment, examining particle behavior in both the bulk plasma and plasma sheath regions.

MODEL DESCRIPTION

The model describes a capacitively coupled rf plasma in a parallel plate reactor. The simulation domain is assumed to be radially large compared to electrode separation, thus numerical analysis is reduced to one dimension. One electrode is grounded and represents the location of the deposition substrate, while the other represents the powered electrode and the location of the gas inlet. A particle model is coupled with a plasma model to simulate the temporal and spatial variation of the nanoparticle-plasma system. In the plasma model, the governing equations include the ion and electron continuity equations, an electron energy balance, and Poisson's equation for the plasma potential. A drift-diffusion approximation describes species flux terms, and an effective ionic field has been applied to the ion equation [5]. The Scharfetter–Gummel scheme is applied in discretizing the plasma equations [6,7]. At the electrodes, negative species are assigned a concentration of zero and the concentration gradient is assumed to be zero for positively charged species. In calculating the plasma potential, the time-dependent applied voltage is prescribed at the powered electrode while the other is assigned 0 V. A constant temperature boundary condition is applied to the electron energy equation. The loss of electrons and ions during particle charging is accounted for in the plasma species balance equations, and the energy required for particle charging is included in the electron energy balance. Additionally, charges residing on particles are accounted for in calculating the plasma space charge.

The aerosol general dynamic equation, eq. 1, describes the temporal and spatial dependence of particle concentration N of a given size v, where Γ is particle flux. The source terms on the right side of eq. 1 describe changes in concentration due to nucleation (R_{nuc}) and growth of particles from other sizes due to surface reactions (G_{sg}) and coagulation (G_{coag}). The subscript v indicates that each term refers to particles of a specific size.

$$\frac{dN_v}{dt} + \nabla\Gamma_v = R_{\text{nuc},v} + G_{\text{sg},v} + G_{\text{coag},v} \tag{1}$$

The present investigation is focused on the behavior of nucleated particles before significant coagulation occurs, thus particle growth terms are neglected. A nucleation rate is estimated from results of Bhandarkar et al. [2], and refers to nuclei of bulk silicon density and a diameter of ~0.7 nm. A nucleation zone is prescribed around the reactor center, based on results of De Bleecker et al. [3]. Approximating the nucleation term in this manner replaces the need for a computationally demanding chemistry mechanism. Rather than assuming a steady-state charge distribution, a finite-rate charging scheme is applied to simulate the charging and neutralization of particles. This is necessary to accurately describe particle charge distributions, especially in the sheath region where charging is relatively slow. A charge limitation based on particle size is applied to the model [8], and a balance equation is solved for each discrete charge value (–1, 0, and +1 for nucleus-sized particles). Applying the above assumptions, the change in concentration of a particle of k unit charges is described by the following equation:

$$\frac{dN_k}{dt} + \nabla\Gamma_k = \nu_{i,k-1}N_{k-1} + \nu_{e,k+1}N_{k+1} - \left(\nu_{i,k} + \nu_{e,k}\right)N_k + R_{\text{nuc},k} \tag{2}$$

In eq. 2, the subscript k indicates particle charge and the size-specifying subscript has been dropped for simplicity. The terms on the right side of eq. 2 represent changes in particle charge due to charging collisions with ions and electrons, and $v_{i,k}$ and $v_{e,k}$ are the ion and electron collision frequencies, respectively, with particles of charge k. Collision frequencies between plasma species and particles are calculated according to orbital motion limited (OML) theory [9], assuming that heavy species (neutral gas atoms, ions, and particles) share the prescribed gas temperature. The particle flux term consists of diffusion, drift, ion drag, convection, and thermophoretic components. In a static gas and uniform temperature field, convection and thermophoresis are neglected. Additionally, ion drag is negligible for particles in the size range of interest [7]. Thus, the flux term is reduced to a drift-diffusion formulation, where the particle electric field is taken from the period-averaged plasma field. Similar to the plasma model, the Scharfetter–Gummel scheme is applied for particles and the governing equations are discretized over the model domain. Negative and neutral species are assigned a concentration of zero at the electrode surface, while a concentration gradient of zero is assumed in calculating the concentration of positive ions at the electrodes. Owing to the difference in time scales between plasma and particle response, the solution of the combined model is obtained by a two-step method. First, the plasma equations are solved over several cycles, then, time-averaged plasma parameters are applied to the charging and transport calculations in the particle model. Plasma balance equations are solved self-consistently with particle charging and transport equations to determine plasma properties as well as spatial and charge distributions of particles.

RESULTS AND DISCUSSION

The plasma-particle system is simulated for conditions of nanoparticle formation during PECVD of silicon thin films [10]. A pressure of 100 mTorr (13.3 Pa) and a uniform temperature of 300 K are assigned to the domain. Electrodes are separated by a 3-cm gap, and a voltage of 200 V is applied to the powered electrode, oscillating at 13.56 MHz. The gas is modeled as argon, and the plasma model includes positive argon ions, neutral argon atoms, and electrons. In the nucleation zone, an initial concentration of 10^9 cm^{-3} uncharged nuclei is introduced into a periodic steady-state plasma (at time $t = 0$), and subsequent nucleation occurs at a rate of 10^{12} cm^{-3} s^{-1} for several milliseconds. As particles acquire and lose charge, they spread throughout the reactor, but accumulate in a well-defined region around the plasma center, as shown in Fig. 1. The peak in the center forms rapidly and continues to grow as particles are added uniformly across the nucleation zone (indicated in Fig. 1). These structures are discussed by examining calculated charging frequencies (Fig. 2) and charge-specific particle concentrations (Fig. 3). In Fig. 2a, the rf period-averaged attachment rate of electrons to neutral and positively charged particles is plotted. In both cases, the lowest frequencies occur near the electrodes and the maximum frequency occurs in the reactor center. These profiles reflect the period-averaged electron concentration profile, and do not visibly change within 1 ms. Figure 2b shows the calculated rf period-averaged ion-particle collision frequencies, corresponding to reactor conditions at 0 and 1 ms. The frequency of ion-neutral particle collisions depends strongly on the ion energy, which reaches maximum values at the electrodes and a minimum value at the plasma center. The frequency of ion attachment to negatively charged particles varies inversely with ion energy resulting in the profile shown in Fig. 2b. Between 0 and 1 ms, both ion-particle collision frequencies increase in a well-defined region in the reactor center. This is caused by an increase in ion concentration in a sharp center region, discussed below.

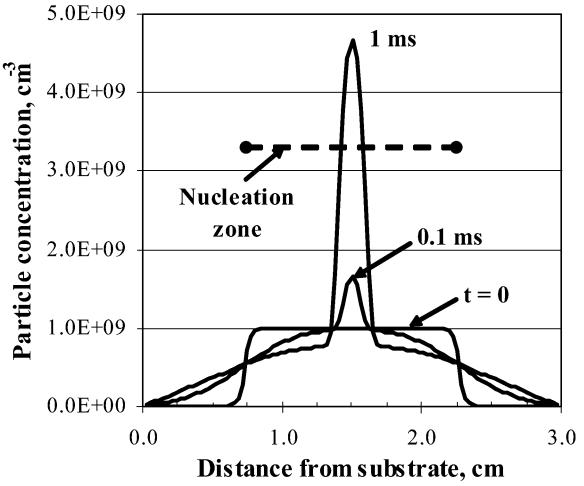

Fig. 1 Total particle concentration at 0, 0.1, and 1 ms after initial particle formation. Nucleation occurs at a prescribed rate in the nucleation zone. Particles spread throughout the reactor but accumulate in a distinct region in the plasma center.

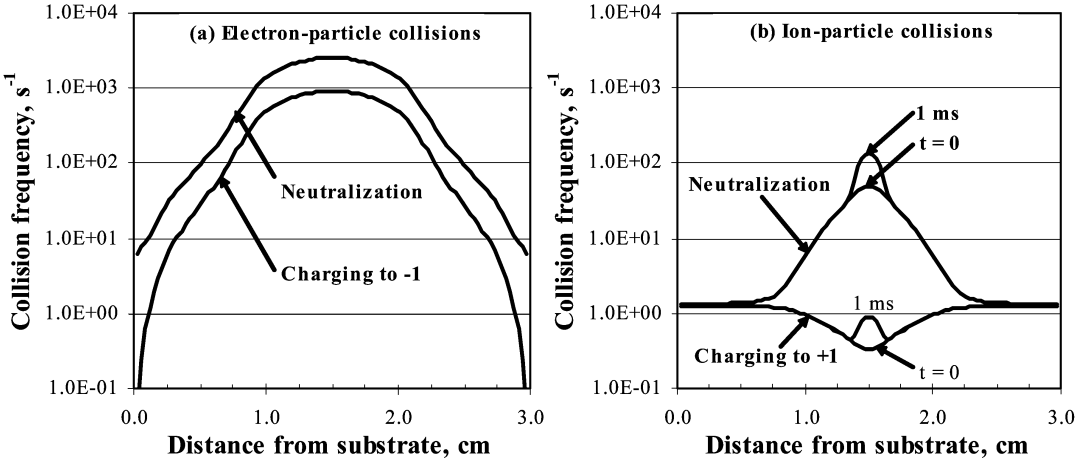

Fig. 2 Collision frequencies for (a) electron-particle collisions and (b) ion-particle collisions. An increase in collision frequency for ion-particle collision occurs in the reactor center between 0 and 1 ms, corresponding to an increase in ion concentration.

Figure 3a shows the concentration of neutral particles between 0 and 1 ms as they appear in the nucleation zone (noted in the figure) and spread throughout the reactor. The maximum electron attachment rate in Fig. 2a corresponds to a charging time on the order of 1 ms, which is the same time scale as neutral particle diffusion under the given conditions. A neutral particle is less likely to become negatively charged as it moves further from the center. Additionally, the frequency of ion-particle collisions occurs on a much slower time scale than neutral particle diffusion. Thus, as shown in Fig. 3a, a significant number of neutral particles diffuse from the nucleation zone toward either electrode, where particles are lost from the system or deposited onto a film substrate. The profile of negatively charged particles, Fig. 3b, shows their accumulation in a distinct region near the plasma center. Negative particles at any location within the reactor are forced toward the center by the electric field, and may only escape if neutralized. However, electron attachment is over 10 times faster than neutralization of a negative par-

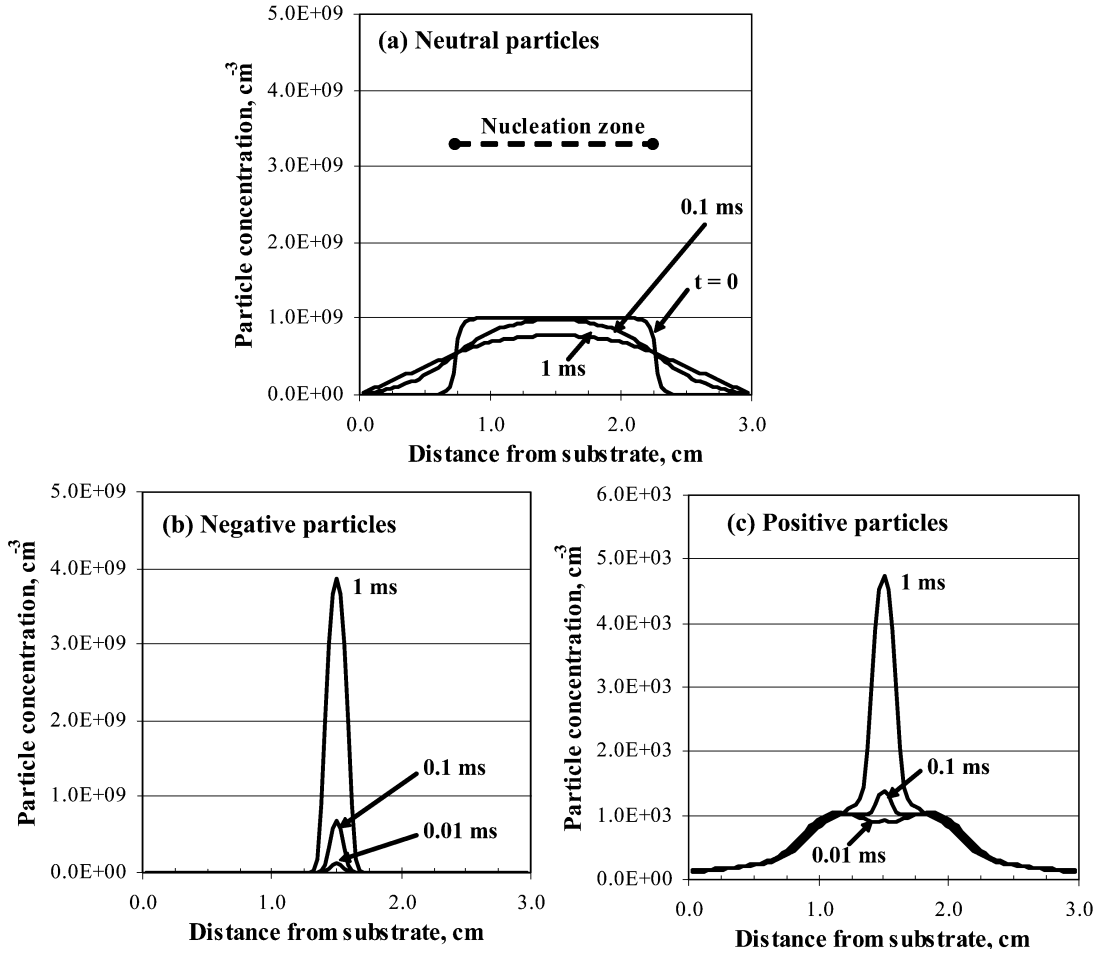

Fig. 3 Concentration of (a) neutral, (b) negative, and (c) positive particles in the reactor up to 1 ms. Neutral particles diffuse toward walls from nucleation zone. Both negative and positive particles have high production rates in the center, but negative particles are trapped in the center while positive particles are accelerated toward either electrode.

ticle in the reactor center (Fig. 2a), causing most particles to become and remain negatively charged. Thus, the accumulation of particles in the center is due to the high electron attachment rate and the trapping of particles by the electric field.

Ion-particle collisions are significantly slower than electron-particle collisions over most of the domain, thus positive particles exist only in low concentrations (Fig. 3c). Initially, a dip in positive particle concentration occurs at the plasma center, corresponding to the location of lowest ion energy and lowest ion attachment rate (Fig. 2b). However, as ion concentration in the center increases, as discussed below, the increased ion-particle collision frequency causes a spike in the positive particle production rate in the reactor center, plotted in Fig. 4. This produces the peak in positive particle concentration shown in Fig. 3c. Local maxima in positive particle production rate appear in Fig. 4 outside the center peak, resulting from the opposing profiles of the particle concentration, minimized at the electrodes, and the ion-neutral particle collision frequency, maximized at the electrodes. Positive particles are forced by the electric field from their production location, away from the plasma center toward the electrodes.

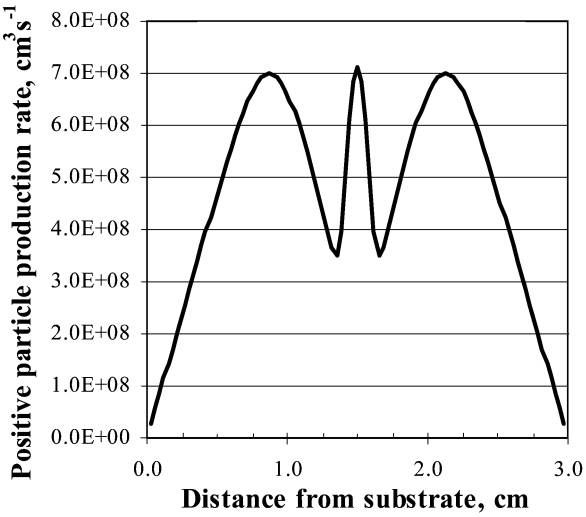

Fig. 4 Positive particle production rate at 1 ms. A peak in production in the reactor center corresponds to the accumulation of positive ions in that location. The peaks away from the center are a result of increasing ion energy but decreasing neutral particle and positive ion concentrations from the center toward the wall.

Positive particles are accelerated as they approach the electrodes and carry high energies when lost from the plasma, thus will deposit on a substrate with high velocity.

After 1 ms, the period-averaged profiles of most plasma variables have not been significantly influenced by the presence of particles. A slight drop in electron concentration in the center is observed due to electron attachment to particles, but changes in electron temperature are unnoticeable. However, the period-averaged ion concentration, Fig. 5, develops a well-defined region of ion accumulation, almost tripling the peak ion concentration at the center of the plasma after 1 ms. Excess ions are produced by a slight increase in ionization and are trapped in the center region by the space charge created by negative particles. Thus, the positive ion concentration grows with the negative particle concentration.

As particles continue to accumulate and become charged in the reactor, the influence on plasma parameters is expected to become more significant due to further depletion of free electrons as nucleation continues to increase particle concentration. The growth of particles is also expected to deplete the free electron supply, as larger particles may become multiply charged. Work in progress includes incorporating particle growth in the plasma-particle model and simulating longer times to further examine interactions between nanoparticles and the plasma during PECVD.

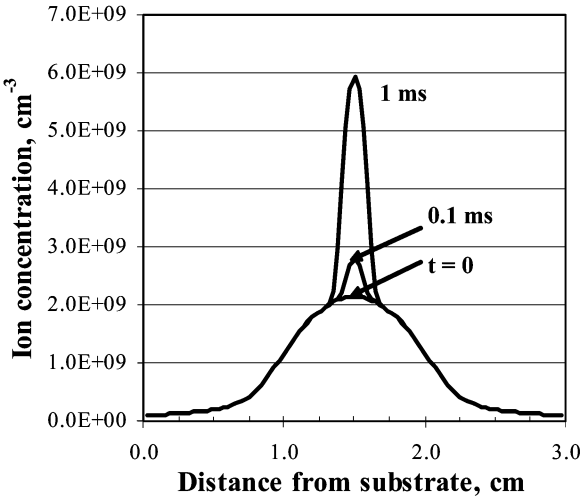

Fig. 5 Ion concentration from 0 to 1 ms. Ion concentration increases in a sharp region near the reactor center, corresponding to the negatively charged particle profile.

SUMMARY

The interactions between nanoparticles and a low-pressure plasma are modeled in the context of PECVD, focusing on the earliest stages of particle nucleation before significant nanoparticle growth has occurred. A 1D model describes the charging and transport of particle nuclei using a finite-rate charging scheme based on OML collision rates. Simulations predict that many neutral particles are able to escape the plasma and deposit on reactor walls or a substrate before becoming negatively charged and trapped in the center region of the plasma. Positively charged particles are shown to exist in low concentrations throughout the reactor and can also deposit in growing films. In the sheath, positive particles are accelerated toward the electrodes due to the strong electric field. The high-energy impact of positive particles on the deposition substrate could influence the morphology of the growing film and change the film properties. The highest production rate of negative particles is found to be in the reactor center where neutral particle and electron concentration are highest. Once charged, negatively charged particles are confined to the center by the plasma potential. Although most plasma parameters change little during the short times discussed here, the ion concentration profile forms a relatively sharp peak in the reactor center, balancing the negative charges residing on particles in the center region. Future work will explore the system at longer simulation times, incorporating growth due to surface reactions and coagulation. Interactions between the plasma and particles are expected to become more significant in time as particles acquire more charge at larger sizes.

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