Monte Carlo hydrodynamic simulation of neutral radical transport in low pressure remote plasma activated chemical vapor deposition

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In electron cyclotron resonance plasma sources for semiconductor processing (1–10 s mTorr), the mean free paths of neutral radical species are commensurate with the dimensions of the reactor. To address these conditions, a hybrid hydrodynamic Monte Carlo simulation has been developed to model the transport of neutral excited state and radical species. The continuity and momentum equations are solved to obtain an average advective flow field. Monte Carlo techniques are then employed to model the trajectories of the neutral particles, while allowing for momentum transfer collisions with the background gas, and chemical reactions. Results are presented for Ar/SiH_4 plasmas where the uniformity of the radical flux and hot atom effects are investigated.

Plasma processing for semiconductor fabrication is moving towards using lower pressures, higher plasma densities and remote plasma sources with the goal of reducing damage, increasing anisotropy, increasing uniformity and reducing particulate contamination.[1,2] Electron cylcotron resonance (ECR) reactors are currently being investigated for both etching and deposition to satisfy these goals.[3] ECR reactors operate at <1 mTorr to 5–10 mTorr, and plasma densities of 10^{11}–10^{12} cm^{-3}. The plasma is typically generated remotely from the substrate in a fairly well confined region located 10 s cm from the wafer. At the pressures of interest, the mean free path for neutral atoms and radicals ($\simeq 8$ cm mTorr) is commensurate with both the distance between the plasma and the substrate, and the transverse dimensions of the reactor.

Another discerning effect occurring at low pressures is the production of hot atoms and radicals during dissociative electron impact excitation of the feedstock gases. Hot radicals are produced when the energy of the transition state of the excited molecule is dissipated into translational modes.[4] In low pressure remote plasma sources, these dissociative processes are the dominant sources of hot radicals which do not undergo symmetric charge exchange with energetic ions.

Modeling transport of neutral radicals in low pressure ECR reactors is problematic since the large mean free path of most radicals nearly places them in the molecular flow regime. These conditions have recently been addressed by Coronell and Jensen[5] in the context of low pressure (1–10 mTorr) thermal chemical vapor deposition (LPCVD). They modeled the transport of reactive gases in cylindrical furnaces using the direct simulation Monte Carlo (DSMC) technique. At pressures exceeding a few mTorr in large reactors, they showed that there are enough collisions to support a pressure gradient. This implies that neutral radicals produced in the plasma zone of an ECR reactor will experience at least a few momentum transfer collisions with the average flow field which directs their motion prior to striking the substrate.

To address these conditions, we have developed a hybrid model for the transport of neutral radicals in low pressure ECR plasma reactors. The model combines hydrodynamic techniques for the advective flow of the background gas with Monte Carlo techniques for the transport of neutral excited states and radicals. It differs from the work of Coronell and Jensen by treating collisions on a particle-mesh basis, as opposed to a particle-particle basis. The model has been applied to study the transport of radicals generated in a confined plasma zone to the substrate.

The model begins by solving for the advective flow field in the reactor while assuming that the conventional hydrodynamic continuity and momentum equations are valid. We acknowledge that the advective flow field is only approximately represented in this manner at pressures of a few mTorr. The advective flow field is not directly used to describe transport of radicals, but rather provides for momentum transfer to those radicals, as described below. The continuity and momentum equations are solved assuming ideal inviscid flow with no slip boundary conditions, couching derivatives in finite difference form, and are integrated with a third order Runga–Kutta technique. The trajectories of neutral excited states and radicals are described using standard Monte Carlo techniques. Collision probabilities are calculated using a modified null cross section technique based on elastic collisions and chemical reactions. A collision cross section is obtained from chemical rate coefficients by dividing by the appropriate thermal velocity. Hard sphere elastic collisions are included with cross sections obtained from Lennard–Jones parameters. Cross sections are assumed to scale as $1/v$, where v is the speed of the neutral particle.

Pseudoparticles representing excited states and radicals are launched from the upstream plasma zone on a quasicontinuous basis. Their initial directions are isotropic with appropriate weighting for the local advective flow field. Their speeds are randomly selected from either thermal or hot distributions. The maximum collision frequency of each species is used to choose a time to the next collision and the equations of motion of the neutral particle are

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integrated for that time. When the collision occurs, a sequence of random numbers is used to determine what type of collision occurs. If the collision is a chemical reaction, the identity of the Monte Carlo particle is revised accordingly and the velocity reinitialized. Particles are removed or added as dictated by the reaction stoichiometry. All particles crossing the plane of the input or exhaust ports are removed from the simulation. Particles striking the walls either reflect, stick, or react based on an assigned reactive sticking coefficient. All particles leaving surfaces are given a Lambertian distribution of velocities (diffuse reflection) with speeds randomly selected from a thermal distribution at the wall (or substrate) temperature.

If a gas phase collision is an elastic momentum transfer collision, we assume that the momentum of the collision partner is given by the velocity components ($\mathbf{v}_a$) of the advective flow field at that location. Recall, however, that the advective flow field is the *net* average velocity of a nearly thermal isotropic distribution of atoms having a thermal speed $v_t \gg v_a$. Accordingly, the velocity of the collision partner is assumed to be the sum of $\mathbf{v}_a$ and a thermal velocity randomly selected from a Maxwell–Boltzmann distribution having the gas temperature. This prevents pseudoparticles from unrealistically pooling near stagnation points in the flow field. The collisional exchange of momentum is calculated using standard elastic collision theory. In this manner the pseudoparticle "senses" the net advective flow field after a statistically meaningful number of collisions. At pressures of many to 10s mTorr the pseudoparticles have enough collisions to nearly come into equilibrium with the advective flow field.

The model system is a two-zone cylindrical ECR reactor (see Fig. 1). The plasma zone (12 cm diam×20 cm long) is located upstream where the gas inlet port is located. The downstream deposition chamber (28 cm diam) is terminated by an annular exhaust port surrounding the substrate holder (22 cm diam). Unless specified otherwise, the substrate is located 30 cm from the end of the upstream plasma zone. For this work, we have simply specified rates of generation of radicals based on results from a separate Monte Carlo simulation. For demonstration purposes, we selected an $Ar/SiH_4=95/5$ gas mixture as used in the deposition of μC-Si. The inlet gas temperature is 300 K, the total flow rate is 100 sccm, and the substrate temperature is 523 K. The species generated in the plasma are Ar(4*s*), H, SiH_2, and SiH_3.

The degree to which the transport of neutral radicals in ECR reactors is affected by the advective flow field is shown in Fig. 1.[6] Here the densities of SiH_3 at 1 mTorr total pressure are plotted as a function of position when momentum transfer from the advective flow field is included (solid contours) and excluded (dashed contours). SiH_3 radicals are primarily generated in the plasma zone from electron impact dissociation of SiH_4 and excitation transfer to SiH_4 from Ar(4*s*). In spite of the modest flow rate, momentum transfer collisions increase the density of radicals downstream compared to the case of pure molecular flow. This results from the fact that the loss of SiH_3 is primarily at the walls. In the case of molecular flow, the

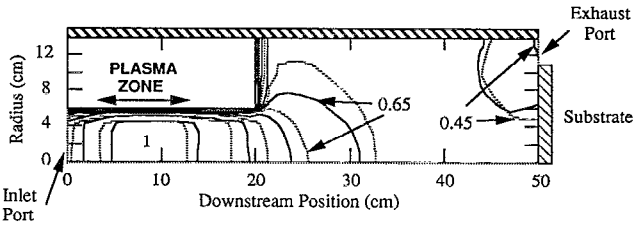

FIG. 1. SiH_3 density as a function of position for a total gas pressure of 1 mTorr. The solid contours show densities (maximum value 4.2×10^{11} cm^{-3}) when including momentum transfer collisions with the flow field. The broken contours show densities (maximum value 4.7×10^{11} cm^{-3}) for molecular flow.

SiH_3 radicals strike the walls more often, thereby decreasing their density. When including momentum transfer with the flow field, SiH_3 is more rapidly directed downstream thereby decreasing the rate of loss at the walls.

The flux of SiH_3 which sticks to the substrate is shown in Fig. 2(a) as a function of radial position on the wafer for three axial locations of the substrate. As the substrate moves further from the plasma zone, the flux is more uniform, though also lower in value. At low pressures, radicals moving ballistically in a critical solid angle defined by the generation zone and the opening to the deposition chamber θ_c, may transport to the substrate without suffer-

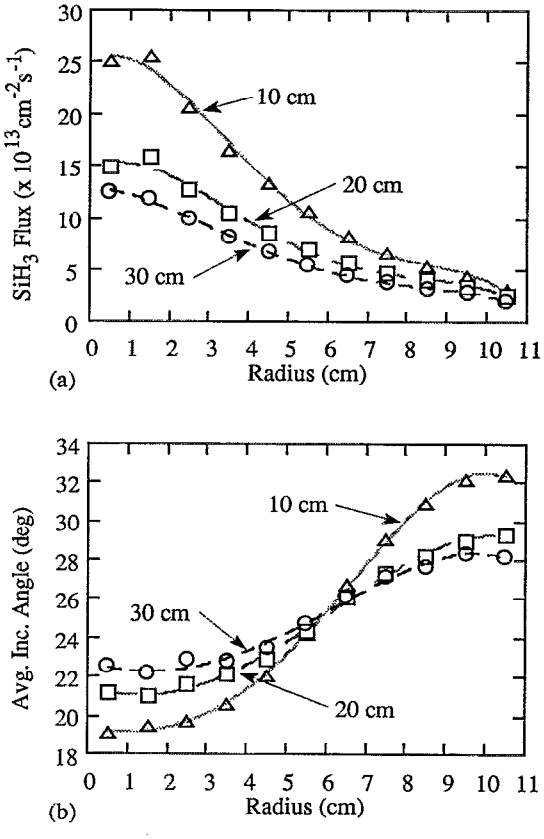

FIG. 2. The flux of SiH_3 sticking on the substrate (a) and the average angle of incidence of particles hitting the substrate (b) as a function of radius on the wafer. Results are shown for various distances between the end of the plasma zone and the substrate.

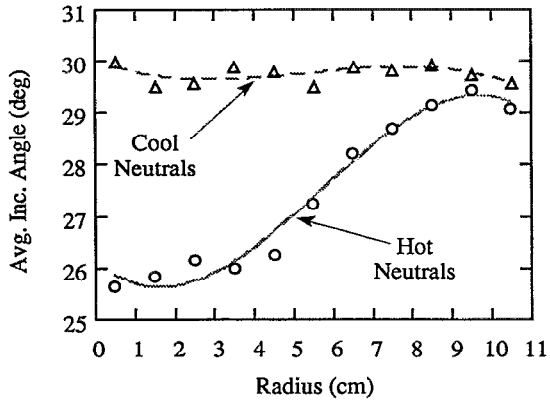

FIG. 3. The average angle of incidence for particles hitting the substrate as a function of radius when radicals are created hot in the plasma zone and when radicals are created at the gas temperature.

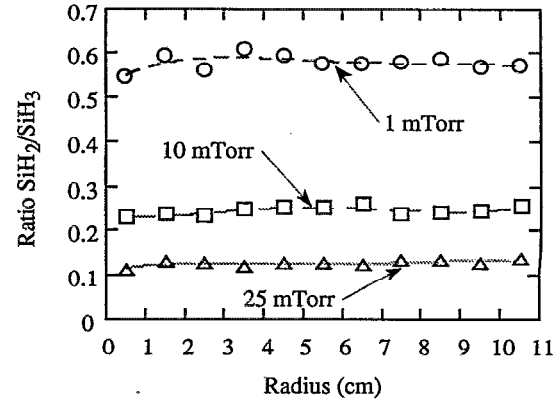

FIG. 4. The ratio of the flux of SiH_2 to SiH_3 sticking to the wafer as a function of radius for various total gas pressures.

ing any wall collisions. Radicals which strike the wafer beyond the area subtended by θ_c must have at least one gas phase or wall collision before reaching the substrate. As the substrate is moved further from the plasma zone, both the area of the wafer subtended by θ_c and the number of collisions increase, thereby making the radical flux to the substrate more uniform.

The ballistic nature of the radical flux also affects the angles of incidence of radicals onto the substrate ϕ. This is shown in Fig. 2(b) where ϕ for all radicals striking the substrate is plotted as a function of position on the wafer for different substrate locations. (Normal incidence has $\phi=0$.) When the stage is close to the plasma zone, radicals strike the wafer with smaller ϕ in the center of the wafer than at the edges. Radicals striking near the center of the wafer have, on the average, had fewer collisions. Radicals striking the edge suffer more collisions and therefore have more isotropic velocities. As the stage is moved further from the plasma zone, the area subtended by θ_c increases and the number of collisions of radicals with gas atoms within θ_c also increases. Therefore, ϕ increases in the center of the wafer, and decreases near the edge.

Hot radical generation can also affect ϕ. Since the collision cross section scales as $\epsilon^{-0.5}$, the mean free path scales as $\epsilon^{0.5}$. To demonstrate the effects of hot radicals in this regard, simulations were performed with radicals created with 2 eV of translational energy and with radicals created with thermal energies. ϕ as a function of radical position on the wafer is shown in Fig. 3. Hot neutrals arrive with more normal angles at all locations compared to thermal radicals, and particularly so in the center of the wafer. This trend is a consequence of the longer mean-free-path of the hot radicals, resulting in there being fewer velocity randomizing collisions.

Although the mean free path of radicals is large at pressures <10 mTorr, the large size of ECR reactors allows a significant number of gas phase chemical reactions to occur. For the pressures of interest, SiH_3 is virtually unreactive in the gas phase and has a low sticking coefficient on surfaces. SiH_2, however, will react with SiH_4

$$SiH_2+SiH_4 \rightleftarrows \overset{Si_2H_6}{\underset{M\uparrow}{Si_2H_6^*}} \rightarrow Si_2H_4+H_2.$$

Since we are in the falloff pressure regime, the preferential branching is to Si_2H_4. SiH_2 also has a higher reactive sticking coefficient on surfaces than SiH_3. The ratio of SiH_2/SiH_3 fluxes to the substrate is plotted as a function of radius on the wafer for 1, 10, and 25 mTorr in Fig. 4. The ratio of these fluxes is nearly constant as a function of radius. The composition of the flux, however, changes significantly with pressure. At low pressures the SiH_2/SiH_3 ratio is determined by the branching ratio of production, somewhat diminished by SiH_2 radicals colliding and sticking to the walls of the narrow plasma zone. As the pressure increases, the SiH_2 flux decreases compared to the SiH_3 flux. This results from there being more velocity changing collisions which increases the flux of SiH_2 into the side walls of the chamber, and from there being a higher rate of gas phase chemical reactions.

In conclusion, a hybrid hydrodynamic Monte Carlo model has been developed for the transport of neutral excited states and radicals at low and intermediate pressures in remote plasma reactors. We used the model to demonstrate the consequences of the ballistic transport of hot and cold radicals to the substrate at low pressure in the context of uniformity of the deposition and angle of incidence.

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[6] A video animation of radical transport using this model can be obtained from the authors. Please enclose a blank standard VHS cassette with your request.