Pulsed plasma-pulsed injection sources for remote plasma activated chemical vapor deposition

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Remote plasma activated chemical vapor deposition (RPACVD) is an attractive fabrication technique owing to the increased selectivity of radical generation which can be obtained compared to deposition techniques in which the substrate is immersed in the plasma. This selectivity can be compromised if the deposition gases, which are typically injected downstream of the plasma zone, back-diffuse into the plasma where indiscriminate electron impact dissociation occurs. In this communication, a new RPACVD technique is described in which the plasma and injected gases are sequentially pulsed to temporally isolate the injected gases from the plasma. This method reduces, or eliminates, indiscriminate dissociation of the injected gases and improves the selectivity of radical fluxes to the substrate.

In conventional plasma enhanced chemical vapor deposition (PECVD), the substrate is located in the plasma chamber where feedstock gases are uniformly mixed.[1] Electron impact dissociation, ionization, and excitation of these gases, followed by chemical and ion-molecule reactions, generate a variety of radicals. Typically, only a subset of these radicals are desired as deposition precursors.[2] Remote plasma activated chemical vapor deposition (RPACVD) is a technique whereby the user has more control over the formation of deposition precursors.[3,4] In RPACVD, the substrate is located outside of the plasma zone. Nondeposition gases, or a subset of the deposition gases, are flowed through the plasma zone. Excited states and radicals flow out of the plasma zone to the downstream deposition chamber where (additional) deposition gases are injected. Excitation transfer and chemical reactions between the plasma activated gases and injected gases produce the deposition precursors. RPACVD affords a greater degree of control over the production of deposition precursors compared to conventional PECVD, since the injected gases are not subject to indiscriminate electron impact dissociation. For example, deposition of μc-Si can be performed by flowing He through the plasma zone and injecting SiH_4 downstream. This arrangement primarily produces SiH_3 radicals by reactions initiated by excitation transfer from He metastables and ions generated in the plasma zone. However, flowing Ar through the plasma zone instead of He produces primarily SiH_2 radicals by reactions initiated by excitation transfer from Ar metastables.[4,5] In this communication, a new RPACVD reactor is described in which deposition precursors can be selectively produced by pulsing the plasma followed by a pulsed injection of the deposition gases.

The basis of selectively producing precursors in RPACVD is that chemical reactions and excitation transfer between plasma activated species and injected gases generate a finite, well-defined set of products. Electron impact dissociation of the deposition gases generally produce any energetically permitted fragments. Therefore, the selectivity of producing deposition precursors in RPACVD is readily compromised if the injected gases are allowed to back diffuse into the plasma zone.[5] At the low pressures (100–300 mTorr) and moderate flowrates (a few hundred sccm) commonly used, the advective residence times of gases in the reactor are tens to hundreds of milliseconds which are commensurate with the diffusion times. Isolating injected gases from the plasma zone is, therefore, difficult, and the selectivity of the downstream reactions are unavoidably compromised by electron impact dissociation in the plasma zone.

A carefully designed reactor can minimize the back diffusion of injected gases into the plasma zone.[5] For example, having a narrow plasma zone compared to the deposition chamber results in jetlike flow of gases through the plasma zone. Diffusion against this flow field, coupled with a smaller opening to the plasma zone, results in a low penetration of the injected gases into the plasma, though it is difficult to eliminate the penetration entirely. Isolating injected gases from the plasma zone by geometry and flowrate will ultimately be limited by practical matters such as pumping speed, and becomes increasingly more difficult as the pressure is decreased. One can, however, obtain almost total isolation of the injected gases from the plasma zone by using temporal as well as spatial isolation. This concept is called pulsed plasma-pulsed injection RPACVD (P^3I-RPACVD).

The basis of P^3I-RPACVD will be discussed in the context of the deposition of μc-Si. The desired deposition precursor is believed to be SiH_3, whereas the undesirable precursors are believed to be SiH_n, $n<3$.[6] SiH_3 radicals can be produced with almost unity branching ratio by hydrogen abstraction reactions with silane;[2]

$$H+SiH_4 \rightarrow SiH_3+H_2. \quad (1)$$

Reactions of H with SiH_3 can produce SiH_2, however, the rate of production of SiH_2 by this process is low since it is a tertiary process. In our demonstration P^3I-RPACVD system a mixture of Ar/H_2 is flowed through the plasma zone and SiH_4 is injected downstream. The plasma is pulsed for few milliseconds while the silane is *not* injected

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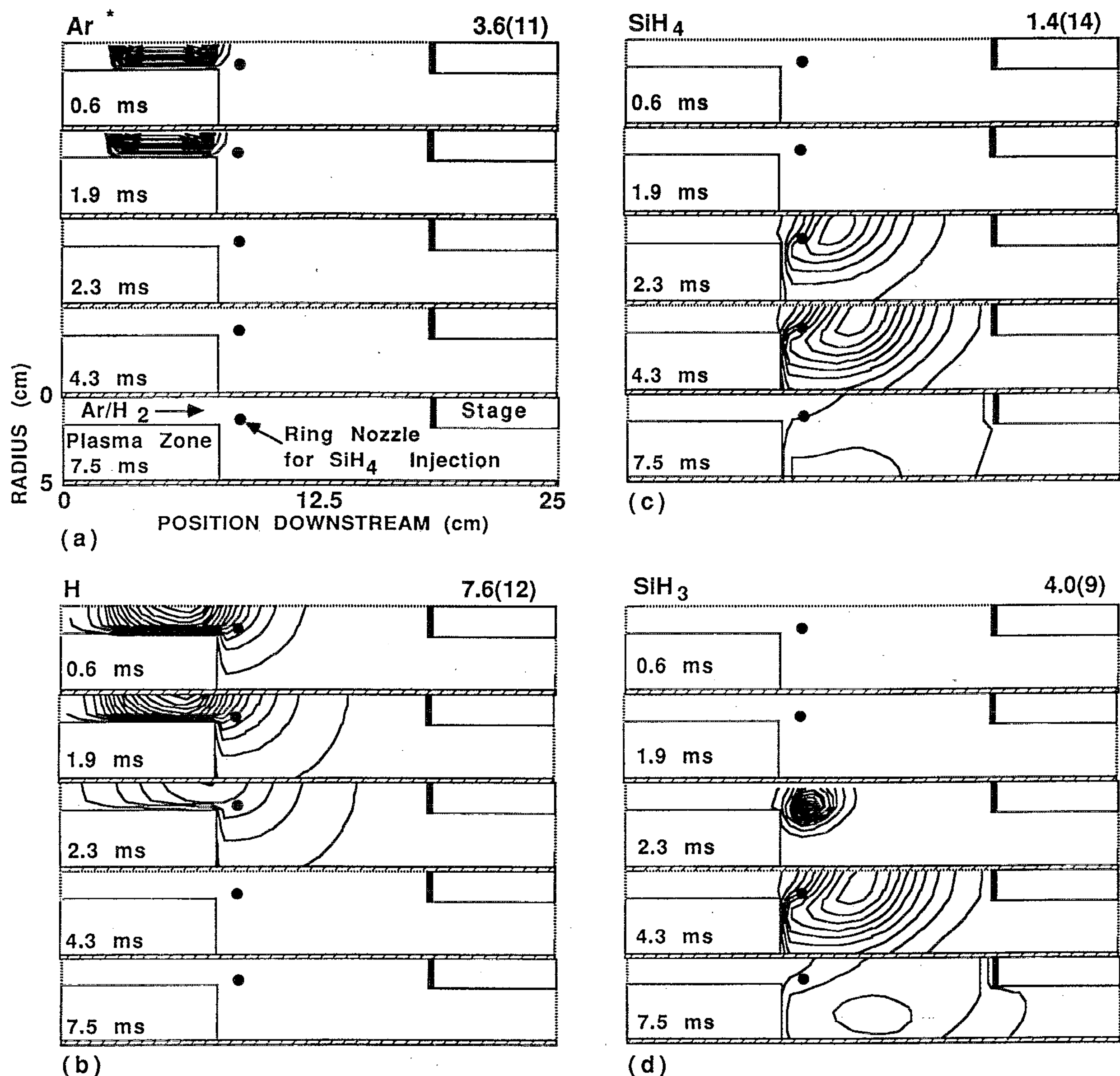

FIG. 1. Densities of selected species during the first P^{3}I-RPACVD sequence (a) Ar(4s), (b) H, (c) SiH_4, and (d) SiH_3. A more detailed schematic of the reactor with dimensions appears in Fig. 2. The maximum densities (cm^{-3}) for the species are shown at the top right-hand side of each figure. Densities are shown at 0.6 ms (during plasma excitation), 1.9 ms (just prior to plasma termination), 2.3 ms (during SiH_4 injection), 4.3 ms (following termination of SiH_4 injection), and 7.5 ms (prior to pulsing the plasma again). The gas pressure is 150 mTorr and flow rate is 400 sccm. $Ar/H_2=80/20$ is flowed through the plasma zone, and SiH_4 is injected through the nozzles at the exit of the plasma zone.

downstream. Electron impact dissociation of H_2 produces H atoms. Electron impact on Ar also produces Ar^+ and excited states which, on the time scales of interest, are immediately quenched by H_2, and do not leave the plasma zone. After a few milliseconds of plasma excitation, a plume of H atoms is produced which convects downstream. The plasma is then extinguished by removing the applied field, and SiH_4 is pulsed through nozzles into the deposition chamber. The plasma recombines and excited states radiatively decay or quench rapidly compared to the convective time scales (ms), and therefore, do not mix with the injected SiH_4. Reactions between the plume of H atoms and the injected SiH_4 produce SiH_3 by reaction in Eq. (1), which convects downstream to the substrate. The injection of SiH_4 is terminated after the H atoms are exhausted. The remaining SiH_4 is allowed to convect downstream, clearing it from the plasma zone before the plasma is pulsed again. With the P^{3}I-RPACVD technique SiH_4 is not in the upstream chamber while the plasma is on, and the only active species which mixes with SiH_4 is H atoms. The reaction chemistry is, therefore, limited to a small subset of those which occur in conventional PECVD,[2] and the selectivity is higher.

P^{3}I-RPACVD has been investigated with a computer simulation. This model was previously described in detail in Ref. 5, and therefore, will only be briefly summarized here. The model is a 2-D (cylindrically symmetric) simulation of the electron kinetics and plasma chemistry of

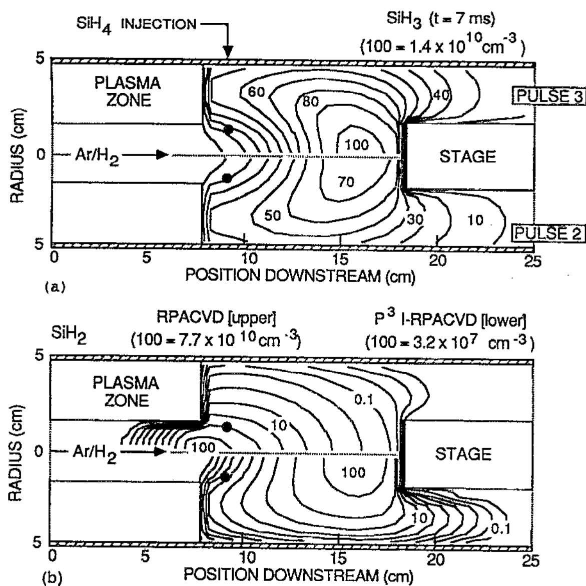

FIG. 2. Densities of radicals during RPACVD. (a) Density of SiH_3 at 7.5 ms (just prior to pulsing the plasma again) at the end of the second P^3I-RPACVD cycle (lower portion of the figure) and at the end of the third P^3I-RPACVD cycle (upper portion of the figure). The conditions are otherwise the same as in Fig. 1. The density of SiH_3 integrates over successive cycles, and the uniformity of the flux of SiH_3 to the substrate improves. (b) Density of SiH_2 during P^3I-RPACVD at the end of the third cycle (lower portion of the figure) and during continuous operation (upper portion of the figure). The production of SiH_2 is significantly suppressed during P^3I-RPACVD.

RPACVD reactors. Continuity equations encompassing kinetics, advection, and diffusion for all species of interest are couched using finite differences and the donor cell method; and integrated using a time slicing technique between kinetics and transport. A companion Monte Carlo simulation is used to generate electron impact rate coefficients. The advective flow field is separately solved for, imported into the model, and uniformly used for all species. The locations of injection nozzles, plasma zone, and substrate are user specified.

The densities of Ar*, SiH_4, SiH_3, and H calculated with the model during the first P^3I-RPACVD cycle are shown in Fig. 1.[7] A more detailed schematic of the reactor containing dimensions appears in Fig. 2. The gas pressure is 150 mTorr, and the flow rate is 400 sccm. An Ar/H_2 =80/20 mixture is flowed through the plasma zone (3 cm diam). SiH_4 is injected at the rate of 15 sccm from nozzles at the exit of the plasma zone in the deposition chamber (10 cm diam). The substrate is located 8 cm from the end of the plasma zone. The plasma is pulsed for 2 ms, followed by 2 ms of injection of SiH_4, and a clearing interval of 3.5 ms before pulsing the plasma again. The density of Ar* [Fig. 1(a)] defines the location of the plasma since it is rapidly quenched by H_2. H atoms [Fig. 1(b)] produced by electron impact dissociation of H_2 and excitation transfer from Ar* drift and diffuse from the plasma zone. At 2 ms, the plasma is terminated, and SiH_4 [Fig. 1(c)] is injected. SiH_3 [Fig. 1(d)] is coincidentally produced by hydrogen abstraction from SiH_4. The H atoms are nearly exhausted by this process. The SiH_3 so produced finally convects downstream to the substrate.

The short duty cycle of the plasma and injection does decrease the rate of generation of radicals compared to continuous excitation and injection. The downstream SiH_3 density will, however, integrate over sequential plasma pulses as shown in Fig. 2(a). This ultimately provides a reasonable density of deposition precursors, and improves the uniformity of the flux of SiH_3 to the substrate.

The selectivity of the P^3I-RPACVD is shown in Fig. 2(b), where the densities of SiH_2 are shown for the conditions of Fig. 1, and when the plasma and injection are continuous. The density of SiH_2 during P^3I-RPACVD is shown at the end of the third cycle ($\simeq$7.5 ms). The density of SiH_2 is approximately 1000 times larger during continuous operation compared to P^3I-RPACVD, largely due to diffusion of SiH_4 into the plasma, which additionally produces SiH_2 by electron impact dissociation, and excitation transfer from Ar*. The density of species which are products of SiH_2 reactions with SiH_4 (e.g., Si_2H_4 resulting from $SiH_2+SiH_4 \rightarrow Si_2H_4+H_2$) are similarly suppressed during P^3I-RPACVD. The close proximity of the injection nozzles to the plasma zone does increase the rate of SiH_2 production during continuous operation compared to locating the injection nozzles downstream. This arrangement is, however, a stringent test of the selective nature of producing radicals which one can obtain with P^3I-RPACVD.

In conclusion, a new method of pulsed plasma-pulsed injection of gases is described for RPACVD which is capable of selectively producing deposition precursors. This is accomplished by isolating the injected gases from the plasma zone both spatially and temporally. The system has been demonstrated by computer modeling where SiH_3 is selectively produced for deposition of μc-Si.

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[7] A video animation of this P^3I-RPACVD sequence can be obtained from the author. Please enclose a blank standard VHS cassette with your request.