Pure Appl. Chem., Vol. 74, No. 3, pp. 483–487, 2002.
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Clustering phenomena in low-pressure reactive plasmas. Basis and applications*

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Abstract: Clustering phenomena of particles below a few nm in size in low-pressure reactive plasmas have been studied in capacitively coupled high-frequency SiH_4 discharges. Clusters nucleate around a size of 0.5 nm, Si_4H_x and subsequently grow due to influxes of Si_nH_x ($1 < n < 4$) and other molecular species. Because of long gas-residence time and small surface loss-probability of clusters, even neutral ones accumulate to nucleate in the reactor. Appearance of negatively charged clusters is considered to become noticeable at around Si_4H_x. The growth of clusters is suppressed by using thermophoretic force, gas flow, periodical discharge modulation, and hydrogen dilution. The reactor has been newly developed to suppress the growth of clusters both by thermophoretic force and by gas flow and evacuation without stagnation. Using the reactor, a-Si:H films of extremely high quality have been successfully deposited.

INTRODUCTION

Formation kinetics of particles in reactive plasmas has been extensively studied using capacitively coupled high-frequency (CCHF) SiH_4 discharges during the last decade. At present, the kinetics has been fairly well understood for particles above a few nm in size [1], and some techniques utilizing it have been proposed to prepare functional powder-materials or films, as represented by a high-quality solar cell utilizing nm-size crystallized particles in argon-diluted CCHF SiH_4 discharges [2]. However, many issues have been left concerning the growth kinetics of clusters, particles below a few nm in size, because there is no method to observe their growth. Understanding of such kinetics is important from viewpoints of their growth suppression and utilization. To study such issues, we have developed two methods for observing *in situ* time-evolution of size and density of clusters: photon-counting laser-light-scattering method applicable in a nm-size range and double-pulse-discharge method applicable in a sub-nm-size range [3,4]. Using the methods, we have succeeded in observing a critical size at which clusters nucleate, and revealed the reasons why the discharge modulation, substrate heating, gas flow, and hydrogen dilution are effective in suppressing the cluster growth.

Recently, we also have developed a reactor which can suppress effectively growth of clusters both using thermophoretic force and realizing gas flow and evacuation without stagnation. The qualities of a-Si:H films deposited with this reactor are much improved as compared to that prepared under the conventional so-called “device-quality” conditions. In this paper, we discuss the growth kinetics and suppression of clusters based on the experimental results obtained using the newly developed observation methods, and show that extremely high-quality a-Si:H films can be prepared by suppressing the cluster growth.

*Lecture presented at the 15th International Symposium on Plasma Chemistry, Orléans, France, 9–13 July 2001. Other presentations are presented in this issue, pp. 317–492.

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CLUSTERING PHENOMENA IN CCHF SiH_4 DISCHARGES

Figure 1 shows size, density, and volume fraction of clusters in a CCHF SiH_4 discharge [4]. There exist two size-groups of clusters: a small size-group which has a constant average size of about 0.5 nm and a density of 10^{10}–10^{11} cm^{-3} during the discharge duration; a large size-group which appears at a time t ~ 10 ms after the discharge initiation and grows up to a few nm at t = 0.5 s, and has a tendency that its density decreases from about 10^{10} cm^{-3} to about 10^9 cm^{-3} due to coagulation. The volume fraction increases monotonously even when coagulations between clusters in large size-group exist. Since clusters of 0.5 nm in size almost correspond to Si_nH_x (n = 4), the result indicates that the clusters in small size-group nucleate around Si_4H_x's. The large clusters Si_nH_x's (n > 4) grow by influxes of Si_nH_x's (n < 4) and other molecular species and/or by coagulation between themselves. The density of clusters observed is quite high compared to that of positive ions, about 10^9 cm^{-3}, in the plasma, and further the density of electrons measured using a microwave interferometer is about 80 % of positive ions, measured carefully with an rf-compensated Langmuir probe, during the discharge. According to ref. [5], the effective attachment rate to clusters tends to increase drastically around a size of Si_4H_x. This suggests that almost all of Si_nH_x's (n < 4) are neutral, and some fraction of Si_nH_x's (n < 4) are charged negatively. In these experiments, the following conditions are satisfied: a cluster growth time is much shorter than a gas residence time T_{res}; a cluster diffusion time to the reactor wall is also much shorter than T_{res}; a surface loss-probability of clusters to the wall, which is deduced from their loss rate after turning off the discharge, is much smaller than unity. Thus, even Si_nH_x's (n < 4) being almost neutral can stay in the reactor during a period long enough for them to nucleate. The growth up to Si_4H_x is considered to be due to the SiH_2 insertion reactions.

A series of such results can be reasonably explained by the following growth model: (1) the short lifetime radicals, especially SiH_2's, generated mainly around the plasma/sheath (P/S) boundary near the powered electrode react rapidly with SiH_4's to produce Si_nH_x's (1 < n < 4); (2) the Si_nH_x's (1 < n < 4) accumulate to nucleate in the reactor because of small surface loss-probability to the reactor wall and long gas-residence time; and (3) the nucleated Si_nH_x's (n < 4), some fraction of which are charged negatively, grow by influxes of Si_nH_x's (1 < n < 4) and other molecular species.

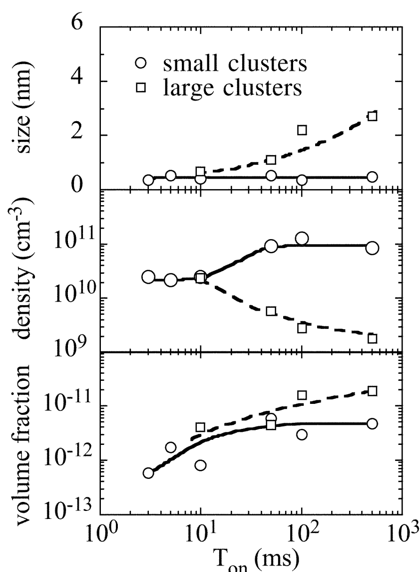

Fig. 1 Time evolution of size, density, and volume fraction of clusters after discharge initiation. Experimental conditions: 100 % SiH_4, 13.3 Pa, 5 sccm (17 cm/s), 10 W (0.18 W/cm^2), 13.56 MHz.

Our experiments have shown a lot of clusters exist even under the conventional device-quality conditions. This implies that some fraction of them are incorporated into depositing films, resulting in their quality deterioration. To suppress deposition of such clusters into films, we have experimentally studied effects of substrate heating, gas flow, discharge modulation, and hydrogen dilution on cluster growth. From these studies, we have obtained the following results: (1) the gas temperature gradient due to heating the grounded electrode is effective in driving clusters above a few nm in size toward the powered electrode of room temperature as shown in Fig. 2 [6]; (2) the gas flow across the radical generation-region around the P/S boundary, is effective in suppressing the cluster growth [7]; (3) the periodical discharge modulation is effective in suppressing the density of clusters when a discharge-off time in one discharge period is long enough compared to a diffusion time of clusters through the radical generation-region [6]; and (4) the hydrogen dilution is effective in suppressing coagulation between clusters in the large size-group [6].

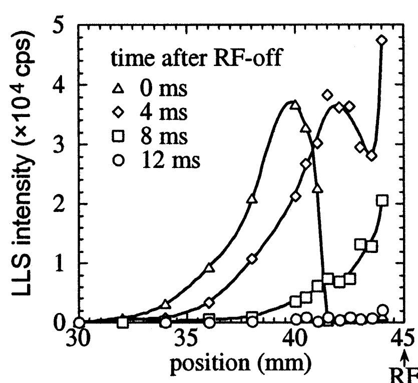

Fig. 2 Transport of clusters toward powered electrode by grounded electrode heating. Experimental conditions: 100 % SiH_4, 13.3 Pa, 5 sccm, 8 W (0.1 W/cm^2), grounded electrode 300 °C.

QUALITY IMPROVEMENT OF a-SI:H FILMS BY SUPPRESSING CLUSTER GROWTH

Clustering phenomena in reactive plasmas are important from two aspects: utilization of them for preparing powder materials of novel or tailored functions and/or high-quality films [2]; production of high-quality films by suppressing cluster growth. Recently, from the latter aspect, we have made a reactor for a-Si:H film deposition, as shown in Fig. 3, in which growth of clusters is suppressed due to gas temperature gradient, gas flow across the radical generation region, and evacuation through both the powered electrode with many holes and four viewing ports on the reactor wall [8]. Figure 4 shows gas-flow-rate dependences of both the ratio R_α of absorption intensity of Si–H_2 stretching mode (2100^{-1} cm) to that of Si–H one (2000^{-1} cm), and the Si–H_2 hydrogen content C_H(Si–H_2) and total hydrogen content C_H(Si–H_2+Si–H), respectively. While the ratio R_α for a-Si:H films under the conventional device-quality conditions is about 0.1, its value for this reactor decreases from about 0.8 at 5 sccm to 0.02 at 20 sccm. Further, C_H(Si–H_2), closely related to efficiency deterioration due to light soaking, also decreases 1 at. % at 5 sccm to 0.2 at. % at 20 sccm, keeping C_H(Si–H_2+Si–H) ~ 6 %. The C_H(Si–H_2) ~ 0.2 % is significantly low compared to about 1 % for the conventional device-quality films. Recently, we have introduced an equipment to make Schottky diode for evaluating the fill factor (FF) of a-Si:H films. The FF value after light soaking of 240 mW/cm^2 for 7.5 h was 0.53. This value is much better than the best ones 0.47 obtained until now. It has been reported that FF and conversion efficiency of a-Si:H solar cell are estimated from the FF value of i-layer [9]. The value of FF = 0.47 above is estimated to correspond to the single junction pin solar cell of FF ~ 0.64 and stabilized conversion

efficiency of about 9.4 %. The FF and conversion efficiency for the a-Si:H of FF = 0.53 in our case are estimated to correspond to 0.78 and 12.3 %, respectively.

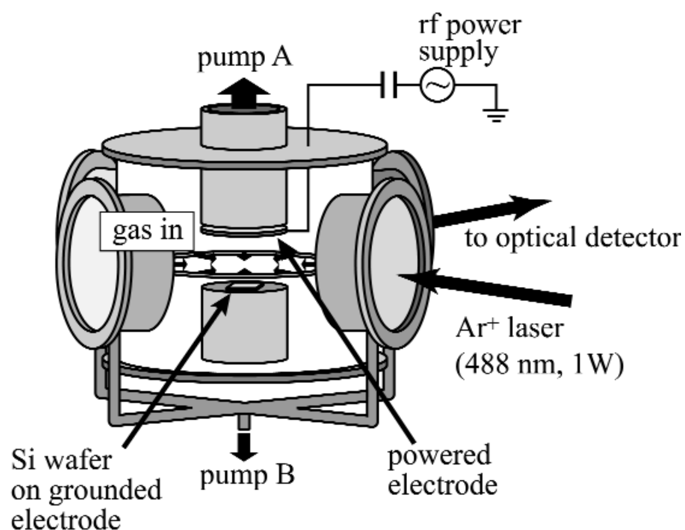

Fig. 3 Newly developed reactor which suppresses cluster growth both by thermophoretic force and by gas flow and evacuation without stagnation.

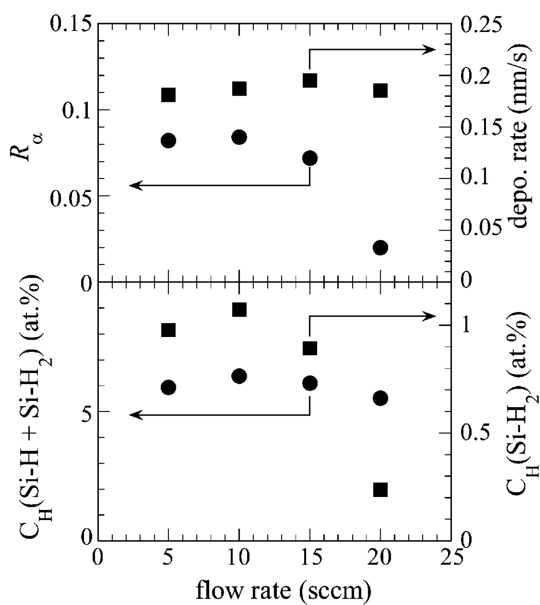

Fig. 4 Qualities of deposited a-Si:H films. Experimental conditions: 100 % SiH_4, 9.3 Pa, 28 MHz, 10 W, grounded electrode temperature 250 °C.

CONCLUSIONS

The clustering phenomena in CCHF SiH_4 discharges have been revealed fairly well using newly developed *in situ* observation methods of cluster growth. The a-Si:H films of quite high qualities compared to those prepared for the conventional device-quality conditions have been obtained by using the reactor in which the cluster growth is suppressed both by thermophoretic force and by gas flow and evacuation without stagnation. This result indicates that the qualities of a-Si:H films are much improved by suppressing the cluster growth even under high-speed-deposition conditions.

Recently, powder formation of various materials, such as SiO_2, SiN and CN, in gas phase have been tried, suggesting the study on clustering kinetics for mixed gases becomes important. While the clusters obtained in our experiments have been amorphous, those for SiH_4 highly diluted by Ar have been nm-size crystallized ones. Also, crystallized clusters have been obtained for SiH_4 highly diluted by H_2. It will be important to identify conditions for which clusters are crystallized, since crystallized clusters may improve film quality, while amorphous ones may degrade the quality.

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