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Surprising temperature dependence of the dust particle growth rate in low pressure Ar/C_2H_2 plasmas

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We have experimentally monitored the growth rate of dust particles in a low pressure Ar/C_2H_2 radiofrequency discharge as a function of the gas temperature T_g and independent of the C_2H radical density and the gas density. Used diagnostics are laser light scattering and measurements of the phase angle between the RF voltage and current. In contrast to most literature, we demonstrate that the growth rate is not a monotonically decreasing function of T_g but shows a maximum around $T_g = 65\,°C$. In addition, we demonstrate that the phase angle is an accurate measure to monitor the particle growth rate. © *2011 American Institute of Physics*. [doi:10.1063/1.3658730]

The possible appearance of dust particles is recognized to be of major importance for almost every application in which chemically reactive plasmas are utilized, e.g., for manufacturing of solar cells, semiconductors, and nanostructures. Also in astrophysics, dusty plasmas play an important role. More recently, the problem of dust particles in nuclear fusion devices, influencing plasma operation, demands for more understanding of the processes that dominate the creation and growth of these particles.[1] An important parameter herein is the gas temperature T_g. Although hydrocarbon plasma chemistry and dust particle formation has been investigated by several researchers,[2–4] experimental data on T_g dependencies are scarce. The few experiments reporting on the T_g dependent particle growth rate R_p in silane and methane all demonstrate decreasing particle growth rates at elevated T_g's.[5,6]

The experiments are performed in a grounded cylindrical stainless steel vacuum vessel (diameter: 300 mm and height: 500 mm), discussed in Ref. 3. The aluminum lid closing this vessel is heated and the gas is supplied towards the showerhead RF powered top electrode (diameter: 138 mm)—ensuring a homogeneous gas flow—through a narrow channel (diameter: 1 mm and length: 80 mm) in the lid material. Since this large length/diameter ratio (80), the supplied gas is safely assumed to have the same temperature as the vessel lid (roughly 13 collisions between gas particles and the lid material). The RF electrode is insulated by a Teflon ring from the grounded setup parts. A grounded cylindrical aluminum plasma chamber (diameter: 140 mm and height: 40 mm) is mounted, electrically and thermally conducting, below the vessel head. The bottom of this chamber consists of an aluminum grid through which the gas can escape without friction. The sidewalls and the bottom have the same temperature as the vessel lid (verified by measurements). Hence, no thermophoretic effects are present. Opposite to each other, the sidewall contains two vertically aligned slits (5 mm in width) through which a vertical sheet of 532 nm laser light is directed radially through the discharge. The pressure p was kept constant at typically 0.3-0.9 mbar. As discharge gas a mixture (8.2 sccm) of 6% C_2H_2 in argon was used. For all measurements, the typical RF (13.56 MHz) plasma power was 5 W. The phase angle between the RF voltage and current φ_{RF} was monitored with 100 ms time resolution by a commercially available radio frequency plasma impedance monitor (PIM) of Scientific Systems. The scattered laser light was collected from below through the bottom grid, after which its intensity I_s was measured with 100 ms time resolution with an Ocean Optics HR2000+ spectrometer.

Formation and growth of dust particles can be described by the four-stage (I-IV) formation mechanism, originally developed for silane discharges;[7] first, negative ions are formed (I) growing due to polymerization chemistry into primary clusters (II). These clusters nucleate into particles of a few nanometers. Once these nanoparticles reach a critical density, they rapidly coagulate (III) to ultimately form permanently negatively charged particles, typically 20-50 nm in size. After coagulation, the particle size increases linearly[4] by deposition of plasma species on their surface (stage IV) while their density n_p remains constant;[7] i.e., the negatively charged particles are confined within the positive plasma potential and no new particles are created since reactive species are rather deposited on the particle's surface than creating new particles. When the particles become too large, the confining electric force is not able to overcome the non-confining ones anymore, the particles are lost from the discharge and n_p starts to decrease. This stage we refer to as stage (V). Figure 1 shows typical measurements of φ_{RF} and $I_s^{1/6}$ for the first 15 s after plasma ignition, demonstrating that it is possible to distinguish between the stages (I), (IV), and (V). Within stage (IV), φ_{RF} increases linearly in good approximation as the growing dust particles extract an increasing amount of free electrons from the discharge, increasing the plasma resistance. The reason for plotting $I_s^{1/6}$ in Fig. 1 becomes clear when realizing that I_s scales with $n_p \cdot r_p^6$. Since in stage (IV) n_p is constant,[7] $I_s \propto r_p^6$ and, consequently, $r_p \propto I_s^{1/6}$. Although no absolute particle sizes can be derived from $I_s^{1/6}(t)$, it does provide an accurate measure for the particle size and the growth rate R_p in relative terms. We define $R_{p,LLS}$ from the slope of the curve in phase (IV) as

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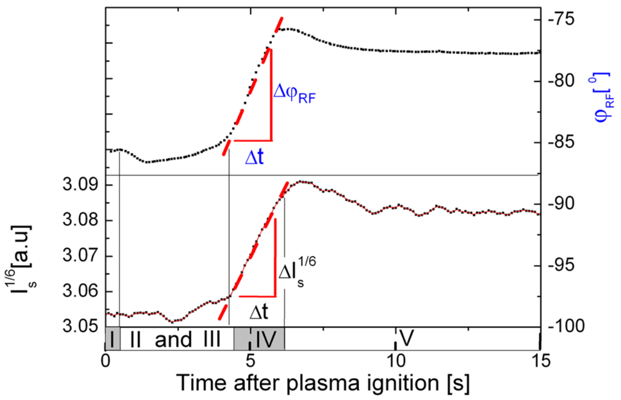

FIG. 1. (Color online) Typical measurements of φ_{RF} (above) and $I_s^{1/6}$ (below) as a function of time after plasma ignition. Below the figure, the several stages of the particle formation and growth mechanism are indicated.

$$R_{p,LLS} = \frac{\Delta r_p}{\Delta t} \propto \frac{\Delta(I_s^{1/6})}{\Delta t}. \qquad (1)$$

As can be observed in Fig. 1, $R_{p,LLS}$ is constant in phase (IV). This is in perfect agreement with constant particle growth rates in comparable Ar/C_2H_2 RF plasmas determined *ex-situ* by means of SEM by Berndt *et al.*[4] Consequently, this is a verification that, indeed, n_p is constant. In Fig. 2, we have plotted the normalized values of $R_{p,LLS}$ at $T_g = 25\,°C$ as a function of p and compared the results with simultaneously measured values of $R_{p,\varphi_{RF}} = \Delta(\varphi_{RF})/\Delta t$. Within the error bars and in relative terms, for each plasma setting $R_{p,\varphi_{RF}}$ shows good agreement with $R_{p,LLS}$. From this, we conclude that $\Delta(\varphi_{RF})/\Delta t \propto R_p$. Since the error bars on the $R_{p,\varphi_{RF}}$ values are the smallest, φ_{RF}-t diagrams were used to determine normalized R_p values as a function of p for five more gas temperatures. Three of those data sets are plotted in Fig. 2.

In Fig. 2, for each value of T_g a pressure p_{pl} exists (see indicated for $T_g = 150\,°C$) below which R_p increases with p and above which R_p becomes independent of p (a plateau is observed). The height of this plateau shows a maximum as a function of T_g (see Fig. 3). For $p < p_{pl}$, at higher pressures the increasing precursor density results into a higher dissociation rate, creating more C_2H radicals per unit of time. Since it was shown that densities of positive ions are lower than the density of radicals by a factor of 1000,[8] and the sticking factor for ions (roughly 1) is close to that of C_2H radicals (0.92 ± 0.05 (Ref. 9)), we assume that dust particles grow due to deposition of mainly C_2H radicals onto their surface. Increasing p thus leads directly to increasing R_p. At constant mass flows, increasing p also leads to an increased residence time τ_{res} of the gas in the plasma volume and apparently, at $p = p_{pl}$, τ_{res} is sufficiently long for all injected C_2H_2 molecules to be dissociated before leaving the plasma volume. For $p > p_{pl}$, the amount of C_2H radicals created per unit of time is independent of p and limited by the constant C_2H_2 inflow. Hence, R_p remains constant. An estimate of the typical dissociation time τ_{diss}, given by $(n_e k_{EID})^{-1}$ with the electron density n_e typical $10^{15}\,m^{-3}$ (Ref. 10) and k_{EID} the electron impact dissociation rate ($6 \times 10^{-16}\,m^3/s$ (Ref. 4) at 2.5 eV (Ref. 10)), gives $\tau_{diss} = 1.7$ s. Indeed, this is in the same order as $\tau_{res} = 2.1$ s (at 25 °C and $p = p_{pl} = 0.47$ mbar). Also, the obtained values of p_{pl} scale with T_g according to the ideal gas law, enhancing the conclusion that $\tau_{diss} = \tau_{res}$ at $p = p_{pl}$. Performing measurements at p_{pl} for each temperature consequently allows to study R_p as a function of T_g independent on gas density (constant) and radical density (100% dissociation of the partial C_2H_2 gas density). Where most experiments and computer simulations reported in literature claim monotonically decreasing growth rates at elevated temperatures, we observe that the growth rate has a maximum around 65 °C. Giving an explanation for the observed maximum without a sophisticated model is rather difficult. However, it might be clear that more temperature dependent effects compete. For instance, at the left-hand side of the maximum, the increase in radical velocity and radical flux towards the particle with increasing temperature likely dominates. At the right-hand side, two effects might play a role. First, the value of n_p might change with temperature. However, the critical density and radius of dust particles before coagulation do not vary with temperature.[11] Second, the residence time of radicals on the particle's surface decreases with gas/particle temperature[9] radicals finding an open bond to strongly chemisorb with becomes less probable, fewer radicals chemisorb and R_p is decreased.

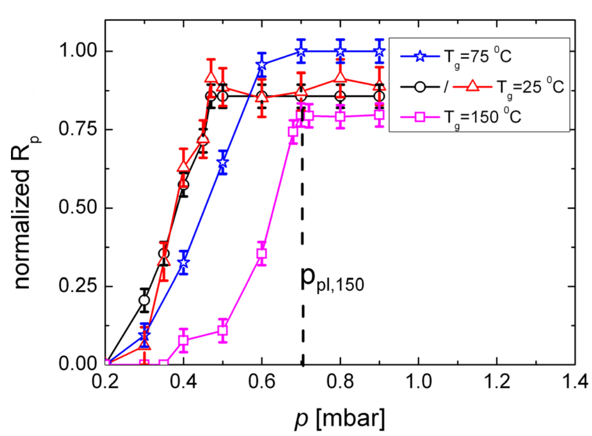

FIG. 2. (Color online) Normalized value of the particle growth rate R_p as a function of pressure for three values of the gas temperature. For $T_g = 25\,°C$, the R_p values determined from φ_{RF} measurements (black circles) show, within the error bars, good agreement with those determined from scatter measurements (red triangles up).

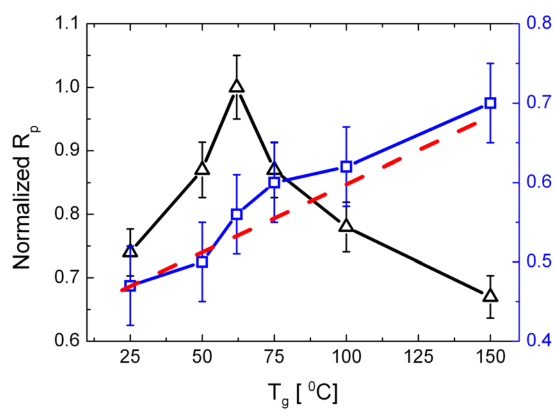

FIG. 3. (Color online) p_{pl} measured as a function of T_g (blue squares) showing good agreement with the ideal gas law (dashed red line) starting from ($T_g = 25\,°C$, $p_{pl} = 0.47$ mbar), together with the normalized R_p (black triangles up) at the corresponding temperature and pressure combination.

In conclusion, we have experimentally obtained the growth rate of dust particles in Ar/C_2H_2 RF discharges as a function of pressure and temperature. The results show a maximum in the particle growth rate around 65 °C. To the best of our knowledge, this has never been observed before.

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