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Gas temperature dependence of coagulation onset times for nanoparticles in low pressure hydrocarbon plasmas

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Onset times for coagulation of nanoparticles in chemical reactive low pressure Ar/C$_2$H$_2$ and Ar/CH$_4$ radiofrequency (rf) discharges have been measured as a function of the gas temperature while either the gas pressure or the gas density was kept constant. As a diagnostic, the phase angle between rf voltage and rf current was monitored. The results demonstrate, within the temperature range 25 °C–150 °C, that for both gases coagulation is delayed significantly (by more than a factor of 10) for increasing temperatures. These results are explained in terms of the temperature dependence of the Brownian diffusion coefficient. © 2013 AIP Publishing LLC.

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Recent significant developments in nanotechnology, micro-electronics, and lithography have triggered even more attention to nanoparticles which are—under many circumstances—spontaneously grown in processing plasmas. Industrial applications where these plasma-grown particles contaminate, i.e., complicate, production processes are those used for etching, for deposition, and for sputtering. Significantly affected are the billion dollar solar cell and semi-conductor industries and production facilities for the fabrication of nanotubes and other nanostructures; in many of these applications, chemical reactive (hydrocarbon) plasmas are utilized. Also in future nuclear fusion devices dust particles formed by plasma-nucleation of wall material influence plasma operation negatively. For all these issues, it is essential that fundamental processes responsible for the formation of nanoparticles in plasmas are well understood. Although the research area regarding plasma chemistry in silane has been developed over the last decades, up to today many details—and especially the observed significant dependencies on the gas temperature $T_g$—are still poorly understood. Generally accepted is the four stage formation path through which dust particles are formed in reactive plasmas: (i) formation of negative ions, (ii) nucleation into protoparticles (several nanometers in size) with time varying charge, (iii) coagulation into larger particles (>20 nm) with permanent charge, and (iv) particle growth by deposition of plasma species on the particle’s surface. Here, the coagulation stage is essential since after coagulation the particles have permanent negative charge, will be confined in the plasma potential, and can grow towards sizes where they are harmful for the application purpose. It was experimentally observed that nucleation in low pressure argon-silane discharges significantly delays when $T_g$ is increased. In order to understand this delay, several explanations have been proposed. Fridman et al. proposed as possible explanation an increased de-excitation of vibrationally excited precursor molecules at elevated $T_g$. Perrin et al. explained this effect by reduced electron attachment rates (at constant pressure) forming less primary anions. Finally, Warthesen et al. proposed a decreased gas density (at constant pressure) explaining the observed effect. Bhandarkar et al. showed in a comparisonal numerical study that—although present—none of these processes could adequately explain the observed delay. Those authors demonstrated that the temperature dependence of the Brownian diffusion coefficient was the most dominant factor in the nucleation delay in silane. With respect to the gas temperature dependence of nanoparticles formation in silane based plasmas, some researchers have discussed processes in terms of diffusion times of protoparticles and their critical density necessary of coagulation onset. For Ar/CH$_4$ discharges, the temperature dependence of the coagulation time has been studied experimentally. However, although acetylene containing discharges are used very often and in many applications, no experimental data on temperature dependent coagulation times have been published in literature up to today.

In this letter, we present measurements of the coagulation onset time $\tau_{coag}(T_g)$ in both Ar/C$_2$H$_2$ and Ar/CH$_4$ discharges and as a function of $T_g$. In order to differentiate form gas density effects, $\tau_{coag}(T_g)$ was measured for both configurations: (a) gas pressure $p_g$ kept constant and (b) gas density $n_g$ kept constant.

The experiments are performed in a grounded cylindrical aluminum plasma chamber (140 mm in diameter and 40 mm in height). The electrically insulated top lid of this vacuum chamber is of the showerhead type (through which gas is homogeneously supplied) and powered with a 13.56 MHz voltage signal. The grounded bottom lid is an aluminium grid with approximately 80% transparency through which the gas can escape without friction. Based on the used pressure and gas flow, it can be assumed that operation is within the laminar flow regime. The temperature of the plasma chamber can be set at a desired temperature while the gas mixture is supplied through a stainless steel tube set at the same temperature. Detailed information about the rest of the experimental setup is given in Ref. 10. Since the length-diameter ratio of the tube is larger than 10, it can safely be assumed that the gas temperature is equal to the set temperature. A Smart PIM radio

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frequency Plasma Impedance Monitor of Scientific Systems measures with 100 ms time resolution the phase angle $\phi_{RF}$ between the rf voltage and rf current. In former studies, we have already shown that the phase angle is an adequate parameter to detect particle growth and—especially—coagulation onset times.  

Fig. 1 shows a typical measurement of $\phi_{RF}$ as a function of time. As is common for capacitively coupled discharges, values close to $90^\circ$ are measured. In the figure, the earlier discussed stages (I-IV) are denoted. On these time-scales, the increased plasma resistivity due to the formation of negative ions can hardly be observed. In stage II, these ions continue to grow, while in stage III, the coagulation process starts. In this phase, the particles gather permanent charge due to which free electrons are extracted from the discharge, altering the plasma towards a more resistive regime. As discussed, in stage IV, the particles grow further and extract even more free electrons from the discharge. In stage V, the particles have grown too large and will be lost from the discharge. From measurements, such as presented in Fig. 1, the coagulation onset time $\tau_{coag}$ (transition from stage II to stage III) can clearly be determined. In Fig. 2, $\tau_{coag}$ in an Ar/C$_2$H$_2$ discharge is plotted as a function of gas pressure for three values of the gas temperature. As can be observed from this figure, both increasing the gas temperature and lowering the gas pressure delay coagulation.

In order to provide more insight in the temperature dependence, $\tau_{coag}$ has been plotted as a function of $T_g$ for constant gas density and for constant gas pressure for an Ar/C$_2$H$_2$ and for an Ar/CH$_4$ discharge in Figs. 3 and 4, respectively. Two main observations can be made from these figures. First, $\tau_{coag}$ in the case of argon-methane is significantly longer than in the case of argon-acetylene. This has been observed earlier and is explained by the fact that— even in methane containing plasmas—the formation of protoparticles is initiated by anion formation starting from C$_2$H$_2$ molecules. Where in argon-acetylene, anion formation starts straight away, in argon-methane, the CH$_4$ precursor molecules first have to be transformed into C$_2$H$_2$. This additional crucial step—of course—delays all the following stages.

Also, it should be noted that in order to initiate dust particle formation in argon-methane discharges, significantly higher plasma powers (~50 W) are necessary when compared with the situation in Ar/C$_2$H$_2$ discharges (~5 W). This, as well, is in agreement with other studies in literature. The second observation is the fact that $\tau_{coag}$ is significantly delayed as a function of gas temperature under both constant pressure and constant density. This applies for both gases.

In order to gain insight in the dependence of $\tau_{coag}$ upon $T_g$, we consider that a certain critical density $n_{cr}$ of protoparticles needs to be reached within time $\tau_{coag}$, where it is assumed that all protoparticles have equal size $r_{cr}$. From literature, it appears that $r_{cr}$ and $n_{cr}$ do not depend on temperature. Furthermore, these protoparticles are neutral or have plus or minus one elementary charge. Just after plasma ignition, the bulk of the protoparticles is neutral. While diffusing towards the boundaries of the discharge, these particles might become positively or negatively charged stochastically. Diffusion of these small particles through a background gas can be described well with the concept of Brownian diffusion. A rough estimation of the diffusion time...
In conclusion, we have monitored experimentally the gas temperature dependence of the coagulation onset time in low pressure Ar/C$_2$H$_4$ rf plasmas. These data are compared with measurements in comparable Ar/CH$_4$ discharges. For both gases and under both constant gas density and constant gas pressure, coagulation times are significantly delayed although the temperature dependence under constant gas pressure is much stronger. The observed trends could be explained in terms of the temperature dependence of the diffusion coefficient for neutral nanoparticles.

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