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Dust Growth Instabilities in Silane-based Plasmas

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Abstract. In this paper we report on two instabilities observed in dusty plasmas, at different stages of dust particle formation. Experiments are performed in a low-pressure Ar/SiH₄ radiofrequency plasma. The first instability, occurring at the transition between nanocrystal accumulation and coalescence phases, is very sensitive to operating conditions. It is shown to be a good indicator of the end of nanocrystal accumulation phase in the plasma. This “coalescence instability” seems to be an attachment induced-ionization instability as observed in electronegative gases. The second instability starts during the second dust generation formation. It exhibits a complex scheme closely linked to dust successive generations. This instability is suspected to be a void instability. Indeed, the occurrence of this “successive generation instability”, combined with laser light scattering and Ar*(750.38 nm) line spectroscopic measurements indicate a possible void region in the dust cloud, as observed in PKE experiments.

Introduction

Plasma is the most common state of matter. It is often said to be 95 to 99% of the Universe, even if this assertion is quite impossible to verify or to disprove! But one thing is quite sure: plasma filling Universe is in most cases a dusty plasma (also called “complex” plasma). Dusty plasmas, as their name indicates, are plasmas containing immersed dust particles ranging in size from a few nanometers to tens of micrometers. They can be found as well in astrophysical environments (solar winds, planet atmospheres, Saturn rings, comet tail...) as in industrial ones (plasma processing such as etching or thin film deposition). Laboratory dusty plasmas are known for a long time now. *Langmuir et al.* [1924] reported on tungsten “solid particles or aggregates” he observed in an electric discharge in 1924. Nowadays laboratory dusty plasmas are produced by different ways: using reactive gases (silane, methane, acetylene...), sputtering a target or a deposited layer (carbon, silicon, polymer...), or injecting calibrated dust particles (silicate, melamine formaldehyde...).

Dusty plasmas generated in radiofrequency (rf) discharges are widely studied since the 90's. First dust particle observations in processing plasmas were reported by *Roth et al.* [1985] in 1985 for silicon deposition plasmas and by *Selwyn et al.* [1989] in 1989 in silicon etching plasmas. A first burst of interest has been induced by those contamination phenomena in industrial plasma reactors. Since then, dust particle formation has been widely studied principally in Europe and Japan. Lots of publications have been produced on this topic (see for example the work of *Watanabe et al.* [1988]; *Bouchoule et al.* [1991]; *Böhm and Perrin* [1991]; *Howling et al.* [1991]; *Stoffels et al.* [1996]). In the 90's the main goal of those studies was to understand dust particle formation to avoid it in industrial reactors. In the 2000's, a second burst of interest has been induced by potential applications of single-crystal and/or polycrystalline dust particles. Indeed, new applications of dust production have emerged. It can be used to produce analog aerosols of planet atmospheres like Titan as demonstrated by *Cernogora et al.* [2005] and *Szopa et al.* [2006]. Single-crystal nanoparticles can also be obtained by this way, and then can be incorporated in thin film layers in order to improve their mechanical and/or optoelectronic properties [*Roca i Cabarrocas et al.*, 2004], or used for single electron device fabrication [*Tiwari et al.*, 1996].

Dust particles immersed in a plasma acquire a negative charge by collecting electrons and ions from the plasma [*Barkan et al.*, 1994]. *Couëdel et al.* [2006] showed that dust particles conserve a part of their charge after plasma extinction. Dust particles experience several forces, some of them are due to their charge, that act either to confine them to the plasma (electrostatic force) or to drag them to the walls (gravity, ion drag, neutral drag, thermophoresis). Depending on the equilibrium between these forces, the dust cloud trapped in the discharge can have various shapes: few layers of dust particles located near the sheaths or 3D cloud filling the whole inter-electrode gap. The slightest modification of the force balance leads to strong modifications of the dust cloud behavior. Most common cases are void formation, instabilities of the dust cloud and/or instabilities of the void. The void, a dust-free region in the dust cloud, has been first observed by *Dorier et al.* [1995] and then by *Praburam and Goree* [1996], *Mikikian*

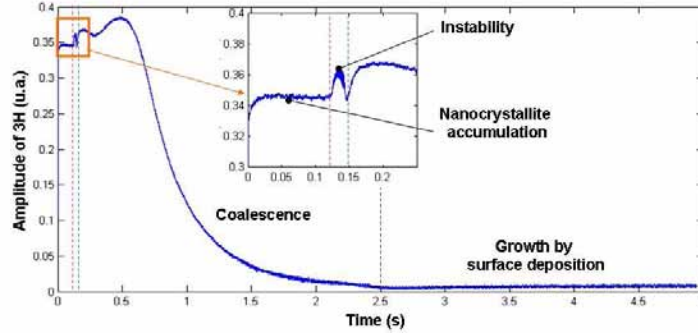


Figure 1. Main formation steps on 3H in an Ar/SiH₄ plasma.

et al. [2003]... It can be observed both in plasma processing discharges and plasma sputtering discharges. The void structure is widely studied on a theoretical point of view [Mamun *et al.*, 2002; Goree *et al.*, 1999]. Lots of instabilities of the dust clouds (streaming, ion drag force induced, dust charge gradient induced, drift wave, parametric instabilities etc...) have been identified [Shukla and Mamun, 2002], and some instabilities of the void region have also been reported. We can cite as examples the filamentary and great void mode reported by Praburam and Goree [1996] and Samsonov and Goree [1999] or the so called “heartbeat” instability reported by Mikikian and Boufendi [2004]. Instabilities linked to dust particle formation and growth in sputtering and deposition discharges have also been reported recently [Cavarroc *et al.*, 2006a; Mikikian *et al.*, 2006].

In this paper, we report on two instabilities observed in an Ar/SiH₄ plasma, and the possible apparition of a void region after the first dust particle generation. The second instability addressed is indeed suspected to be a void instability.

Experimental set-up and diagnostics

The experimental set-up used to carry out this work has already been described in detail in previous papers [Boufendi *et al.*, 1992, 1993; Bouchoule *et al.*, 1991]. The rf discharge is produced in a grounded cylindrical plasma box (13 cm diameter). The plasma box is closed at the bottom by the driven electrode (3.3 cm for inter-electrode distance). It is a shower-head one in order to ensure a homogeneous gas distribution at the entrance of the plasma zone. This electrode is connected to a 13.56 MHz rf generator through a matchbox including a blocking capacitor. The whole system is enclosed in a vacuum chamber. The power can be varied from 0 up to 20 Watts. The gas temperature can be varied from -40°C up to 150°C and is measured in the gas flow just below the plasma box by a thermocouple. Typical experimental conditions are: argon-silane mixture with a total pressure around 120 μ bar.

As dust grains affect many of the physical properties of the plasma (electron density and temperature, electric field, impedance, ...) it led us to use a diagnostic based on the time evolution of the amplitude of the discharge current third harmonic (3H) and the amplitude of the self-bias voltage (V_{dc}) [Boufendi *et al.*, 2001]. This electrical diagnostic has been developed in the GREMI laboratory. The probes are inserted between the matchbox and the rf electrode. Curves are visualized on a scope and results are recorded via a computer. This diagnostic has been shown to be able to follow dust particle formation and growth in different chemistries such as silane and methane based ones [Mezghrane *et al.*, 2004]. Thus, in a pure argon plasma, the amplitude of 3H and V_{dc} remains constant in time, while when silane is added to the mixture, i.e. in a dust forming plasma, V_{dc} and 3H show a time evolution due to dust formation and growth in the discharge. The main formation steps can be clearly identified thanks to this electrical diagnostic (figure 1). Even though, some uncertainties are remaining concerning the exact transition from one step to another. As can be seen in figure 1 insert, an instability occurs in between accumulation and coalescence phase [Cavarroc *et al.*, 2006a].

Coalescence instability

This instability occurs at the transition between two formation steps (accumulation and coalescence). A complete study concerning both fundamental aspects and potential applications has been performed by Cavarroc *et al.* [2006a,b]. This instability appears as oscillations on all the diagnostics used: potential measurements (V_{RF} , V_{dc} , V_f), current harmonic measurements (1H, 3H) and ion flux measurement (V_i).

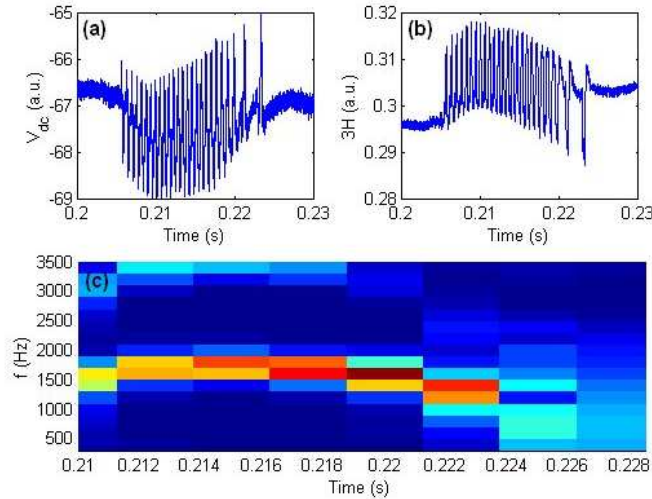


Figure 2. Time-evolution of V_{dc} (a) and $3H$ (b) during the coalescence instability, (c) spectrogram of $3H$.

Figure 2 shows an example of this instability both on $3H$ and V_{dc} . It affects many properties of the dusty plasma. Its typical characteristics have been determined: frequency in the kHz range, duration of a few to a few tens of ms and appearance time between 100 and 200 ms after the plasma ignition. In order to understand this phenomenon, we needed to know its exact location with respect to dust formation steps. Some depositions were performed just before, during and after the instability and analyzed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), leading to the conclusion that the instability onset exactly corresponds to the coalescence beginning (i.e. end of accumulation phase). The instability frequency has been shown to evolve in time thanks to a FFT analysis (using a sliding window). This evolution can be explained by the increase of the particle mean mass during the instability, leading to modifications of the plasma-dust frequency.

The effects of operating conditions on the instability have also been investigated. A pressure threshold of disappearance around $150 \mu\text{bar}$ has been evidenced. The rf injected power and the silane flow rate have been shown to have a significant effect on the instability characteristics (appearance, duration, frequencies...) [Cavarroc *et al.*, 2006a]. The gas temperature, investigated from -24°C to 120°C has also a significant effect on the instability duration, but does not seem to affect the appearance of the phenomenon. Finally, a very particular case of instability, showing a short replica of its end, has been evidenced in two very tight sets of parameters. An experimental criteria for the instability appearance in the most common cases has been determined.

Thanks to a comparison with the work of Descoedres *et al.* [2003], a possible explanation of the instability is given. It seems to be an attachment induced-ionization instability as observed in electronegative gases [Nighan and Wiegand, 1974; Descoedres *et al.*, 2003]. Nighan and Wiegand [1974] gave a criterion for the appearance of the instability:

$$R = \frac{\partial k_a / \partial T_e}{\partial k_i / \partial T_e} > 1, \quad (1)$$

where k_a and k_i are respectively the attachment and ionization coefficients and T_e the electron temperature. We showed that in our conditions the criterion is met. The instability we observe can thus be linked to the attachment induced-ionization instability [Cavarroc *et al.*, 2006a].

Moreover, its exact location at the end of nanocrystal accumulation phase makes it a very good mark for single-crystal silicon nanoparticle deposition. Indeed, nanocrystals are single-crystal silicon nanoparticles of 2-3 nm in diameter in the FCC phase [Viera *et al.*, 2002] at room temperature. Nanocrystals obtained by this way can be incorporated in thin film layers in order to improve their mechanical and/or optoelectronic properties [Roca i Cabarrocas *et al.*, 2004], or used for single electron device fabrication [Tiwari *et al.*, 1996].

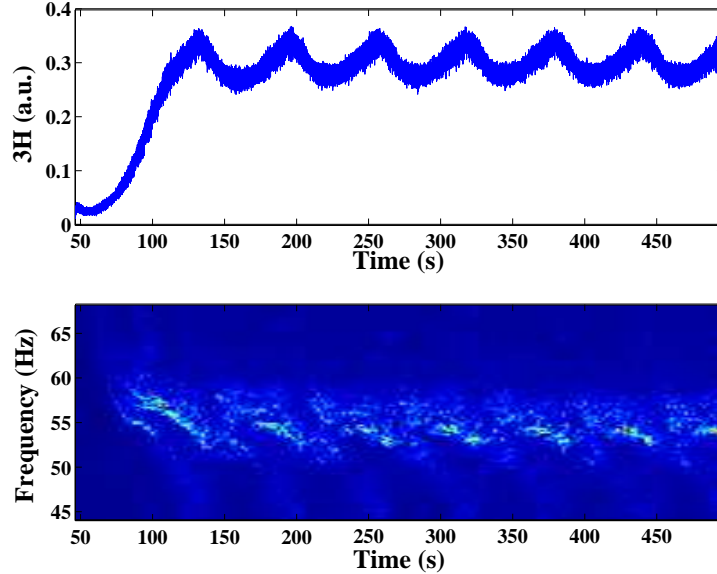


Figure 3. Time-evolution of 3H and spectrogram of 3H during successive dust generations.

Successive generation instability

A second instability has been observed on 3H and V_{dc} during the growth of successive generations of dust particles. Dust particle successive generations can be identified by a pseudo-sinusoidal evolution of the signal, exhibiting a period of several tens of seconds ($\simeq 70$ s in figure 3). If we have a look at the inner structure of the signal during the successive generations, it exhibits a highly unstable behavior, occurring once the second dust generation starts to grow in the discharge. This unstable phase exhibits a complex spectrogram (time-evolution of the frequency) as can be seen in figure 3. This low-frequency instability presents frequencies generally comprised between 45 and 60 Hz, depending on operating conditions. It is a long-lasting instability (more than 400 s in figure 3) which does not stop by itself: it lasts as long as the plasma is on. In opposition to the “coalescence instability”, this instability seems to be little-sensitive to experimental parameters such as rf power or silane flow rate.

The instability seems to develop following two steps. First, a well-organized phase with decreasing frequency is observed during the new generation growth (for example between 150 and 200 s in figure 3). Then a second phase during 3H decrease, which is less organized than the previous one but not chaotic as far as we can observe. This instability, closely linked to successive generation formation, could be a void instability. Indeed, on experimental set-up such as PKE experiment, new dust particle generations are known to grow in a previously formed void region [Mikikian *et al.*, 2003], which is often unstable [Mikikian and Boufendi, 2004]. On Laser Light Scattering (LLS) measurements, we noticed that between each new dust generation, no scattered photons are detected for a while. As the detection system is focused on the plasma center, these signal extinctions let us surmise that a void region could be responsible for these extinctions. Moreover, by following Ar^* (750.38 nm) line, we observed that LLS extinctions correspond to an increase in the line emission indicating an increased ionization. This last results could also suggest a void region in the plasma [Mikikian and Boufendi, 2004]. Presently, some experiments are underway in order to make some observations of the assumed void region, using a standard CCD camera. Furthermore, a high speed camera is currently used to analyze this possible void instability.

Conclusion

In this paper, we reported results concerning two different instabilities occurring during dust formation process in a silane-based discharge. Experiments have been performed in a low-pressure rf discharge, in a mixture of argon and silane (92:8). Instabilities are followed thanks to an electrical diagnostics, based on the discharge current third harmonics, which is very sensitive to dust particle formation and growth in the discharge. The first instability we observe (“coalescence instability”) takes place exactly at the end of nanocrystal accumulation in the gas phase. Its typical characteristics are the following: appearance

time between 100 and 200 ms, frequencies of a few kHz, and duration up to a few tens of ms. This instability is directly linked to charge variation due to coalescence beginning, and is similar to attachment induced-ionization instability observed in electronegative gases. The second instability (“successive generation instability”) starts with the formation of the second dust particle generation in the plasma. Its typical characteristics have been determined: appearance time a few seconds after plasma ignition, low frequency around 40-60 Hz, very long duration (as long as plasma is on). This instability is suspected to be a void instability since LLS and spectroscopic measurements suggest a possible void region in the dust cloud.

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