Particle Decharging and Agglomeration in Pulsed, Particle Dense Dusty RF Plasmas

Toshisato Ono[1], Zhili Zuo[2], Changgong Wang[2], Song-Moon Suh[2], Christopher J. Hogan[1], and Uwe R. Kortshagen[1]

[1]*Dept. of Mechanical Engineering, University of Minnesota, Minneapolis*
[2]*Applied Materials*

Abstract: We examine the decharging and subsequent agglomeration of particles in pulsed, dusty RF plasmas using laser light scattering. We find that periodic pulsing of the plasma containing micrometer sized particles leads to (1) particle decharging, and (2) at high polydisperse particle loadings, rapid particle agglomeration, which is made possible because Coulombic repulsion is minimized upon decharging. This study provides new insights into the dynamics of particles in afterglow and in non-steady state plasmas.

Keywords: Low-pressure plasmas, Dusty plasma, Particle agglomeration

1. Introduction

Dusty plasmas are encountered naturally in interstellar systems and industrially, either intentionally (for particle manufacturing and processing) or inadvertently (when contaminant particle form or are unintentionally introduced in a process) [1], [2]. With regards to the latter, in semiconductor manufacturing, there have been multiple efforts to eliminate particle contamination on wafers, which can occur in plasma enhanced vapor deposition and etching processes [3]–[8]. Such contamination arises because of either particle formation in the plasma system from precursor materials or because of particle generation from reactor walls or system component material. A central issue in addressing particle contamination in industrial plasma systems is that once formed, particle behavior is often only qualitatively understood in the plasma environment as well as on plasma boundaries and in afterglows, hence their propensity to remain in the reactor or to deposit is not easy to predict [9]–[11]. There is therefore a need to carry out fundamental studies of particle behavior in not only steady-state dusty plasmas, but also transient plasmas (time varying, pulsed systems) and dusty afterglows (short-lived systems wherein electron densities and temperatures rapidly decay).

Along these lines, the purpose of this research is to carry out fundamental investigations of the decharging and agglomeration of particles in transiently pulsed plasmas. Previous works focusing on particle behavior in dusty plasmas have largely focused on steady-state, parallel-plate non-thermal plasmas [12]–[15]. In large part, these studies show that particles are strongly negatively charged. Negative charge is known to arise because of the mobilities of electrons as compared to ions. All theories predicting the flux rate of ions to electrons show that the flux rates balanced only for highly negatively charged particles [16]–[18]. Particles hence repel one another and do not coagulate in steady-state plasmas. Prior research shows that the trapping location nearly coincides with the boundary of the plasma volume and the onset of the plasma sheath at this location, the forces on particles appear to balance [4], [5], [8], [19]–[21]. Less understood is particle behavior, when the steady-state plasma is disturbed, i.e. when it is pulsed or turned off. The charging (excess collisions with electrons) and decharging (either collisions with ions or emission of electrons) of particles are the most important reactions governing the motion of particles not only in a steady-state system but also in transient plasmas (pulsed plasmas or afterglows); transient plasmas are also important steps in most industrial processes, usually as part of start-up or completion [16], [22], [23]. If particles decharge quickly in the afterglow relative to the time scale of particle motion, the space-charge effect on their motion will be minimal, and neutral drag (i.e. gas flow), gravitational forces, diffusion, and possibly thermophoretic forces, will control particle motion, as in is the case for particles in aerosol systems [3], [24], [25]. However, if decharging is relatively slow compared to timescale of particle motion, because of residual fields in a transient plasma or afterglow (which are common because of residue potential on electrodes), and because of space charge effects, particles may display unique behavior from an aerosol system, and furthermore, their behavior may be highly size and chemical composition (material) dependent. In this research, laser light scattering measurements have been conducted to monitor particle migration and trapping. Rectangular wave pulses have been added to RF sinusoidal wave, which enables us to conduct repeatable afterglow experiments.

2. Experimental

Experiments have been conducted in a parallel plate capacitively coupled plasma (CCP) reactor shown in Figure 1. In this reactor, a plasma is maintained between two planar electrodes each 19.2 cm in diameter and separated by 2.5 cm. The upper electrode is connected to an RF power supply through a matching network, which enables the reflected power to be minimized during experiments. To introduce and generate a dusty plasma, the reactor is first pumped down to a pressure near 500 mTorr and the plasma is ignited with argon gas continuously flowing at a rate of 200 sccm. Next, the argon flow is ceased while pumping is used to further drop the pressure to 100 mTorr or lower. The main pump is disconnected, leaving a sealed, steady-state plasma reactor. Argon gas is then pulsed through a side injection tube; the pulse is initiated over a particle bed loaded with a prescribed mass of particles of a desired chemical composition (purchased commercial nanopowders or micropowders). The pulsing of Argon disperses particles quickly into an aerosol which enters the plasma chamber via a diffuser (diverging nozzle). Visual inspection of the particles presently suggested that the dispersed particles are submicrometer (>100 nm) to several micrometers in size when introduced, i.e. particles are partially agglomerated upon introduction, but large microparticles (> 10 micrometers) likely do not enter the chamber. The pulse not only results in particle dispersal within the plasma but also an increase in the chamber pressure to 1-2 Torr.

To observe particle migration and trapping, a diode laser (405 nm wavelength) beam, expanded to a sheet light by a Plano-concave lens, is continuously introduced into the plasma reactor, with a CCD camera positioned at a 90^{o} angle from the sheet direction (Figure 1). This setup enables detection of scattered laser light by particles (i.e. the laser light scattering, or LLS technique), which can not only be used to monitor particle migration and trajectories, but via application of Mie light scattering theory [26] particle size and shape. The LLS method is widely applied in particle monitoring, as it is a non-invasive method and in the micrometer size range, it can have single particle sensitivity. However, emission from plasmas can lead to large interferences in the visible wavelength range, hence the laser wavelength needs to be chosen properly to not coincide with an Argon emission wavelength, the optical signal received by the camera must be filtered, and background substraction is often necessary. Towards these ends, a band-pass filter (405 ± 5 nm) is placed on the camera lens, and a mechanical chopper system is utilized on the laser beam; this enables both elimination of many plasma interference wavelengths as well as subtraction of 405 nm background signal (there is some degree of Argon emission within the bandpass transmission range). A rectangular shaped waveform is imposed on the RF sinusoidal waveform to repeat the afterglow measurements with a fixed particle weight. Figure 2 shows the input waveform for the RF pulsed plasma measurement. The plasma is in a steady-state during when rectangular waveform is the “on” position, and the particle dynamics in the afterglow can be observed between these steady-state phases.

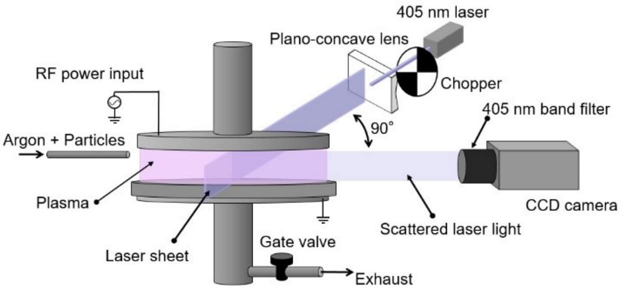

Fig. 1. A schematic diagram of the CCP plasma reactor and LLS diagnostics system used to monitor particle migration and trapping. 405 nm diode laser is converted into a sheet of light by Plano-concave lens. Particles scatter laser light when they across the laser sheet, and CCD camera captures the emissions.

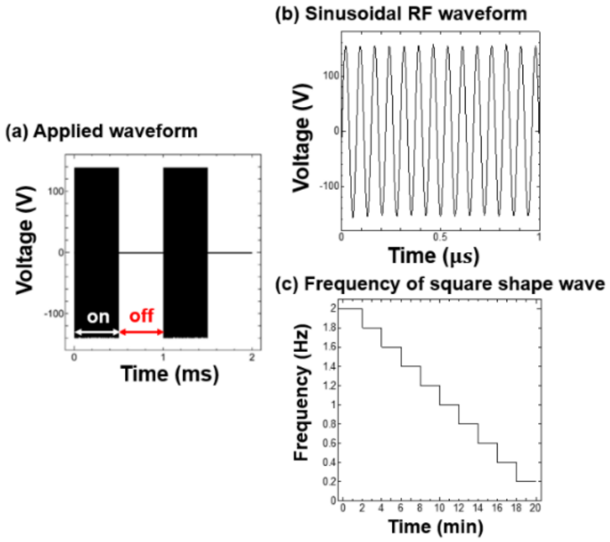

Fig. 2. (a) Imposed rectangular shape modulation wave for the afterglow RF pulsing experiments. (b) Sinusoidal RF waveform for steady-state conditions. (c) The changes in the frequency of the rectangular shape modulation wave. The initial frequency was 2 Hz and reached at 0.2 Hz after 18 minutes.

3. Result and discussion

Photographs of suspended test particles in the steady-state plasma and particle trajectories in the transient plasma are shown in Figure 3 and 4. Particles, upon introduction to the plasma, are observed to immediately migrate towards trapping locations at either the top or bottom electrode, as is depicted in Figure 3 (a). Particles do not remain bound at the trapping location when the plasma is extinguished. As in Figure 3 (b), some particles both gravitationally settle, while others migrate towards the upper electrode; the latter appear to be driven by residual negative charge (slow decharging), and residual positive voltage on the top electrode when the plasma is extinguished.

RF pulses hence induce particles to have differential velocities in both speed and direction. Upon restriking the plasma, such motion is reversed, and all particle return to the trapping location. Differential motion (both settling and migration velocities) is known to be an efficient method of agglomeration, and we find that when decharging occurs, particle agglomeration occurs rapidly in a pulsed plasma system, with larger agglomerates evident simply from laser light scattering images. However, the agglomeration rate appears to decrease as particles grow larger. Figure 4 shows agglomerated particles after 20 minutes of RF pulsing. We tested two cases for the particle agglomeration observation; Figure 4 (a) shows particles after 20 minutes of pulsing with fixed rectangular shape wave frequency at 2 Hz, and Figure 4 (b) shows particles after 20 minutes of pulsing using a variable rectangular shape wave frequency with a monotonic decrease in frequency of 0.1 Hz every 2 minutes (the frequency steps are shown in Figure 2 (c)). Significantly more agglomeration was observed in the variable frequency case. Approximately, agglomerated particles reached 500 µm in size 20 minutes with variable frequency. This is presumably because as agglomerates increase in size, the characteristic decharging time increases, hence with fixed frequency there is a critical size for agglomerates in a pulsed plasma.

We additionally provide evidence that the mechanism of decharging is not simply ion-particle collision, but may be driven by electron emission, which is material (dielectric constant) dependent. Figure 5 shows a photograph comparison of particle clouds of different materials exposed to identical pulsed plasmas with initial similar submicrometer range particle size distributions and the same loaded particle mass. High dielectric constant particles appear to have agglomerated siginificantly less, suggesting they decharge more slowly, conistent with electron emission as the main mode of decharging.

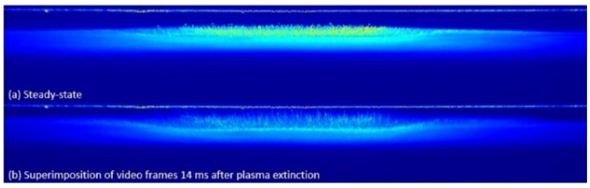

Fig. 3. (a) A LLS image of a particle cloud in steady-state Ar plasma. (b) Superimposition of video frames after plasma extinction with 14 ms exposure time. Some particles migrate towards the top electrode, while others settle due to gravitational forces.

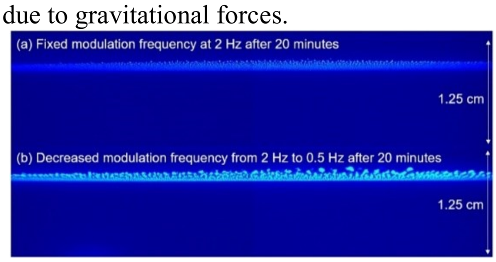

Fig. 4. LLS images of particle clouds after 20 minutes of RF pulsing. (a) The modulation frequency was fixed at 2 Hz whole 20 minutes. (b) The modulation frequency was decreased by 0.2 Hz every 2 minutes, starting at 2 Hz.

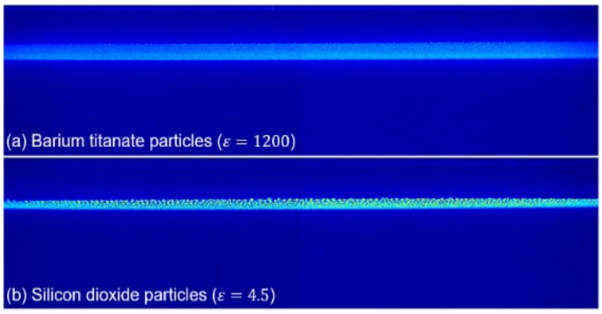

Fig. 5. LLS images of particle clouds after 14 minutes of RF pulsing with variable frequency. (a) Barium titanate particles (b) Silicon dioxide particles.

4. Conclusions

We have carried out fundamental investigations of the decharging and agglomeration of particles in transiently pulsed plasmas using laser light scattering. Few prior studies have examined particle dynamics under such conditions. In transient plasmas, when the plasma is off, particles decharge, and differential gravitational settling can drive particle agglomeration, hence pulsed plasmas are a means of controlling the extent of particle agglomeration over orders of magnitude in size. The rate of particle decharing appears to decrease as agglomeration proceeds.

Acknowledgments

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