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Interaction of nanosecond UV laser pulses with reactive dusty plasma

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Even though UV laser pulses that irradiate a gas discharge are small compared to the plasma volume ($\lesssim 3\%$) and plasma-on time ($\lesssim 6 \times 10^{-6}\%$), they are found to dramatically change the discharge characteristics on a global scale. The reactive argon–acetylene plasma allows the growth of nanoparticles with diameters up to $1\ \mu\text{m}$, which are formed inside the discharge volume due to spontaneous polymerization reactions. It is found that the laser pulses predominantly accelerate and enhance the coagulation phase and are able to suppress the formation of a dust void.

Plasmas containing nanoparticles, generally referred to as dusty plasmas, play a tremendous role both for the understanding of fundamental plasma physical processes and for technological applications. In particular reactive dusty plasmas, where nanoparticles grow spontaneously, are in the focus of the applied research: either with the aim to avoid the formation of nanoparticles as e.g. in fusion devices and during the fabrication of microelectronic circuits where nanoparticles are often considered as killer particles or with the aim to produce them in a controlled way and to use them as building blocks for further applications (e.g. nanocomposites, biomimetic surfaces and quantum dots).^{1–5}

This letter deals with the interaction of nanosecond UV laser pulses with a reactive dusty plasma. The experiments are performed in capacitively coupled discharges operated in a mixture of argon and acetylene at a gas pressure of 10 Pa. This type of plasma allows the growth of nanoparticles (with diameters up to $1\ \mu\text{m}$ in our case, see figure 1 for a typical scanning electron micrograph of collected particles), which are formed inside the discharge volume due to spontaneous polymerization reactions.

The basis for the formation of particles in the plasma volume are gas phase reactions which are leading to

the formation of nanometer-sized clusters or proto-particles.^{6–10} This homogeneous nucleation has been observed in several kinds of discharges and gas mixtures and is the first step in the production of larger particles. In particular for acetylene discharges, it has been shown that negative ions play a crucial role in this phase.¹¹ At this stage, the charging of the clusters is mostly governed by the random arrival of both positive and negative species. Net nanoparticle charge will not be high (several elementary charges), and can therefore easily (temporarily) change sign. The second step is the abrupt coagulation phase when the particles reach a critical density, pushing proto-particles together and ‘fusing’ them, provided they are not electrostatically repelling each other. The result is the formation of particles with diameters up to some tens of nanometers; which quickly attain a permanent negative net charge due to the efficient collection of electrons. As a result, further coagulation stops and the nanoparticles are trapped (confined) in the plasma. The last step is a continuous growth of the particles due to the accretion of ions and radicals from the plasma.

A frequent observation in laboratory and industrial dusty plasmas is the development of a so-called dust void. This is a macroscopic region devoid of large (coagulated) nanoparticles. In experiments, a void can easily be visualized using laser light scattering.¹² The void develops as a result of the interplay of the different forces acting on the particles as e.g. the ion drag force and the electrostatic force. In particular in reactive plasmas where the particles grow in time, the dust void may show a dynamic behavior: in the beginning of the process, when the particles are rather small, the whole chamber is filled with dust particles. During the further growth process however forces like the ion drag force or gravity become more and more important.¹³ As a consequence, the particles are pushed out of the center of the discharge and the void starts to develop. This dust-free region, which is separated from the dust-containing region by a sharp pronounced boundary, is continuously increasing during the further growth of the particles until a new cycle of nanoparticle formation can start in the void region.¹⁴ Then the process repeats itself, resulting in a periodic behavior of the whole phenomenon. Examples of this kind of behavior can be found for different discharges as e.g. in argon–silane¹⁵ and argon–acetylene^{12,16–18} low-

FIG. 1. Typical scanning electron microscopy image of particles collected from our discharge.

FIG. 2. Schematic top view of the setup. A dusty plasma is generated in a parallel-plate capacitively coupled RF discharge. For Setup A, gas enters the vessel through the top shower-head electrode, whereas for Setup B, gas enters through a side port located near the top of the vessel. A laser generates short UV laser pulses with a repetition frequency of 10 Hz. The light coming from the dusty plasma and radiating particles (incandescence) is recorded by a video camera, which is triggered by the laser.

pressure plasmas.

It will be shown in this Letter that short (nanosecond and even sub-nanosecond) high-energy UV laser pulses can strongly influence the formation of nanoparticles and can change substantially the whole behavior of the discharge – even though the laser irradiates only a relatively small volume of the discharge. The most obvious effect of the laser pulses concerns the heating of the nanoparticles. Our plasma-confined particles reach a temperature of about 3000 K after irradiation by the UV laser pulses. As a result, they emit thermal radiation even in the visible part of the spectrum. This radiation can be seen as a white-ish trace in the plasma at places where irradiated particles are present. The phenomenon is in this case usually referred to as laser-induced incandescence and can be used as a particle diagnostic.^{19–21} The diagnostic potential of laser-induced incandescence is also studied for the experiments presented in this Letter, the results of which will be discussed in a forthcoming paper.²² The temperature and radius of the particles were determined with microsecond time resolution by measuring and analyzing the spectra of blackbody-like emission from the particles after irradiation.

The global setup is schematically drawn in figure 2. Two variations of this setup are used (referred to as Setup A and Setup B), see table I. Power is coupled capacitively to the plasma using an in-house built L-type matching circuit at a frequency of 13.56 MHz. The plasma is electrically characterized using a commercially available probe (Scientific Systems SmartPIM), placed between the matching circuit and powered electrode of the plasma. This device measures the voltage, current, phase angle, power and impedance up to the fifth harmonic at a sample frequency of 10 Hz. The phase angle signifies the phase difference between the voltage over the discharge and the current flowing through it. Just as in conventional electronics, a phase angle of -90°

means a pure capacitive behavior, whereas values closer to zero indicate a more resistive behavior. Nanoparticles present resistive losses in a dusty plasma, meaning that the nanoparticle formation process can be followed by inspecting the plasma phase angle. Gas pressure inside the vessel is 10 Pa. Nanoparticles are synthesized by the plasma following initial polymerization of acetylene. Once coagulated, the particles are permanently negatively charged and are trapped in the plasma. Without void formation, the particle cloud completely fills the plasma volume, except for the sheath regions which are several mm wide. The laser wavelength is 355 nm and the pulse repetition frequency is 10 Hz. The laser beam enters the vacuum vessel through a quartz window, is directed radially through the electrode system and has a beam diameter of about 1 cm. This means that the laser irradiates both the plasma volume containing nanoparticles and the sheaths. In our calculation of the percentage of plasma volume irradiated, the sheath areas contribute to the total “plasma volume”.

Figure 3 shows two measurements using Setup A, one performed at roughly 60 mJ pulse energy and one at about 75 mJ pulse energy. The dissipated RF power was in both cases 5 to 6 W. The plasma and incandescence emission are calculated from the video (figure 4a). A comparison between figure 3a and 3b clearly shows that the high-energy pulses traversing the plasma change the discharge characteristics dramatically even on a global level. At low pulse energy, cyclic void formation is observed, indicated by the periodic behavior of the plasma emission, plasma phase angle and incandescence signal. At high laser energy, however, the cyclic void growth is completely suppressed.

Another aspect concerns the size distribution of the particles. Without laser irradiation, the size distribution in Setup A is rather narrow (the standard deviation for the particle radius is < 15 nm). Due to the irradiation of the discharge with high-energy UV pulses, the particle size distribution becomes much broader (see figure 1).

In contrast to the situation in Setup A, there is no void formation observable in Setup B. Nevertheless, the ability of UV laser pulses to change the plasma on a global scale is also observed for this discharge. Using Setup B, three dusty-plasma experiments were conducted successively differing only in the presence of laser pulses in the plasma volume:

1. Laser pulses traversing the plasma during the complete experiment.
2. No laser pulses traversing the plasma during the complete experiment.
3. Laser pulses traverse the dusty plasma between 136 s and 259 s.

The temporal evolution of the plasma phase angle and plasma emission is shown in figure 5. It should be noted that the results are shown only for three experiments, but they were repeated several times and showed good

TABLE I. Experimental details of the setups A and B.

	Setup A	Setup B
Electrode distance (cm)	4.0	2.8
Top electrode (RF-driven)	13-cm diameter shower head	12-cm diameter plate
Bottom electrode (grounded)	15-cm diameter metal mesh	12-cm diameter plate
Gas inlet	Shower head	Vessel side port
Argon flow (sccm)	15.4	10
Acetylene flow (sccm)	0.9	1
Laser	Ekspla SL312 Nd:YAG	Quantel Brilliant Nd:YAG
Laser pulse width (approx.)	150 ps	6 ns
Laser pulse energy (mJ)	up to ~ 75	~ 20
Camera	Grayscale CMOS	Grayscale CCD

FIG. 3. The effect on the global discharge characteristics of short (150 ps) and intense UV (355 nm) laser pulses traversing equivalent dusty plasmas for a pulse energy of about (a): 60 mJ and (b): 75 mJ. The sharp jump in the phase angle around 525 s in panel b is probably an artifact of the measuring device (SmartPIM) because it is not seen in the other discharge parameters. During the experiment at low pulse energy, cyclic void formation is observed, whereas it is completely suppressed at high pulse energy.

FIG. 4. Sample video frame of the laser-irradiated discharge. (a): Setup A. The plasma emission is taken as the average pixel value of the pixels enclosed by the lower black rectangle. The incandescence emission is the average pixel value of the pixels enclosed by the upper black rectangle, subtracted with the plasma emission. (b): Setup B. The plasma emission is taken as the average pixel value of the pixels enclosed by the black rectangle. Emissions are corrected for the background before plasma operation.

reproducibility. The plasma emission is calculated from the video (figure 4b). The discharge is switched on at $t = 0$. Especially in the first 100 s the plasma behaves very differently, when the laser is switched on. The fast rise of the plasma phase angle and plasma emission during this period is caused by coagulation of nanoparticles in the plasma volume, see for example Beckers *et al.*²³ This means that the UV laser pulses greatly influence the physics and chemistry of (the phases leading up to) coagulation and seem to accelerate and enhance this period (compare the blue graph with the red graph). The effect

FIG. 5. The effect on the global discharge characteristics of short (6 ns) and intense (20 mJ) UV (355 nm) laser pulses traversing a dusty plasma. (1): *With* laser pulses traversing the dusty plasma during the complete experiment. (2): *Without* laser pulses traversing the dusty plasma during the complete experiment. (3): *With* laser pulses traversing the dust plasma between 136 s and 259 s. The yellow block symbolizes the period in which laser pulses are traversing the dusty plasma for curve number 3.

of the laser pulses at later times is much less pronounced (yellow graph). This means that UV laser pulses predominantly affect the early phases of dust particle formation. It is difficult to pinpoint with certainty the reason for the observed global effect on the dust particle formation processes due to their inherent complexity. However, one plausible cause is a laser-induced change in the polymerization routes.

Photons with a wavelength of 355 nm have an energy of 3.49 eV. This means that these photons can detach electrons from the C_2H^- anion,²⁴ by laser-induced photodetachment, producing the C_2H radical. Usually negative ions as the C_2H^- ion are assumed to play a key role in the nucleation process since negative species are trapped in the plasma region and can thus build up large densities. However, the polymerization rate for the C_2H

TABLE II. Polymerization reactions in acetylene plasmas between acetylene and anions or radicals.²⁵

Reaction	Rate constant ($m^3 s^{-1}$)
$C_{2n}H^- + C_2H_2 \rightarrow C_{2n+2}H^- + H_2$	$\sim 10^{-18}$
$C_{2n}H + C_2H_2 \rightarrow C_{2n+2}H_2 + H$	6.6×10^{-17}

radical is more than ten times higher than for the C_2H^- anion, see table II. Both pathways have acetylene as reaction partner and can therefore be compared directly. Consequently, if a UV laser pulse suddenly increases the C_2H radical density, the polymerization rate increases dramatically. In turn, this would result in an accelerated dust particle formation process (i.e. onset of coagulation) if the resulting neutral clusters stay sufficiently long in the plasma to contribute to the particle growth process. Another possible explanation concerns the charge distribution of the particles, which can be changed by the laser pulses, enhancing in this way the coagulation rate (due to the collisions between positively and negatively charged clusters).

In conclusion, the irradiation of a reactive dusty argon-acetylene plasma by high-energy and short UV laser pulses is found to alter the discharge substantially and globally. At sufficiently high pulse energies, the formation of a dust void in the center of the discharge – which occurs without laser irradiation – is totally suppressed. The presence of laser pulses is also found to alter (the phases leading up to) coagulation. It should be stressed again that the laser light propagating through the plasma affects only $\lesssim 3\%$ of the total plasma volume and is present only $\lesssim 6 \times 10^{-6}\%$ of the plasma-on time. Although the effects are not yet fully understood, it is striking how these localized short scale laser pulses can influence the plasma so dramatically on a global scale.

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- ¹J. Winter, Plasma Physics and Controlled Fusion **40**, 1201 (1998).
- ²G. Selwyn, J. Singh, and R. Bennett, Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **7**, 2758 (1989).
- ³J. Berndt, H. Acid, E. Kovacevic, C. Cachoncinlle, T. Strunskus, and L. Boufendi, Journal of Applied Physics **113**, 063302 (2013), 10.1063/1.4789949.
- ⁴A. Kuzminova, A. Shelemin, O. Kylián, M. Petr, J. Kratochvíl, P. Solář, and H. Biederman, Vacuum **110**, 58 (2014).
- ⁵U. Kortshagen, Journal of Physics D: Applied Physics **42**, 113001 (2009).
- ⁶L. Boufendi and A. Bouchoule, Plasma Sources Science and Technology **3**, 262 (1994).
- ⁷A. Bouchoule and L. Boufendi, Plasma Sources Science and Technology **2**, 204 (1993).
- ⁸L. Boufendi, J. Hermann, A. Bouchoule, B. Dubreuil, E. Stoffels,

- W. W. Stoffels, and M. L. de Giorgi, *Journal of Applied Physics* **76**, 148 (1994).
- ⁹E. Kovačević, J. Berndt, T. Strunskus, and L. Boufendi, *Journal of Applied Physics* **112**, 013303 (2012), 10.1063/1.4731751.
- ¹⁰C. Hollenstein, W. Schwarzenbach, A. A. Howling, C. Courteille, J.-L. Drier, and L. Sansonnens, *Journal of Vacuum Science & Technology A* **14**, 535 (1996).
- ¹¹J. Berndt, E. Kovačević, I. Stefanović, and L. Boufendi, *Journal of Applied Physics* **106**, 063309 (2009), 10.1063/1.3224874.
- ¹²F. M. J. H. van de Wetering, R. J. C. Brooimans, S. Nijdam, J. Beckers, and G. M. W. Kroesen, *Journal of Physics D: Applied Physics* **48**, 035204 (2015).
- ¹³J. Goree, G. E. Morfill, V. N. Tsytovich, and S. V. Vladimirov, *Physical Review E* **59**, 7055 (1999).
- ¹⁴F. M. J. H. van de Wetering, *Formation and dynamics of nanoparticles in plasmas*, Ph.D. thesis, Eindhoven University of Technology (2016).
- ¹⁵M. Cavarroc, M. Mikikian, Y. Tessier, and L. Boufendi, *Physical Review Letters* **100**, 045001 (2008).
- ¹⁶E. Kovačević, I. Stefanović, J. Berndt, and J. Winter, *Journal of Applied Physics* **93**, 2924 (2003).
- ¹⁷I. Stefanović, C. Scharwitz, E. Kovačević, J. Berndt, and J. Winter, *IEEE Transactions on Plasma Science* **36**, 1018 (2008).
- ¹⁸S. Hong, J. Berndt, and J. Winter, *Plasma Sources Science and Technology* **12**, 46 (2003).
- ¹⁹W. W. Stoffels, E. Stoffels, G. M. W. Kroesen, and F. J. de Hoog, *Journal of Vacuum Science & Technology A* **14**, 588 (1996).
- ²⁰G. S. Eom, C. W. Park, Y. H. Shin, K. H. Chung, S. Park, W. Choe, and J. W. Hahn, *Applied Physics Letters* **83**, 1261 (2003).
- ²¹L. A. Melton, *Applied Optics* **23**, 2201 (1984).
- ²²F. M. J. H. van de Wetering, W. Oosterbeek, J. Beckers, S. Nijdam, E. Kovačević, and J. Berndt, *Journal of Physics D: Applied Physics* (2016), submitted.
- ²³J. Beckers and G. M. W. Kroesen, *Applied Physics Letters* **99**, 181503 (2011).
- ²⁴“*CRC Handbook of Chemistry and Physics*: Table Electron Affinities, Internet Version,” (2015).
- ²⁵K. De Bleecker, A. Bogaerts, and W. Goedheer, *Physical Review E* **73**, 026405 (2006).

ACCEPTED MANUSCRIPT

2 μm

Driven electrode

Incandescence

Grounded electrode

Driven electrode

Incandescence

Grounded electrode