Dust formation and charging in an Ar/SiH₄ radio-frequency discharge

Citation for published version (APA):

Stoffels - Adamowicz, E., Stoffels, W. W., Kroesen, G. M. W., & Hoog, de, F. J. (1996). Dust formation and charging in an Ar/SiH₄ radio-frequency discharge. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 14(2), 556-561. <https://doi.org/10.1116/1.580144>

DOI:

[10.1116/1.580144](https://doi.org/10.1116/1.580144)

Document status and date:

Published: 01/01/1996

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Dust formation and charging in an Ar/SiH₄ radio-frequency discharge

E. Stoffels, W. W. Stoffels, G. M. W. Kroesen, and F. J. de Hoog

Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

(Received 4 October 1995; accepted 13 December 1995)

The formation and charging of submicrometer dust particles in a low pressure argon/silane radio-frequency (rf) discharge was studied using laser-induced photodetachment in combination with a microwave resonance technique. This method allows a measurement of the spatially averaged electron density, the spatially resolved negative ion density, and/or the charge on small clusters in the plasma as a function of time during particle formation. The loss frequency of photodetached electrons yields information about the recharging of small clusters. During the first second after plasma ignition dust particles are formed. Simultaneously, the electron density decreases from about $2 \times 10^{15} \text{ m}^{-3}$ to about $4 \times 10^{14} \text{ m}^{-3}$. In the first 10 ms after discharge ignition, charged particles are not present in the plasma and the photodetachment experiment gives a negative ion density of $4 \times 10^{15} \text{ m}^{-3}$. During the first 50 ms after plasma ignition, nanocrystallites are formed, which is reflected by a strong increase of the loss frequency of photodetached electrons. After 50 ms the particles start to coalesce and acquire a negative charge, which results in a strong increase of the photodetachment signal. After 1 s of plasma operation, the charge density on particles is about $8 \times 10^{16} \text{ m}^{-3}$. The photodetachment signal decreases with the gas flow rate, indicating that the clusters are expelled from the plasma by the gas flow. © 1996 American Vacuum Society.

I. INTRODUCTION

An extensive research effort was undertaken to elucidate the behavior of macroscopic particles suspended in a plasma.¹ Dust formation in a silane discharge has especially been extensively studied. Low pressure silane discharges are commonly used to produce thin silicon layers for a wide variety of industrial applications. Typically, the highest deposition rates of Si are reached and the best layers are formed in conditions where abundant dust formation also occurs. However, the presence of particles is not necessarily harmful for the layers if powder formation and transport in the plasma are controlled. In order to obtain a better understanding of the transport processes in the discharge it is necessary to study various forces acting on a particle.

A dust grain, like all floating objects in a plasma, acquires a negative charge due to a difference in mobility between the electrons and positive ions. This charge is responsible for trapping the particle in the positive plasma glow. Beside Coulomb interactions, there are other forces that act on a particle: the neutral drag force, the ion drag force, the thermophoretic force, etc. The competition of these forces determines the behavior of dust particles, their spatial distribution, and their residence time in the plasma. A study of the negative charge is thus very important to obtain good control of the particle formation process. Knowledge of the charging and trapping of nanometer scale clusters in the plasma would be helpful in understanding the initial stages of particle growth. In this period trapping is essential due to the low densities of active species and their short residence time in a low pressure discharge.

Howling *et al.*² showed by means of mass spectrometry that negative ions are involved in the early phase of particle formation in SiH₄. They detected negative ions up to Si₁₆H_x⁻ in the plasma afterglow, while the largest positive ion

was Si₅H_x⁺. The time evolution of the particle size was studied by Bouchoule and Boufendi using transmission electron microscopy.^{3,4} In the same studies they also used laser light scattering to determine *in situ* particle density. However, due to the r^6/λ^4 dependence of the Rayleigh scattering, the minimum particle radius they could observe was about 10 nm. Smaller particles, in the earlier formation phase, were studied using laser-induced heating.⁵

It has become clear that dust formation in an Ar/SiH₄ discharge is a stepwise process. The first step is the formation of large molecules, which in turn form 2 nm crystallites. Then, in the next step, these crystallites coalesce, producing larger scale particles ($r \approx 10$ nm). Further particle growth by coalescence is believed to be prevented by a permanent negative charge on the particles. After the coalescence phase the charged particles continue to grow by deposition of radicals and ions. At a certain size the particles are expelled from the plasma, in our case because the neutral drag force becomes larger than the electrostatic force.⁶

There is very little experimental data available on the charging of dust particles in the plasma. Most measurements are indirect and limited to the case of large particles. Also, modeling of the charging of clusters is not that insignificant. The simple orbital motion limited theory for isolated macroscopic dust grains does not give reliable results in the case of overly high particle densities. Bouchoule and Boufendi⁷ have shown that for conditions of interest interactions between the particles take place and the particle cloud should be described as a Coulomb liquid rather than a suspension of individual grains in the plasma. Furthermore, for small clusters statistical fluctuations in the charge must be taken into account. Also, the macroscopic treatment of electron and ion capture is not valid for these small particles. Consequently,

FIG. 1. A scheme of the electrode configuration. The direction of the gas flow is indicated.

charging of nanometer scale clusters is an unresolved problem.

In this article preliminary measurements of the charging of dust particles, including nanometer scale grains, are presented. Both the charge and the charging time are measured in a dusty Ar/SiH₄ rf plasma by means of laser-induced photodetachment in combination with a microwave cavity. This experimental technique provides a unique opportunity to study the charge and charging of nanometer scale particles, which are very difficult to detect by standard diagnostics and for which simple charging models are not valid.

II. EXPERIMENT

The experimental setup consists of a capacitively coupled 13.56 MHz plasma confined in an aluminum cylinder (diameter: 17.5 cm, height: 5 cm). A 12-cm-diam, water cooled rf electrode is situated at the bottom and the rest is grounded. The gas is introduced homogeneously through a 2 mm slit around the rf electrode. The top of the cylinder consists of a wire grid (grid size: 0.5 mm) to provide for a laminar gas flow through the plasma. Two vertical slits in the side walls of the plasma box allow for laser diagnostics. A schematic view of the plasma box is shown in Fig. 1. Typical conditions in this work are 120 mTorr pressure and 10 W rf power input. The gas mixture consists of 5% SiH₄ in argon. Further details on the setup can be found in Refs. 8 and 9.

The scheme of the setup for laser diagnostics is shown in Fig. 2. The method was described extensively elsewhere.^{8,9} Briefly, in order to measure the electron density a microwave resonance technique is used in which the plasma box serves as a cavity. For this purpose a low power microwave signal of variable frequency is coupled into the cylinder by means of an antenna, exciting the TM₀₂₀ mode (frequency $\approx$ 3 GHz). The transmission of the cavity is recorded by another antenna and processed by a digitizing oscilloscope. The transmission curve is determined by stepping the microwave frequency. Finally, the resonance frequency of the cavity as

FIG. 2. A schematic view of the setup used for the photodetachment experiments.

well as its quality factor (width at half height) are found by fitting the experimental data. The resonance frequency of the cavity depends on the number of free electrons inside. From the shift of the resonance frequency with respect to its value in vacuum the average electron density in the cavity is deduced. This method allows a measurement of the spatial average of the electron density, with a time resolution determined by the quality factor (in our case about 50 ns). This technique is thus well suited to study electron density transients in the plasma, like ignition and afterglow,¹⁰ or extra electrons created in laser-plasma interactions.

In the past this technique has been used in combination with laser-induced photodetachment to determine the negative ion density.^{8,10,11} Besides negative ions, the technique can be applied to strip the negative charge from dust particles. A high power pulsed Nd:YAG laser (pulse width: 10 ns, max power 30 mJ at $\lambda=532$ nm) is used and the extra shift in the resonance frequency caused by the photodetached electrons is measured. If the effect is saturated, this shift, multiplied by the ratio of the cavity and the laser beam volume, gives the total amount of charge stripped from negative ions and particles. If the signal originates from the particles, the charge per particle can be deduced, provided the particle density is known. The laser beam passes through two slits in the plasma container, making vertical scans possible. The spatial resolution is determined by the diameter of the laser beam, which in our case is collimated and diaphragmed into a 2 mm pencil-like beam.

The shift of the resonance frequency after the laser has been fired through the plasma is monitored as a function of time so the recharging of the dust particles can be studied. This yields information about the typical time scales for charging of initially neutral particles. Note that for high particle densities the observed time scale is not related to the electron flux towards the particle in the *stationary* state. Immediately after photodetachment the electron density is much larger, while the average electron energy is very low; typically a few tenths of an eV (the difference between the photon energy and the detachment energy). As the recharging

FIG. 3. Time behavior of the electron density after switching the Ar/SiH₄ discharge on at 120 mTorr, 10 W, and 30 sccm.

time decreases with increasing particle size,⁹ the charge and charge kinetics of micrometer scale particles cannot be studied at the present time resolution.

The geometry of our plasma box and the plasma conditions are similar to those described by Boufendi and Bouchoule.^{5,12} However, the gas flow in their configuration is directed downwards and injected through a showerhead piece. The steady state electron densities, measured in these two systems under typical conditions for particle formation, are the same.¹³ Even though some differences are observed in the electron kinetics, it is expected that the particle growth mechanisms in these two discharges should be comparable.

III. RESULTS AND DISCUSSION

The formation of a large amount of dust particles in the plasma has a strong impact on the discharge properties.¹⁴ The fact that the clusters acquire a negative charge influences the electron density in the course of powder formation. We have studied the behavior of the electron density in an Ar/SiH₄ discharge in the absence of particles as well as during dust formation.⁶ In the absence of dust (e.g., at pressures lower than 50 mTorr) the dependencies of the electron density on plasma parameters are typical for a low pressure rf discharge: the electron density increases weakly with pressure, is linear with the rf power input, and does not change with the gas flow rate. Moreover, it stabilizes in a fraction of a millisecond after plasma ignition. When the pressure is high enough and particle formation occurs (around 50 mTorr), the electron density becomes strongly dependent on the plasma operation time. In Fig. 3 the behavior of the electron density after the plasma has been switched on is shown. The electron density is high immediately after switching on the plasma and it decreases rapidly during the first 100 ms of discharge operation. This reflects the time needed for the first crystallites to reach the coalescence phase, as is determined by the laser heating technique.⁵ After 1 s, when the coalescence is finished, the electron density increases slightly again. The long-term behavior of the electron density depends on the

FIG. 4. The height of the photodetachment signal as a function of the axial position after several minutes of plasma operation. The rf electrode is at 0 mm and the grounded electrode at 50 mm. The conditions are 5 W rf power, 100 sccm total gas flow rate, and 120 mTorr pressure.

gas flow rate. As particles are periodically removed by the gas flow, oscillatory behavior, visible in Fig. 3, can be observed at low flow rates.⁶

Interactions of the laser beam with a dusty plasma result in a release of extra electrons. The actual photon energy needed to free an electron from the cluster surface is subject to discussion. In the solid state approach this energy would be equal to the work function of Si (3.59 eV); in this case photodetachment would not occur at the laser wavelengths longer than 345 nm. However, the irregular structure of the particle surface, with many adsorbed hydrogenated silicon radicals, enables the electrons to attach to some of the terminal $-\text{SiH}_x$ groups. In the latter case the negative charge is chemically bound to the surface and the corresponding detachment energies are expected to be close to the electron affinities of SiH_x radicals (~ 1.5 eV). The experiments were performed using $\lambda = 1064$ and 532 nm (fundamental and doubled frequency mode of the Nd:YAG laser). In the first case no signal was observed. Using $\lambda = 532$ nm, it is possible to detach electrons from negative hydrogenated silicon ions. However, the observed photodetachment signal at this wavelength in typical dusty plasma conditions corresponds to a much higher (factor of 10) negative ion density than the one expected for the weakly electronegative SiH₄. This gives a very strong indication that the measured signal is due to stripping of the electrons from the particles and that their detachment energy is lower than the work function of Si. The fact that the observed photodetachment signal originates from stripped dust particles is supported by axially resolved measurements of the extra electron density, shown in Fig. 4. The axial profile, obtained after several minutes of plasma operation, is the expected particle density profile for these conditions.^{15,16} The maxima at the plasma-sheath boundaries correspond to higher particle densities in these regions, where the dust grains are trapped by the Coulomb interactions.

One of the most interesting problems is the charging of

FIG. 5. Typical photodetachment signals at two different plasma operation times: (a) 10 ms and (b) 1 s. The laser is shot at $t=1 \mu\text{s}$ and at the axial position $z=15 \text{ mm}$. The conditions are 120 mTorr pressure, 10 W rf power, and 30 sccm flow rate. Note the different scale on the y axis between (a) and (b).

very small clusters in the beginning of the powder formation process. This first phase coincides with a rapid decay of the electron density (Fig. 3). The height (Δn_e) and time decay (τ) of the photodetachment signal depend strongly on the plasma operation time. Typical behavior of the extra electron density for two operation times is shown in Fig. 5. The height of the signal, recorded in a dust free plasma (after 10 ms of plasma operation) corresponds to a negative ion density of $4 \times 10^{15} \text{ m}^{-3}$, which is a reasonable value for a weakly electronegative gas, like SiH₄. On the other hand, the negative ion density in a dusty plasma (1 s of plasma operation) determined this way would be $8 \times 10^{16} \text{ m}^{-3}$. This is not realistic in a silane plasma and therefore multiply charged species must be stripped during the laser shot.

The spatially averaged electron density and the height of the photodetachment signal during the first second after plasma ignition are shown in Fig. 6. In the first 50 ms after switching the plasma on the photodetachment signal does not increase. In this period nanometer scale crystallites are formed. As their density is expected to be higher than the negative ion density, the photodetachment signal suggests that the negative charge on the crystallites is very small. After 50 ms the photodetachment signal increases. This cor-

FIG. 6. The electron density n_e (full curve) and the height of the photodetachment signal Δn_e (●) as a function of the plasma operation time at 120 mTorr, 10 W, and 30 sccm.

responds to the start of the phase in which the particles begin to coalesce and acquire negative charge. As the time needed for the dust grains to obtain their negative charge is shorter than the residence time of active species in the plasma ($\sim 300 \text{ ms}$ at 120 mTorr and 30 sccm), most of the precursors can be trapped and consequently a high particle density can be reached in these conditions. The charge on the particles increases during the first second of plasma operation as the particles continue to grow. Afterwards all particles have a permanent charge and coalescence stops due to Coulomb repulsion.

The quasineutrality condition for the plasma requires that the positive ion density increases as a function of time after plasma ignition, while simultaneously the electron density decreases. Therefore the ionization rate must increase. The electron loss due to presence of the particles is compensated by an increase of the electron temperature, as reported by Bouchoule and Boufendi³. This effect is of similar nature as the simultaneous increase of the ion density and decrease of the electron density during the transition between an electropositive and an electronegative plasma.^{9,11}

Special attention should be given to the decay of the extra electrons after the laser shot. Note that the time needed for the electron density to return to the steady state depends strongly on plasma operation time (Fig. 5). Furthermore, it is clear that the decay kinetics in the presence of particles is rather complex. Nevertheless, we can define the decay time as the time needed for the extra electron density to decay to half of the maximum value (Δn_e). The decay time of the extra electrons reflects the rate of the dominant electron loss process in the plasma. In Fig. 7 the decay time of the photodetached electron density is shown as a function of time after switching on the plasma. In a dust free discharge (10 ms after plasma ignition) the decay can be due to dissociative attachment to SiH₄ or transport to the wall. Dissociative attachment to SiH₄ is a relatively slow process, with a rate constant of $5 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ at an electron energy of 2.5 eV.¹⁷ In our conditions (5% SiH₄ at 120 mTorr) this results in

FIG. 7. The decay time τ of the photodetached electron density as a function of the plasma operation time at 120 mTorr, 10 W, and 30 sccm.

a decay frequency of $\sim 10^3 \text{ s}^{-1}$. This is slower than the typical loss frequencies of electrons to the wall ($\sim 10^4 \text{ s}^{-1}$). Therefore, the decay time of the photodetachment signal in a dust free SiH₄ plasma is probably governed by the electron transport. Consequently, the slow decay of the extra electrons, recorded after 10 ms of plasma operation, is not surprising in a dust free plasma. In the presence of dust, however, the recharging of dust particles after photodetachment is a very fast process. The charging frequency of a particle is proportional to its radius. Therefore, the decay frequency of the extra electrons, created by photodetachment in a dusty plasma, depends on the particle radius and particle density. During the first 50 ms, when crystallites are formed, the decay time decreases strongly. This suggests that effective recombination sites for electrons are created in the plasma. In the coalescence phase, the decay time of photodetached electrons remains more or less constant. Note that the photodetachment technique yields not only the total negative charge on particles, but also information on charging dynamics. Therefore it is a sensitive technique that allows detection of the transition between the dust free and the dusty plasma.

In the GREMI laboratories the particle density and size were measured.^{5,12} If we assume that our conditions are comparable to those of Boufendi and Bouchoule, we can estimate the charge per particle (note: the discharge geometries and the used regimes of the external parameters are comparable in the two reactors). After a plasma operation time of 1 s the particle density is about $3 \times 10^{15} \text{ m}^{-3}$ and the average radius is 5 nm.¹² If we assume that the photodetachment signal corresponds to the accumulated charge on the particles, this gives 25 elementary charges per particle.

The height of the photodetachment signal as a function of the gas flow rate ($\mathcal{F}$) is shown in Fig. 8 for $\mathcal{F} \geq 30 \text{ sccm}$. For lower gas flows ($\leq 30 \text{ sccm}$) the electron density in the plasma shows oscillatory behavior (see Fig. 3). The density of extra electrons is roughly inversely proportional to the gas flow, indicating that the dust grains, or their precursors, are flushed out of the discharge by the gas flow. For the same

FIG. 8. The height of the photodetachment signal Δn_e and the decay time of the extra electrons τ as a function of the flow rate at 120 mTorr and 10 W.

reason the decay time of the extra electrons increases at high flow rates. A similar conclusion for lower flow rates was found earlier by studying the time scale of the electron density fluctuations in a dusty plasma.⁶

IV. CONCLUSIONS

We have shown that laser-induced photodetachment on dust particles allows measurement of the charge on the clusters in a plasma. Furthermore, it gives information about charging kinetics. The formation of silicon clusters in argon/silane rf plasmas occurs in several stages. In the first 10–50 ms 2 nm crystallites are formed; they then coalesce into larger structures. The photodetachment signal in the first period is low, indicating that the total negative charge on the crystallites is very small. Nevertheless, the electron loss frequency increases and the electron density decreases in their presence. This suggests that both strongly attaching species and strong recombination sites are created in the plasma on this time scale. The particles formed during the coalescence period of the crystallites acquire a nonzero average negative charge, sufficient to trap them in the plasma glow. Simultaneous with the charging of particles, the photodetachment signal increases strongly. This implies that the positive ion density increases in the course of particle formation. As the electron density drops during this process, the electron temperature must increase to provide a higher ionization rate.

ACKNOWLEDGMENT

This work was supported by the BRITE-EURAM programme of the European Community under Project No. 7328 and Contract No. BRE2-CT94-0944.

¹Plasma Sources Sci. Technol. **3** (1994).

²A.A. Howling, L. Sansonnens, J.-L. Dorrier, and Ch. Hollenstein, J. Phys. D **26**, 1003 (1993).

³A. Bouchoule and L. Boufendi, Plasma Sources Sci. Technol. **2**, 204 (1993).

⁴L. Boufendi, A. Plain, J.-Ph. Blondeau, A. Bouchoule, C. Laure, and M. Toogood, Appl. Phys. Lett. **60**, 169 (1992).

- ⁵L. Boufendi, J. Hermann, A. Bouchoule, B. Dubreuil, E. Stoffels, W.W. Stoffels, and M.L. de Giorgi, *J. Appl. Phys.* **76**, 148 (1994).
- ⁶W.W. Stoffels, E. Stoffels, G.M.W. Kroesen, and F.J. de Hoog, *J. Appl. Phys.* **78**, 4867 (1995).
- ⁷A. Bouchoule and L. Boufendi, *Plasma Sources Sci. Technol.* **3**, 292 (1994).
- ⁸E. Stoffels, W.W. Stoffels, D. Vender, M. Kando, G.M.W. Kroesen, and F.J. de Hoog, *Phys. Rev. E* **51**, 2425 (1995).
- ⁹E. Stoffels and W.W. Stoffels, Ph.D. thesis, Eindhoven University of Technology, 1994.
- ¹⁰M. Haverlag, Ph.D. thesis, Eindhoven University of Technology, 1991.
- ¹¹E. Stoffels, W.W. Stoffels, D. Vender, G.M.W. Kroesen, and F.J. de Hoog, *J. Vac. Sci. Technol. A* **13**, 2049 (1995).
- ¹²L. Boufendi and A. Bouchoule, *Plasma Sources Sci. Technol.* **3**, 262 (1994).
- ¹³L. Boufendi, T. Hbid, F. Vivet, P. Lefauchaux, and A. Bouchoule, *Euro-physics Conference Abstracts, ESCAMPIG 94*, edited by M.C.M. van de Sanden (European Physical Society, Eindhoven, 1994), Abstract 18E, p. 79.
- ¹⁴Ph. Belenguer, J.Ph. Blondeau, L. Boufendi, M. Toogood, A. Plain, A. Bouchoule, C. Laure, and J.P. Boeuf, *Phys. Rev. A* **46**, 7923 (1992).
- ¹⁵A.A. Howling, Ch. Hollenstein, and P.-J. Paris, *Appl. Phys. Lett.* **59**, 1409 (1991).
- ¹⁶J.P. Boeuf, Ph. Belenguer, and T. Hbid, *Plasma Sources Sci. Technol.* **3**, 407 (1994).
- ¹⁷J. Perrin, C. Böhm, R. Etemadi, and A. Lloret, *Plasma Sources Sci. Technol.* **3**, 252 (1994).
- ¹⁸D.E. Carlson, J.I. Pankove, C.R. Wronski, and P.J. Zanzucchi, *Thin Solid Films* **45**, 43 (1977).