International Journal of Mass Spectrometry 223–224 (2003) 313–325
www.elsevier.com/locate/ijms

Plasma–powder interaction: trends in applications and diagnostics

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Received 13 December 2001; accepted 15 May 2002

Abstract

The research effort in the area of dusty plasmas initially aimed at avoiding particle formation and controlling the contamination level in industrial reactors. Nowadays, dusty plasmas have grown into a vast field and new applications of plasma-processed dust particles are emerging. There is demand for particles with special properties, and for particle-seeded composite materials. Low-pressure plasmas offer a unique possibility of confinement, control and fine tailoring of particle properties.

The interaction between plasma and injected micro-disperse powder particles can also be used as a diagnostic tool for the study of plasma surface processes. Examples for determining the electric field in front of electrodes and for determining the particle charge are given as well as for obtaining information on the energy fluxes in the plasma. (Int J Mass Spectrom 223–224 (2003) 313–325)

Keywords: Dusty plasma; Low-pressure plasma; Plasma–particle interaction

1. Introduction

The interest in the field of plasma–particle interaction in respect to dusty plasmas has grown enormously during the last decade. At present, the interest is due to applied research related to material science and surface processing technology [1–7] and, recently, also in respect to plasma diagnostics [8–10]. But powder formation has also been a critical concern for the micro-electronics industry, because dust contamination can severely reduce the yield and performance of fabricated devices. Sub-micron particles deposited on the surface of process wafers can obscure device regions, cause voids and dislocations, and reduce the adhesion of thin films [11,12].

Nowadays, dust particles are not anymore considered as unwanted pollutants. Some positive aspects of dusty plasmas have emerged and they have even turned into production goods. Powders produced using plasma technology have very interesting and potentially useful properties, e.g., very small sizes (nanometer to micrometer range), uniform size distribution, and chemical activity. Size, structure and composition can be tailored to the specific requirements, dependent on the desired application [3,5,13,14].

There are several links between dusty plasma physics and material science. In the light of the applications, two major trends can be distinguished in applied dusty plasma research. The first one is similar to the well-established surface modification technology, except that now the surface of dust particles is the subject of treatment. The aim is to tailor particle properties for specific purposes. Here one can think

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PII S1387-3806(02)00867-9

of coating, surface activation, etching, modification, or separating of clustered grains in the plasma. In this type of processing, particles are either grown in the plasma or they are externally injected [14–17]. A second important trend in applied dusty plasma research is the incorporation of dust particles in plasma enhanced chemical vapour deposition (PECVD) environment. By this way, new materials are obtained by seeding of thin films with dust particles. Especially nanostructured materials, like thin films with an inclusion of nanometer size particles, are a hot topic in material science [18,19]. Naturally, advanced treatment of particle surface as well as handling of powders in PECVD reactors requires a good control of particle properties.

It is obvious that fundamental knowledge of plasma interaction with particle surfaces must be available to optimise the various applications and to support the industrial developments. These interaction mechanisms have been studied in a more basic research field of dusty plasmas in relation to astrophysics and Coulomb crystallisation [20–24]. The astrophysical questions are related, for example, to the formation of stars in interstellar clouds [25] or processes in cometary tails and planetary magnetospheres [26,27].

The interaction between plasma and injected micro-disperse powder particles might also be used as a tool for the study of plasma–wall processes in technological applications of low-pressure plasmas, such as thin film deposition or etching. The idea to employ powder particles as a kind of micro-probes has been triggered, for example, by the basic research on the particles of plasma crystals [28,29].

In the present paper, some issues related to applications of particle processing in plasma will be reviewed, and the potential of dust particles in a plasma for the use in plasma diagnostics will be summarised.

2. Plasma–particle interaction

If dust particles are injected into a plasma, they become negatively charged by the currents towards the particles and can be confined in the discharge. The trapping is due to the balance of the forces acting on the particles. However, trapping capacity of a plasma is quite limited. Good confinement is obtained only in a rather narrow range of external plasma parameters (e.g., pressure, power input, gas flow) which does not necessarily match the optimal conditions for the technological treatment of dust particles.

The equilibrium net charge Q of a powder particle, which is already reached after a very short time ($\sim 10^{-6}$ s), is a consequence of the charge carrier fluxes and their surface interaction at the particle surface. In Section 5 a simple model for particle charging on the basis of plasma–surface interaction is provided.

Under typical experimental conditions, where the diameter $2r_p$ of the particles ($\sim 10^{-6}$ m) is always small in comparison to the Debye length λ_D ($\sim 10^{-4}$ m) and the mean free path λ_{mfp}($\sim 10^{-2}$ m), the orbital motion limited (OML) theory for a spherical particle holds [30]. The electron flux density j_e for a Maxwellian electron energy distribution function (EEDF) can be calculated by:

$$j_e = n_e \sqrt{\frac{kT_e}{2\pi m_e}} \exp\left(\frac{-e_0 V_{bias}}{kT_e}\right) \quad (1)$$

while the ion flux density j_i may be obtained by:

$$j_i = n_i \sqrt{\frac{kT_i}{2\pi m_i}} \left(1 + \frac{e_0 V_{bias}}{kT_i}\right) \quad (2)$$

where n_e is the electron density, n_i the ion density, T_e the electron temperature, T_i the ion temperature, m_e the electron mass, m_i the ion mass, k the Boltzmann constant and e_0 the elementary charge.

Since dust grains are small isolated substrates in a plasma environment, they rest always at floating potential V_{fl} and it is $V_{bias} = V_{pl} - V_{fl}$ (V_{pl}: plasma potential). As electrons are much more mobile than ions, the grain surface collects a negative charge, repelling electrons and attracting positive ions until a stationary state is reached. In this equilibrium state the electron and ion flux densities towards the particles are equal: $j_e = j_i$. As a result, the net charge $Q = Ze_0$ of a micron-sized particle can be in the order of a few thousands of elementary charges e_0. In principle, the charge Q on a micro-particle can be obtained by equating the fluxes of electrons and positive ions towards the particle surface and their recombination, see Section 5. However, in reality for non-Maxwellian EEDF the current balance becomes more difficult [31]. Several authors have studied both theoretical and experimental aspects of charging the dust grains in capacitively coupled rf discharges, see for example [28,32–37].

However, the above approach holds only for relatively large objects, which are able to absorb the incoming fluxes of charged species. For nanometer size particles, which are merely macromolecules, one has to consider specific cross-sections for electron/ion capture. Therefore, one cannot a priori predict the charge of an arbitrary nanometer particle, and charge fluctuations for these objects are common [38].

The charged particles interact with the electric field in front of the electrodes or walls, respectively, and they are often observed as levitated dust clouds forming rings or domes in the high-potential boundary regions of a plasma. The electrostatic force has to be balanced by various other forces in order to confine the particles.

Understanding particle behaviour in plasmas is the base of both fundamental and applied dusty plasma research. Detailed knowledge of forces acting on particles and particle motion is necessary to proceed in astrophysical studies, and/or in analysis of wave phenomena. This knowledge is also applied in surface-processing reactors to determine the responses of particles to varying external plasma parameters, and the position of the particles with respect to the processed surface. All these problems have to be considered while aiming at reducing surface contamination, or while attempting to produce or to process particles in plasmas.

Neutral gases containing a suspension of particles are well known and thoroughly described objects. The most common systems are atmospheric aerosols, for example combustion/disposal gases, nebulae and volcano clouds. Such aerosols typically contain large particles, ranging in size from a few to a few hundreds of micrometers. At atmospheric pressures fluid models are often applied to describe the gas–particle interactions, and particle behaviour is determined by gas flows, turbulence, thermal gradients and gravitation. Basic knowledge of fluid dynamics and aerosol physics is to some extent applicable to low-pressure laboratory plasmas, too. In a study of dust particles in plasmas, some of the above mentioned interactions are taken into account, others are neglected or modified, and few specific plasma-related forces are introduced [3].

These forces, which have been discussed extensively by several authors, are the gravitation, the neutral and ion drag, thermophoresis and photophoresis [39–41]. But only some of these forces will play a role in laboratory plasmas. Commonly, the electrostatic field and the gravitational force are important. The superposition of both effects results in a parabolic potential trap [42]. It should be mentioned that the contributions to the force balance of the particles can be additionally influenced by external effects like strong laser radiation [43,44], temperature gradients by heating of the surrounding walls [45], or magnetic fields [46].

In laboratory plasmas, Coulomb interactions of charged particles with electric fields in the plasma provide the unique mechanism of dust trapping. The Coulomb force:

$$F_{\mathrm{C}} = Ze_0E_0 \quad (3)$$

where E_0 is the local electric field, is therefore the most interesting force acting on the particles. In plasma regions with uniform free charge density, the Coulomb force can be simply expressed as ‘vacuum’ force. Although a charged particle in the plasma develops its own sheath (so-called ‘dressed particle’), this sheath does not screen an external electric field. When the ‘dressed particle’ is present in a region with charge density gradients (plasma sheath), additional polarisation force F_{p} emerges, due to deformation of the sheath around the particle:

$$F_{\mathrm{p}} = \frac{(Ze_0)^2}{16\pi\varepsilon_0\lambda_{\mathrm{D}}}\frac{\nabla n_{\mathrm{e}}}{n_{\mathrm{e}}} \quad (4)$$

where λ_{D} is the Debye length ($\lambda_{\mathrm{D}} \gg r_{\mathrm{p}}$) and ε_0 marks the dielectric constant. Generally, $F_{\mathrm{p}}/F_{\mathrm{C}}$ is in the order of r_p/λ_D. Therefore, polarisation effects may be neglected [3] and a vacuum force can be taken also for particles in the vicinity of the plasma sheath. This problem was treated in detail by Hamaguchi and Farouki [47] and by Daugherty et al. [40]. Typical electric fields in the plasma sheath are in the order of 10^4 V/m. Under the simplified assumption of a spherical capacitor [3], the particle charge Ze_0 is proportional to the radius r_p ($Z \approx 10^3 r_p$, where r_p is in micrometers) and the Coulomb force is about $10^{-13} r_p$ (in Newton). This makes Coulomb repulsion the most important interaction, which prevents the particle from falling onto the surface. During discharge operation particles seek regions with lower electric fields, and typically they remain suspended at the edge of plasma glow and sheath.

The ion drag force F_i, acting on particles in a pre-sheath of a low-pressure radio-frequency plasma is in the order of 10^{-14} to $10^{-13} r_p^2$ (in Newton) (r_p is in micrometers), dependent on the ion density [3]. Ion drag pushes the particles towards the surface, contrary to the Coulomb force. Since F_i scales as r_p^2 and F_C as r_p, particles present in the pre-sheath may fall onto the surface during plasma operation when their size exceeds a few micrometers. It has been observed that trapping of micrometer-sized particles is possible only at low plasma power levels, when the ion density is below 10^{16} m^{-3}. Failure of confinement at higher powers might be due to the action of the ion drag force.

Concluding, electrostatic interactions due to the particle charge lead to a unique situation. The behaviour of charged dust in a low-pressure medium under the influence of the electrostatic and ion dynamic forces is different than in other systems containing particles. Particles levitate in the plasma glow, repelled from the surface by the Coulomb force. However, forces that remove the particles from the glow have a stronger dependence on the particle size than the Coulomb force ($F_C \sim r_p$). Thus, when the size exceeds a certain limit, particles can deposit on the surface because of ion drag (r_p^2), gravitation (r_p^3) and thermophoresis (r_p^2) (but the direction depends on the temperature gradient), or be evacuated from the reactor by the gas flow (r_p^2) [3].

The balance of the different forces acting on the particles is doubtless the essential issue for their trapping in the plasma boundary regions as well as for the removal out of sensitive plasma regions. Vice versa, by observing the position and movement of the particles in dependence on the discharge parameters, information can be obtained on the electric field in front of electrodes and substrate surfaces—which gives the opportunity of a rather new diagnostic tool [8,9,29], as it will be illustrated in Section 5.

In addition to charging and trapping, the powder particles also undergo a thermal power balance which takes into account the several energy fluxes arriving at and leaving from the particle surface. The different contributions may include kinetic energy of electrons and ions, ion recombination energy, heat of chemical reactions at the surface, thermal conduction, and radiation. Measurement of the particle temperature T_p yields valuable information about these different fluxes. Thus, the particles can also be used as microscopic thermal probes [10,48].

3. Disturbing side effects of dust particles in process plasmas

"Almost all surface processing technologies are concerned with particle-induced failures, which has been well known for ages in micro-electronics industry. The fact that plasma processes, heavily implied in semiconductor device processing, could be involved in inducing dust problems in manufacturing tools has been one of the major inputs for the development of many basic and technological studies devoted to dusty plasmas" [3,12]. Especially in plasma-enhanced dry etching of semiconductors, the industry has always to fight against problems of surface contamination by dust. It is obvious that small particles, which fall onto the wafer surface during plasma treatment and stick in the wafer trenches, can cause defects and, hence, make the integrated circuit chips useless. The fact that the size of plasma-etched structures has decreased down to the sub-micrometer range and will be reduced to below 100 nm in the near future implies the importance for avoiding 'killer particles' down to the nanometer region. The problems become even more important by using modern processes as inductively coupled plasma (ICP) where the electric field in front of the substrates is rather weak and the particles can easily reach the surfaces. It is not surprising that the main goal of early dusty plasma investigations was to obtain a good control of contamination in plasma-processing reactors, either by eliminating dust particles from the gas phase or by preventing them from getting into contact with the surface. As a result of numerous elaborated studies [3,49–51], dust contamination by relatively large (>100 nm) particles is at present under control.

The sources of particle contamination during the plasma surface processes are:

- formation of large molecules, mesoscopic clusters and particles in the plasma by chemically reactive gases, and
- formation of macroscopic particles at surfaces by means of plasma–wall interaction.

The plasma process itself promotes the particle formation by excitation, dissociation and reaction of the involved species in the gas phase. Typical examples are plasma polymerisation [52] and thin film deposition in silane-containing PECVD processes. The formation of particles proceeds via three steps as it has been described in [52,53,55]. The different stages of the particle growth in the plasma can be observed by mass spectrometry [15], laser-induced evaporation [56] photo detachment [53,57], IR absorption [58], microwave cavity measurements [53], Mie scattering [59], and self excited electron resonance spectroscopy (SEERS) [9,60]. The generated particles can be analysed by transmission electron microscopy (TEM).

Examples for generation of particulates from the surrounding surfaces are reactive ion etching (RIE) [61,62] surface sputtering of targets [63,83], vacuum arc deposition [64–66], and in hollow cathode processes [67].

In order to minimise the influence of dust particles in thin film deposition and etching, it is important to develop either new processes avoiding dust generation or to develop process cycles in dusty plasmas without contamination at the relevant substrate regions, which are sensitive against dust fallout. This means an active influence on the collection of particles as well as their trapping behaviour and their movement, respectively. There exist several chances of such active influences, for instance:

- intelligent arrangement of electrodes and substrates [68],
- construction of special electrode shapes ('grooved' electrodes) [49,50,69],
- square wave plasma modulation [70,71],
- fast transport regimes of the reactive species [72],
- additional electrostatic forces by an external potential supply [73,74],
- additional other forces based on neutral drag (gas flow) or thermophoresis (temperature gradient) by

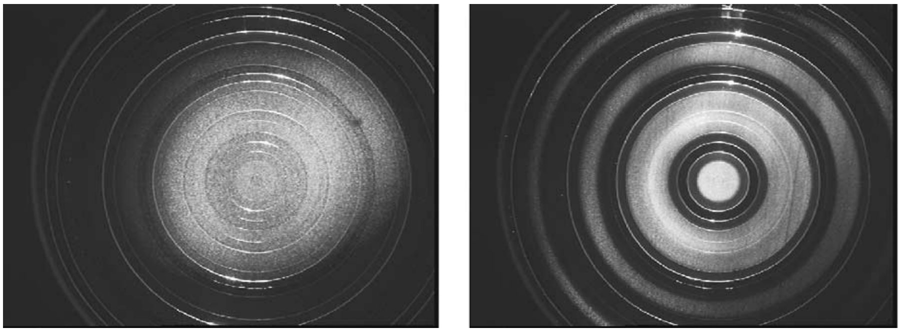

Fig. 1. A compact cloud of SiO_2 powders (∼1 μm) confined in an argon rf-plasma ($p = 10$ Pa, $P = 5$ W) (left) has been separated and stored in rings in different grooves of an aluminum plate which has been placed onto the rf-electrode (right) [68].

external heating [45,75], or photophoresis (laser irradiation) [43].

For example, the basic idea for the introduction of square wave plasma modulation with 'on-off' cycles is that the small and negatively charged dust precursors are not allowed to grow in size and concentration during the 'on' sequence and leave the plasma volume during the 'off' sequence. By taking into consideration the characteristic times for both sequences the optimal modulation frequency should be in the order of a few kilohertz [3,84].

Another approach in order to avoid dust formation is to develop a fast transport regime of the species, so that particles would not have the possibility of growing during their flow through the reactor [72].

The introduction of special electrode shapes and additional forces will result in changes of the equilibrium planes where the dust particles are trapped (Fig. 1). By means of these peculiarities the particles can be actively pushed towards regions in the reactor where their presence is not dangerous [73].

4. Formation and modification of powder particles in a plasma for different industrial applications

In contrast to the disadvantages of dust particles in plasma, as mentioned in the last section, particles which are produced and/or modified in plasma can also have valuable properties for specific applications. In particular, the increased knowledge and ability to control particles in a plasma environment has recently led to new lines of technological research, namely the tailoring of particles with desired surface properties.

Present and potential applications of plasma-treated particles are numerous as it will be given in the following points:

- treatment of soot and aerosols for environmental protection [76],
- powder particle synthesis in high- [77,92–94] and low-pressure [54] plasmas,
- illumination technology, cluster lamp [78],
- enhancement of adhesive, mechanical and protective properties of powder particles for sintering processes in metallurgy [79,89],
- fragmentation of powder mixtures in order to sort them [73],
- improvement of thin film properties by incorporation of nanocrystallites for amorphous solar cells [18] and hard coatings [80,81],
- coating of lubricant particles [88],
- application of tailored powder particles for chemical catalysis,
- functionalisation of micro-particles for pharmaceutics and medical application,
- production of colour pigments for paints,
- improvement of surface protection against corrosion of fluorescent particles [82,90,91],
- tailoring of optical surface properties of toner particles [14], etc.

The different methods for particle production, modification and application as well as their various possibilities of employment are schematically summarised in Fig. 2.

Particle production can start in the plasma using a reactive gas mixture. Alternatively, particle formation can be initiated by external sources. Armand et al. [85] reported formation of fullerene clusters

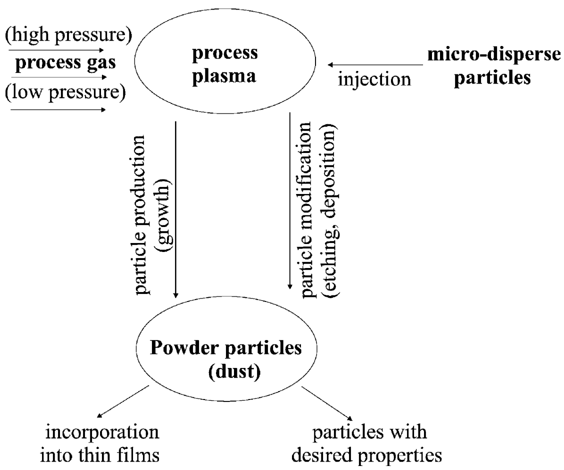

Fig. 2. Different ways of particle treatment in process plasmas [68].

by irradiation of various hydrocarbon gases at atmospheric pressure with a CO_2 laser ($\lambda = 10.6\,\mu m$). In case of an infrared laser, particle formation occurs by non-resonant heating and pyrolysis of the gas. High-purity ultra-fine SiC powders can be synthesised in a laser-driven discharge in SiH_4/C_2H_4 mixtures at atmospheric pressures [86]. In low-pressure plasmas the third harmonics of the Nd:YAG laser ($\lambda = 355\,nm$) was used to initiate particle nucleation in a low-pressure radio-frequency methane discharge [87]. In the studied conditions (low-power plasma at 70 Pa), spontaneous gas-phase nucleation in CH_4 plasma was not observed. The high-power UV laser beam was focused in the plasma and operated at a repetition frequency of 10 Hz, and particles were detected after seconds of such treatment. The clusters obtained this way are in the nanometer-size range and continued to grow by agglomeration and plasma polymerisation to (exceptionally large) chain-like structures of some millimeters in size (Fig. 3).

The plasma-produced particles can be used for further applications. For example, it is possible to produce composite coatings, where the properties of various materials are combined. An example is the deposition of a wear-resistant self-lubricating coating. In this process, which is schematically shown in Fig. 4, small lubricating MoS_2 particles are included in a hard titanium–nitride matrix [88]. The resulting layer will have the hardness and chemical stability of a TiN layer. However, as the layer wears off during its lifetime, the embedded MoS_2 particles will emerge at the surface and form a lubricating layer. This is the principle of a self-lubricating hard coating. It is expected that introduction of such nanostructured layers for coating of heavy-duty mechanical tools on the industrial scale will bring huge economical benefits, for existing as well as novel process technologies and materials. In addition, there will be large environmental implications, as mechanical processing will become much cleaner, safer and more energy efficient.

Since all these materials are prepared under low-pressure PECVD conditions, the new development uses the knowledge gained in the studies of dusty plasmas. Nanometer size particles are extremely difficult to handle outside the processing reactor. Therefore, integrated process of dust particle fabrication in the plasma and co-deposition in the layer is the most promising technology for the production of composite material.

Examples for the modification (coating, etching) of externally injected grains have been discussed elsewhere [68].

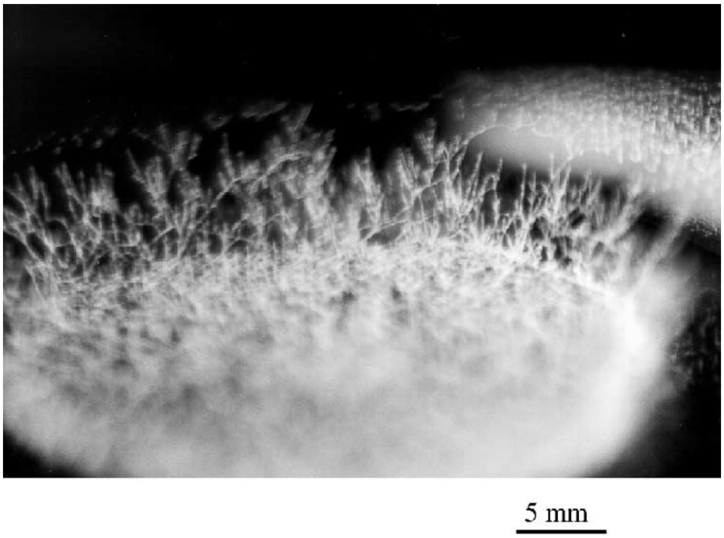

Fig. 3. Chain-like structures of polymers grown in a CH_4 plasma by UV radiation, after [87].

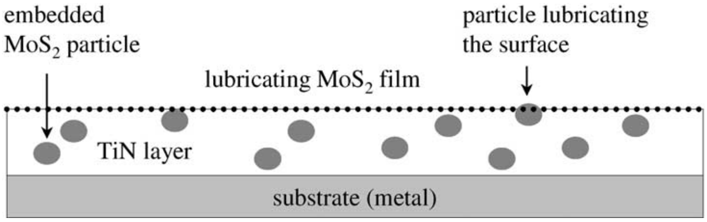

Fig. 4. The idea of a self-lubricating coating: small grains of lubricant are included in the hard matrix. When the surface is exposed to friction and wear, small amounts of lubricant are released to form a thin protective film over the surface. Such hybrid coatings are both effectively lubricated and environmentally clean.

5. Possibilities for using dust particles as micro-probes for plasma diagnostics

The interaction between plasma and injected micro-disperse powder particles can also be used as diagnostic tools for the characterisation of:

- electric fields in the plasma sheath (particles as electrostatic micro-probes) [9,29],
- energy fluxes in the plasma and towards surfaces (particles as micro-calorimeters) [10,48],
- plasma–wall interaction (particles as micro-substrates) [9,59].

By observing the position and movement of the particles dependent on the discharge parameters, information can be obtained on the electric field and the potential distribution in front of electrodes and substrate surfaces where other plasma diagnostic methods fail. Hence, powder particles can be used as a kind of electrostatic micro-probes for the determination of plasma parameters.

Under typical low-pressure plasma process conditions, on a confined micro-particle mainly act the gravitational force F_g and the electric field E. To trap such a particle the responding electric field force F_{el} must have the same value:

$$F_g = mg = F_{el} = QE(z_0) \qquad (5)$$

This simple balance equation implies the determination of the field strength at trapping position z_0 of the particles with mass m. But for using this method the particle charge Q must be known. For the determination of the grain charge Q different procedures have been suggested by several authors, as for example:

- driven particle oscillation about equilibrium by superposition of an external low-frequency voltage [95],
- laser-induced photodetachment of charge and subsequent detection by microwave interference methods [53] or probes [57],
- formation of Mach cones by moving dust particles [96],
- measurement of electron density drop of the surrounding plasma by particle injection [9],
- estimations by model assumptions based on the particles spherical capacity [3] or on the currents of charge carriers towards the dust grains [9], respectively.

As a rather new method for the determination of particle charge, the decrease of electron density n_e during particle injection should be mentioned shortly. Since the injection of powder particles into a plasma disturbs the discharge for a short time until the equilibrium conditions are reached, the related transient changes have been observed by SEERS. While the bias voltage shows only a slight variation when micro-disperse powder particles are injected the response of the electron density is remarkable. As an example, in Fig. 5 a typical behaviour of n_e during powder injection is presented. In the undisturbed argon rf-plasma the electron density shows a rather constant value. If the powder particles are injected the plasma density drops immediately for a short time. After charging n_e relaxes again to the original value. However, the depth and width of

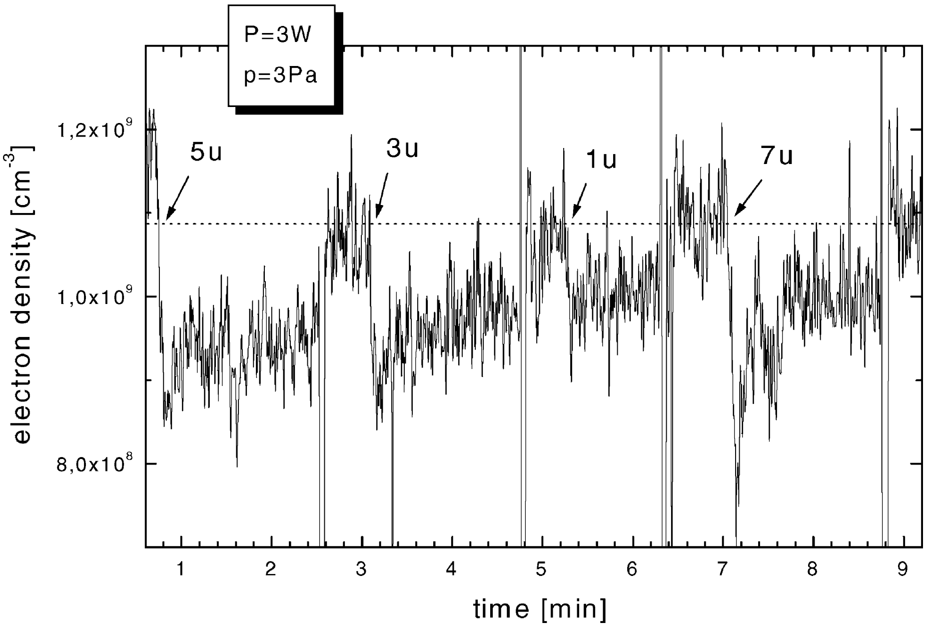

Fig. 5. Mean electron density during powder injection as measured by SEERS, after [9]. The units 'u' indicate the amount of injected dust particles. The dashed line marks the density of the pristine plasma.

the electron density drop depends on the amount of injected dust particles which is indicated as relative units 'u' in Fig. 5. By knowing the powder density n_d, which can be obtained by light scattering, the acquired charge per single dust grain can be determined. The results are comparable with values obtained by other methods.

In respect to the mentioned field measurements, it is even possible to measure not only the static field strength $E(z_0)$, but also the field gradient $\mathrm{d}E/\mathrm{d}z$ via a driven oscillation method as recently suggested by Allen and co-workers [97] by using powder particles which are confined in the plasma sheath.

In addition to charging and trapping the powder particles also undergo a thermal power balance which takes into account the several energy fluxes arriving at and leaving from the particle surface as kinetic energy of electrons and ions, ion recombination energy, thermal conduction, and radiation. Measurement of the particle temperature T_p yields valuable information about these different fluxes [10].

The thermal balance of the particles can be written as an equality between the thermal influx Q_{in}, the temporal derivative of the particle enthalpy $\dot{H}_p$ and the thermal outflux Q_{out}:

$$Q_{in} = \dot{H}_p + Q_{out} \tag{6}$$

In the stationary situation of the particle being suspended in the plasma, $\dot{H}_p = mc(\mathrm{d}T_p/\mathrm{d}t) = 0$. The fluxes Q_{in} and Q_{out} are the surface integrals of the related energy flux densities J_{in} and J_{out}, respectively, over the particles surface A_p: $Q_{in} = \int_{A_p} J_{in}\,\mathrm{d}A$, $Q_{out} = \int_{A_p} J_{out}\,\mathrm{d}A$. In general, for an inert gas plasma the total energy influx J_{in} is the sum of the influxes due to the kinetic energy of electrons (J_e) and ions (J_i), and the energy which is released when a positive ion recombines at the surface of the floating particle (J_{rec}):

$$J_{in} = J_e + J_{ion} + J_{rec} \tag{7}$$

The kinetic energetic contributions (J_e, J_i) of the electrons and ions, respectively, are products of the particle fluxes (j_e, j_i, see Eqs. (1) and (2)) and the mean kinetic energy of the species which is determined by the EEDF for the electrons and the particles bias potential for the ions. In the stationary case, where the particles are heated to their equilibrium temperature T_p, the energy fluxes are equal: $J_{in} = J_{out}$. Hence, by knowledge of the outgoing flux J_{out} which consists of the thermal conduction J_{th} and the radiation J_{rad} the total energy flux towards a powder particle can be obtained and compared with model calculations for J_{in} [98]. Of course, in chemically reactive plasmas also heating terms by exothermic reactions have to be taken into consideration.

The latter issues open new ways for an access to study plasma–surface interaction in respect to measurements of the involved mechanisms. In comparison to conventional plasma diagnostics one has the chance to get additional information by the observation of the particles force balance which is immediately influenced by the plasma parameters.

Since the charge of the particles confined in a plasma plays a key role, at the end of this part a simple model for its determination based on elementary mechanisms of plasma–wall interaction will be presented. The model for the explanation for charging of 'insulated' dust particles based on studies for insulating surfaces [99] includes the following elementary processes at the surface: adsorption of incoming charges carriers, deposition of charge carriers, and surface recombination of the incoming charge carriers, including the concept of their surface diffusion.

Modelling of the plasma–particle interaction is performed in the framework of a 'two-dimensional surface plasma' as first proposed by Emeleus and Coulter [100]. This means that the ions at the particle surface are considered to be fixed and the electrons are moving along the surface by diffusion. In the stationary case, we have an equilibrium between the adsorbed charge carriers and those that desorbed again or recombine, respectively. Hence, the balance equations of the desorbed particles may be written as follows:

$$\frac{d\sigma_e}{dt} = (1 - \Theta_e) S_e j_e - \frac{\sigma_e}{\tau_e} - \alpha_R \sigma_e \sigma_i \qquad (8)$$

$$\frac{d\sigma_i}{dt} = (1 - \Theta_i) S_i j_i - \frac{\sigma_i}{\tau_i} - \alpha_R \sigma_e \sigma_i \qquad (9)$$

where σ_e and σ_i are the electron and ion number densities on the particle. For many conditions the fluxes can be approximated by Eqs. (1) and (2). Here j_e and j_i are the current densities towards the particles, S_e and S_i the sticking probabilities, τ_e and τ_i the residence times of adsorbed particles, Θ_e and Θ_i the fractions of coverage and α_R is the recombination coefficient. The temperature dependence of the residence times are given as:

$$\tau_l = \tau_{lo} \exp\left(\frac{E_{des,l}}{kT_p}\right), \quad l = e, i \qquad (10)$$

where T_p denotes the particle temperature, k is the Boltzmann constant, τ_{eo} and τ_{io} are the vibrational periods of the adsorbed electrons and ions, $E_{des,e}$ and $E_{des,i}$ the corresponding desorption energies. The negative particle charge, finally, is given by the net charge:

$$\Delta\sigma_e = \sigma_e - \sigma_i = \frac{Q}{A_p} \qquad (11)$$

where A_p is the surface area of the powder particle.

The present model was applied to the description for the experimentally obtained charging of MF particles in a helium plasma [28] and to Fe particles in an argon plasma. The values for the surface data listed in the following table were taken from the literature [99] and in some cases slightly modified.

τ_{eo}	1.8×10^{-9} s
τ_{io}	1×10^{-11} s
S_e	0.95
S_i	1.00
$E_{des,e}$	0.185 eV
$E_{des,i}$	0.10 eV
T_p	$380 \cdots 470$ K
T_g	300 K
α_R	$0.3\sqrt{\frac{T_p}{T_g}}\ \mathrm{cm^2\ s^{-1}}$

Fig. 6 shows the results for the calculations of the charging of MF particles in a helium plasma compared with measurements given in [28] dependent on input power. The model, combined with the appropriate coefficients for the recombination, sticking and

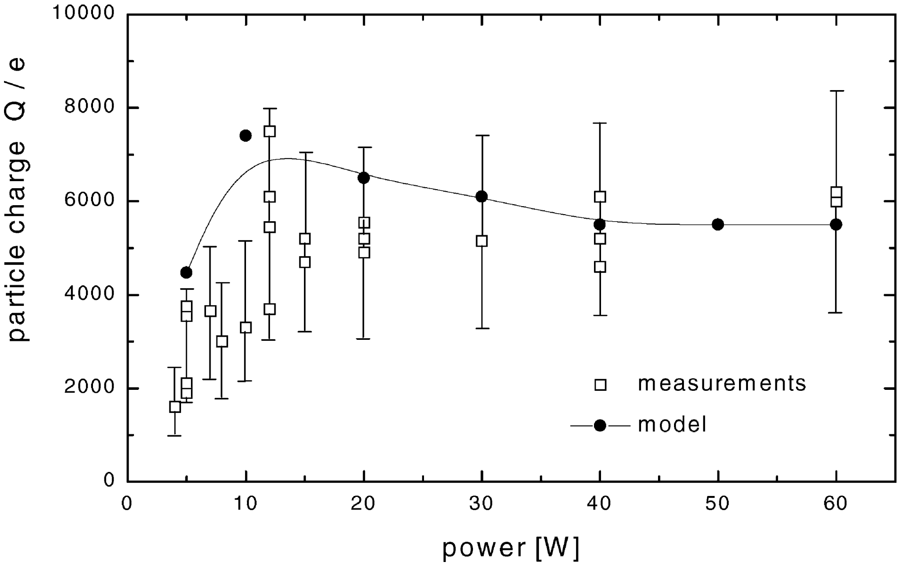

Fig. 6. Measured particle charges of MF particles in a helium plasma (from [28]) are compared with calculations based on the suggested model and the related plasma data (see text).

desorption, describes the 'shape' of the measurements satisfactorily. In a similar manner, we determined the charge of the iron particles used in our experiments in the same way to be in the order of $Q = 7000e$, which is a reliable value.

6. Conclusion

Powder formation, modification and trapping in laboratory discharges have received growing interest in the past decade. The unique possibility of dust particle confinement and control in the gas phase makes plasmas to excellent media for particle handling and treatment. Applications of dust particles are numerous, most of them emerging in modern material science. Established and new technological applications on particle processing have been reviewed.

Vice versa, the interaction between plasma and injected micro-disperse powder particles can be used as a diagnostic tool for the study of plasma surface processes in low-pressure plasmas. For instance, by observing the position and movement of the particles in dependence on the discharge parameters informations are obtained on the electric field in front of the electrode and on sheath structures. Moreover, the measured heat balance of confined particles provides information on the energy fluxes in the plasma and towards the surfaces.

All these applications make complex plasmas a rapidly expanding field of research in the frontier between plasma physics, material processing, and diagnostics. In the coming decade a large amount of novel and exciting developments in fundamental research as well as in technology of powder particles in plasmas can be expected.

Acknowledgements

This study was supported by the Deutsche Forschungsgemeinschaft under SFB 198. The authors would like to thank H. Boldt, G. Thieme, M.Hähnel, and A. Knuth for their support. The research of E. Stoffels and W.W. Stoffels has been supported by fellowships of the Dutch Royal Society (KNAW).

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