Non-equilibrium processes and dust formation in low pressure reactive plasmas

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Abstract. Plasma polymerisation and growth of the dust particles are still in the scope of the plasma community. We analyze the morphology and constitution of plasma polymerized carbonaceous dust particles. The dust particles were grown under different discharge conditions with the different background gas constituents and different monomers. The strong non-equilibrium between electron and ion transport properties causes the charging of the dust in plasma. This, on the other hand, produces changes in the discharge properties, such as: mean electron energy, plasma potential, excitation profiles and sheath dynamics. We report here some of our most relevant results on the properties of complex plasmas.

1. Introduction

Dust formation and growth in low temperature plasmas [1, 2] have been in the focus of many extended studies in the last two decades. At first separated in two different research areas, technology and application of processing plasmas in microelectronics [3–8] and astrophysical observations and studies of the dust in interstellar media (ISM) [9], the explanation of dust formation, its structure and basic properties had become a common field of interest to the larger scientific community. Plasmas containing nano- to micro-sized particles of solid material are also commonly named “complex plasmas”.

The presence of the dust particles in plasmas launches various physical phenomena such as dust acoustic waves, wake fields, voids and vortices [10, 11]. Due to the strong non-equilibrium character of the low temperature plasma - the large difference between ion and electron transport properties – the dust particles are able to collect charged particles, in the way similar to the electrical probes. The dust particles are playing the role of an additional loss mechanism for the electrons and thus change the properties of plasma, like the mean electron energy.

Depending on the plasma conditions the particle charge can be either positive or negative [12] but usually, the dust particles in laboratory plasmas are negatively charged.

We have investigated the properties of the dust and the complex plasmas by the use of infrared absorption spectroscopy, emission spectroscopy, laser light scattering (LLS), current and voltage measurements and mass and energy analysis of the neutral and ion fluxes. As we grow the particles on the purpose we were also interested in their internal structure and chemical properties. After collecting the particles we exposed them to the different ex situ analyses such as Scanning Electron
Microscopy (SEM), Transmission Electron Microscopy (TEM), Rutherford Backscattering (RBS), Nuclear Reaction Analysis (NRA) and Deuterium Induced Gamma Emission (DIGE) [13]. We also did some numerical calculations based on simplified models to describe the properties of complex plasmas [14].

In following sections we shall present the results of measurements on plasma polymerised dust and discuss some of non-equilibrium processes of dusty plasmas.

2. Experimental set-up

The dust particles were formed in capacitively-coupled RF plasma through plasma polymerization of acetylene monomer diluted in noble gases (Fig. 1) [15, 16]. The capacitively coupled parallel plane electrode discharge was connected to a 13.56 MHz RF power source. The standard power applied was 15 W. The electrode system consist of two symmetrically powered electrodes so that the electrode self-bias was kept small. Continuous flow of a background/acetylene gas mixture, with 8 sccm to 0.5 sccm flow ratio was fed into the discharge chamber. Argon, helium or xenon [15], were used as a background gases as well as nitrogen [17]. We also added some small amount of oxygen for testing the chemical composition of the particles [17]. We could trace the particle growth and measure the plasma properties with various diagnostics, such as laser light scattering (LLS), Fourier Transform Infra Red (FTIR) spectroscopy, plasma ion mass spectroscopy, and light emission spectroscopy [15--19].

![Figure 1. Experimental set-up.](image)

The size of the deposited, monodisperse particles was controlled by the discharge running time, with the previously measured particle growth-rate [13, 15]. For collecting the dust a specially designed dust sampling probe was applied [13], which used either the electrostatic force or thermophoretic force.

The current and voltage waveforms were measured with current and voltage probes and stored in the digital storage oscilloscope. The discharge was run either in the continuous wave mode or in the pulsed mode with different pulse frequencies and duty cycles [18]. More details of the experimental setup and diagnostics could be found in [15--19].
3. Dust morphology and composition

In our experiment we were able to design and grow the particles of different sizes (from 20 nm up to 300 nm in radius) and different chemical composition. We could trace their presence, density and diameter by the use of a light scattering, either LLS or infrared scattering. On figure 2 we present the time development of the infrared light scattering signal for the 5000 cm$^{-1}$ wavelength. This wavelength was chosen because there was no characteristic absorption features and we detected only the scattering signal. The scattering signal behaves periodically following the dust particle formation and growth. At the certain stage the balance of different forces brakes (for details of dust dynamics and forces on the dust in plasmas see [1]) and the dust particles leave the plasma volume (the decrease in scattering signal). Immediately after the new growth cycle starts and the process repeats. As the balance of forces is different for the different regions of plasma (due to the space distribution of different plasma properties like plasma density) the dust free regions inside the plasma could form, known as voids.

Figure 2. Infrared dust particle scattering signal vs. discharge time. The scattering signal follows the particle growth and disappearance from the plasma.

Thus the process of dust particle formation and growth is relatively long in time and periodical (for our experimental conditions) we were able to measure and manipulate them in different ways. Here follow some of the experimental results.

3.1. Dust particle morphology

Figure 3 shows a scanning electron microscope (SEM) image of a cauliflower shaped particle with fractal surface texture collected 20 minutes after the ignition of the Ar/C$_2$H$_2$ plasma [19]. The particle radius is about 150 nm. Spheroid grain shape and fractal surface texture have already been observed in several kinds of dusty plasmas [20]. Such kind of a microstructure is a product of columnar growth by ballistic deposition during the accretion phase [20, 21]. Maximum achieved diameter, at the end of one growth cycle (minimum of scattering signal, figure 2) is about 600 nm. The growth speed is thus, in the accretion phase, about 20 nm/min.

The TEM picture (figure 4) and the diffraction pattern (figure 5) suggest that the material is essentially amorphous due to the diffuse halo and ring pattern. A crystalline material would be characterized by sharp concentric rings. Due to the limited resolution we cannot exclude, however, a small fraction of nanocrystalline inclusions in the otherwise amorphous matrix.

However, we note that in the very early growth phase of plasma produced particles, the material properties and the growth texture are different [22], resulting in higher core density. TEM measurements performed so far show an amorphous structure of the particles (figure 4) [15].
3.2. Dust particle composition
Infrared absorption spectroscopy was used to detect the particle composition in situ, during the particle growth. Figure 6 shows FTIR–spectra in the wavenumber region between 500 cm\(^{-1}\) and 6500 cm\(^{-1}\) after the base-line correction [16].

**Figure 3.** SEM image of a plasma polymerized nanoparticle collected 20 min after the beginning of the growth cycle. The particle radius is about 150 nm. Plasma discharge conditions are: Ar/C\(_2\)H\(_2\) = 8/0.5 sccm (standard cubic centimeter per minute), gas pressure 0.1 mbar, RF power \(-15\) W.

**Figure 4.** TEM picture of the particle grown in Ar/C\(_2\)H\(_2\) discharge. The particle was collected 8 minutes after ignition of the plasma and its radius is about 125 nm.

**Figure 5.** Diffraction pattern of a particle with a radius of about 125 nm. The plasma discharge conditions are similar to the conditions described in figure 3, except for the discharge running time.

Numerous aliphatic bonds are detected: CH\(_3\) symmetric bending modes at 1375±5 cm\(^{-1}\), CH\(_3\) asymmetric bending (deformation) modes at 1450±20 cm\(^{-1}\) and a very strong triple peak at 2770 –
3100 cm$^{-1}$ (-CH$_3$ symmetric stretching modes (2870 cm$^{-1}$), and asymmetric modes (2960 cm$^{-1}$), and -CH$_2$- asymmetric stretching modes (2926 cm$^{-1}$)). This triple peak correlates with the 3.4 µm feature observed in astronomical spectra in the diffuse interstellar media (DISM) and is very important in analysis of astrophysical dust [17]. The presence of triple C≡C bonds is also indicated by the weak, sharp absorption peak at 2110 cm$^{-1}$ (C≡C stretching of monosubstituted acetylene). The nearby peak at 2330 cm$^{-1}$ originates from traces of carbon dioxide. The absorption band at 3300 cm$^{-1}$ that was attributed to ≡C-H stretching mode of monosubstituted acetylene by Stoykov, Eggs and Kortshagen [23] is, in our case, a broad band and we attribute this band to the presence of trapped water/OH stretching vibrations steaming from the plasma[24--26].

![FTIR spectrum of dust particles during the particle growth](image)

The peak at 1604 cm$^{-1}$, appearing as a shoulder within the broad peak between 1500 and 1730 cm$^{-1}$, is characteristic of aromatic C=C stretching vibrations. The presence of aromatic compounds is strongly confirmed by weaker peaks observed at 757 cm$^{-1}$, 851 cm$^{-1}$ and 885 cm$^{-1}$ which originate from C-H deformation vibrations of (differently substituted) aromatic hydrocarbons [24--26]. A ≡C-H stretching band at 3030 cm$^{-1}$ due to either an aromatic or an alkene origin [27] is overshadowed by the strong, broad bands near 2900 cm$^{-1}$ and 3300 cm$^{-1}$ (the latter being connected to trapped water).

The strong peak between 1500 and 1730 cm$^{-1}$ can be attributed to carbonyl C=O stretching vibrations [24--26]. The latter results from the oxidation of carbon caused either by water contamination or oxygen which has been deliberately added [27]. To confirm this assumption, we added a small amount of oxygen to our gas mixture, and these results will be discussed in the following.

In addition to the carbonyl C=O stretching vibrations, the broad band between 1500 and 1730 cm$^{-1}$ contains OH (a deformation vibration at about 1640 cm$^{-1}$ corresponding to the stretching OH stretching vibration around 3300 cm$^{-1}$) and C=C stretch bands. The OH deformation and C=C stretching band are blended into a shoulder of the strong carbonyl band.

Beside the astrophysical relevance of the observed triple 2960 cm$^{-1}$ peak [9, 19], this spectral feature, together with its corresponding bending modes, is a common feature observed in amorphous and diamond-like carbon films [28]. By analyzing the spectrum between at 1000 – 2000 cm$^{-1}$ it could be distinguished between higher and lower $sp^2$ content and its delocalization [28].

By changes in the working gas mixture it was possible to influence the dust constitution. In Figure 7 we present the FTIR spectra of the dust particles grown in the Ar/C$_2$H$_2$=8/0.5 sccm mixture with the small amount of oxygen added: 0.02 and 0.08 sccm respectively. In spite of the small amount of oxygen the carbonyl C=O stretching vibrations are strongly increased together with OH stretching vibration around 3300 cm$^{-1}$.

Changing the monomer from acetylene to methane reflects on the changes in FTIR spectrum of dust (figure 8). To initiate the dust formation in methane we had to generate the protoparticles in
plasma in the way that was already described [2, 29]. In this experiment we first made the dust particles in the argon/acetylene mixture and than exchanged acetylene with methane. After disappearing of the dust particles of the “first generation” (the dust grown from acetylene monomer) the next generation of the dust in methane started to grow. The aliphatic CH₃ stretching and bending modes are still present but with some shift of the 1450 cm⁻¹ asymmetric bending line. The reason is that the asymmetric modes are more sensitive to the strength of the skeleton C-C bonds then symmetric modes. The disappearing of the 1000-1300 cm⁻¹ absorption feature, 880 and 1604 cm⁻¹ line show that aromatic component of the carbon material becomes less important. The sp² content and its delocalization become lower and the carbonaceous material becomes more diamond-like or polymer like [28] depending on the hydrogen content. Independent Mie-ellipsometry [22] and TEM measurements [15] showed that our dust particles are softer and polymer like.

![Figure 7. FTIR spectra of the dust particles after adding 0.02 and 0.08 sccm of oxygen, respectively.](image1)

![Figure 8. FTIR spectra of the dust particles grown from two different monomers: acetylene and methane.](image2)

4. Non-equilibrium processes in dusty plasma
The formation and growth of the dust particles in plasma is a strongly non-equilibrium process. Many attempts were made to understand the formation and growth of the dust particles through plasma polymerization, especially for the silane system [1, 3--8]. The common picture is that this process can be separated in a few stages [1]: formation of the singly charged protoparticles either positively or negatively charged, agglomeration phase that creates particles larger than 10 nm and accretion phase. There is only limited knowledge about the first two stages because the particles are too small to be efficiently detected.

The charging of dust particles in plasma is the source of different physical phenomena connected with the complex plasmas. Due to the presence of dust and the strong non-equilibrium between the electrons, ions and neutral gas properties the dust can charge up to few hundreds or even thousands elementary charges. The free electron density drops one order of magnitude and causes different changes of plasma properties. Here are presented only a few results that we obtained in our experiment.

4.1. Electron density in dusty plasmas
The electron density was measured by the means of heterodyne microwave interferometry [18]. In this way we obtained only the line-in-site integrated value but we escape the problems connected to the conventional electric probe measurements: the film deposition on the probe in reactive plasma and the disturbing of the dust distribution in front of the probe due to the probe floating potential. The time resolved measurements of the electron density are presented on figure 9 (a) (the whole measurement) and first few minutes after adding the acetylene on (b).
After running the plasma 5 min in a pure argon, 0.5 sccm of acetylene was added and the electron density is immediately increased from $3.6 \times 10^9$ cm$^{-3}$ to $4.8 \times 10^9$ cm$^{-3}$. It is obvious that plasma density increases due to the lower ionization potential of acetylene. After approximately 20 s, the electron density decreases strongly (figure 9 (b)). The reason for the decrease is the formation of the dust particles that collect electrons. At the end of the agglomeration phase (6 min after adding the acetylene) the density is about four times less. Latter on, the decrease of free electron density follows the increase of the dust particle radius: as the particles are growing they collect more electrons. This process is much slower in comparison to the early stage of the dust particle coagulation (figure 9 (b)). The further decrease can not be traced as the maximum sensitivity of the microwave interferometer had been reached ($0.2 \times 10^9$ cm$^{-3}$).

![Figure 9](image)

**Figure 9.** (a) Electron density vs. time during the two and half cycles of the dust formation. (b) The time development in the first few minutes after admixing of the acetylene. The discharge parameters are the same on both figures.

The second characteristic feature is found 23 min after admixing of the acetylene. The density peak corresponds to disappearance of the dust particles from the plasma bulk (or the formation of the void through the plasma bulk) and at the same time the disappearing of the large electron loss mechanism. Immediately after the new dust formation and growth cycle starts (see figure 2) and the electron density decreases. This process periodically repeats.

**4.2. Electron density in dusty plasma afterglow**

The dynamics of the dust particle charging/discharging processes were studied in plasma pulsed experiment [18]. The anomalous electron density behaviour in plasma afterglow was detected [18]. Switching of the plasma is followed by a short decrease of the electron density that can be explained by the surface recombination processes. The increase in the electron density afterwards can be explained by the discharging of the dust particles. The usual picture of the dust charging takes into account only ion an electron current to the dust particles. To explain the dust discharging we introduced an additional term $I_{e\text{ free}}$ responsible for processes that can release electrons from the dust: secondary electron emission from ion-dust, electron-dust or metastable-dust collisions, photo-emission, field emission and thermionic emission [18]:

$$\frac{dQ}{dt} = (I_i - I_e) + I_{e\text{ free}}$$ (1)

The discharging of the dust particles apart from the recombination is often neglected in plasma modeling. We showed that all this processes could be included by using an effective secondary emission coefficient similarly to the electron yields on the cathode [30]:

$$\text{secondary emission coefficient} = \frac{I_{e\text{ free}}}{I_i - I_e}$$
\[ I_{\text{free}} = \gamma I \]  

(2)

Figure 10 show the experimental results parallel to the results of the simple model based on OML probe theory [18, 31]. The only two fitting parameters used are electron energy time decay constant and the \( \gamma \) coefficient. The model explains the first 300 s after switching off the plasma well – at latte stages the other plasma decay processes that are not in cluded in the model (e. g. diffusion loss) take the leading role and the results of the model depart from the experimental ones.

**Figure 10.** The electron density vs. time after switching off the plasma. The mean electron energy time decay constant was 50 s and \( \gamma=1 \). For the details see ref. [18, 31].

4.3. Light emission from dusty plasma and sheath dynamics

One of the most important characteristic of the complex plasmas is the lack of free electrons. After formation of the dust particles the electron density drops by a factor of about 4 – 10 and according to the plasma quasineutrality the dust particles become multiply charged. The electric field increases and the ionization become stronger to account for the electron losses. Immediately the light emission from the plasma increases by an order of magnitude, as can be seen on figure 11 (a).

In pure argon plasma, before adding the acetylene, the light emission is similar to the radio-frequency glow discharge with the maximum emission at the sheath edge. As the dust particles form the light distribution change and maximum shifts towards the discharge centre. The small asymmetry in the excitation profile is probably due to a small difference in dust density near different electrodes. Plasma model of the discharge with similar conditions like ours showed that the excitation profile follows the dust density profile [32].

The calculated excitation profile of the simple model [14] showed the same behaviour as the measured light distribution (figure 11 (a)). According to the model, the electron density drops with the particle growth and the electron temperature increases to account for the electron losses. This behaviour was already described in the literature [33]. The calculations showed [14] that the Ohmic heating part in the plasma heating mechanism increases with the particle radius up to 90% of the input power.

The presence of large negatively charged dust particles and the lack of the electrons make the situation similar to the electronegative plasma. As it was already discussed [34] in electronegative plasmas the sheath is contracted. Our experimental results and model [14] show the same behaviour. About 4 min after adding of acetylene the excitation profile changes its form: the negative glow as a strongest emission region disappears (figure 11 (b)) and the sheath width shrinks for about 2.5 mm.

5. Conclusion

The plasma polymerisation of carbonaceous dust particles and their influence on the plasma properties were investigated. We used various in situ and ex situ diagnostic techniques to analyze the dust chemical constitution and morphology. The dust particles grown are cauliflower like and their internal
structure seems to be mostly amorphous. The smallest traceable particles in our experiment were about 50 nm in diameter that constrains the possibility of examining the early particle structure.

Due to our dust polymerisation and confinement technique we were able to change the dust constitution and structure either by adding different chemical elements or changing the monomer. We show that adding a small amount of oxygen increases the OH and carbonyl component of the dust. Using the methane as the monomer changed the dust structure probably decreasing $sp^2$ content and its delocalization.

![Figure 11](image-url)

**Figure 11.** The axial distribution of the excitation profile of ArI 750.4 nm line. (a) After adding C$_2$H$_2$ the dust forms, the light emission increases and 180 s later the maximum of intensity is shifted to the plasma bulk. (b) After having reached the maximum intensity the emission profile changed, the negative glow disappeared and the sheath width contracted. Discharge conditions were: discharge pressure $p = 13$ Pa, the input power 15 W, Ar/C$_2$H$_2 = 8/0.5$ sccm gas mixture.

The strong non-equilibrium conditions between the electrons and the ions in the low temperature plasmas govern the behaviour of the dust particles. The dust particles act as a small Langmuir probes and become multiply negatively charged. The plasma becomes electronegative and electron density becomes significantly smaller than ion density. We measured an electron density 4 times less in the complex plasma than in the absence of dust. The decrease in electron density is compensated by the increase of the electric field strength, plasma potential and the excitation. Measured excitation profiles of the ArI 750.4 nm line support the results of our model [14]. Similar to the electronegative plasmas the sheath width decreases.

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