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Initial growth of C-nanoparticles and its correlation with external discharge parameters studied by Mie-ellipsometry

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Abstract. Plasma generated nanoparticles play an important role in modern materials technology, in catalysis and, for instance, in astrophysics. The development of measuring systems for the study of the transition from macromolecules to coagulated nanoparticles makes it possible to gain insight in to the growth process of nanoparticles. In this work two correlated measurement methods will be investigated. The first method, the so-called Mie-ellipsometry, is based on the measurement of the polarization state of the scattered light. The second method is based on the analysis of the Fourier components of the power coupled into the plasma. The Mie-ellipsometry allows the determination of the particle size, the size-distribution and the dielectric properties of the particles. Changes of the Fourier components however indicate non-linear changes of the global plasma. The correlation between this power measurement and the direct particle diagnostic with Mie-ellipsometry allows us to interpret the changes of the global behavior and to deduce a parameter for process control. We have analyzed the initial phase of particle growth in Ar-CH_4 and Ar-C_2H_2 capacitively coupled RF-plasmas. It was possible to attribute a size-scale to the 7^{th} harmonic signal. Careful analyses of the ellipsometric angles Ψ and Δ allows us to push the sensitivity down to a few 10 nm particle size. The time resolution of the present system is about 1s. A Mie-ellipsometry system with time resolution of a few 10 ms is in preparation and will give better insight into the early growth phase and is expected to yield further improved sensitivity.

INTRODUCTION AND EXPERIMENTAL ARRANGEMENT

Particle diagnostic by Mie-ellipsometry is done by a measurement of the polarization state of scattered light. The particles are laterally irradiated with laser light. The polarization state of the light, which is scattered from the particles is measured under a defined angle and is analyzed based on the Mie-Theory [1]. The Mie-Theory describes the correlation between the polarized scattered light, the particle form and size and the dielectric properties of the particles. This measurement technique was suggested for the first time in 1994 by Hayashi and Tachibana [2]. This field of activities was continued e.g. by Swinkels [3] in 1999 and Gebauer [4] in 2001. The Mie-Theory assumes the scattering of plane electromagnetic waves from a homogeneous isotropic spherical particle. The particle size distribution and multi-layered particles have been taken into account for the theoretical description of the results. The polarization state of the scattered light is determined by its modulation. Acetylene/Argon and Methane/Argon mixtures are used as discharge gases with a pressure between 10 and 20 Pa and a mixing ratio between 2:8 and 2:15. The energy density was 0.025 to 0.5 W/cm^3 at a frequency of 13.56 MHz in a capacitively coupled parallel plate reactor. With this experimental arrangement the polarization state of the scattered light is measured. Equation 1 defines the el-

lipsometric angles Ψ and Δ, which result from the ratio of the scattered electric field strengths parallel and perpendicular to the plane of incidence.

$$\tan(\Psi)\exp(i\Delta) = \frac{E_{\parallel}}{E_{\perp}} \qquad (1)$$

INITIAL GROWTH OF C-NANOPARTICLES

The growth of particles can be divided into several steps as described by Perrin [5]. In the first step primary clusters of atoms are formed. When a critical size of about 30 atoms is reached nucleation takes place. When the particle size reaches 10^5 atoms the particle growth is continued by coagulation. These growth processes can be observed by Mie-ellipsometry, which are characterized by the time variation of the ellipsometric angles Ψ und Δ. The results of a measurement for Ar/CH_4 are shown in figure 1 and 2.

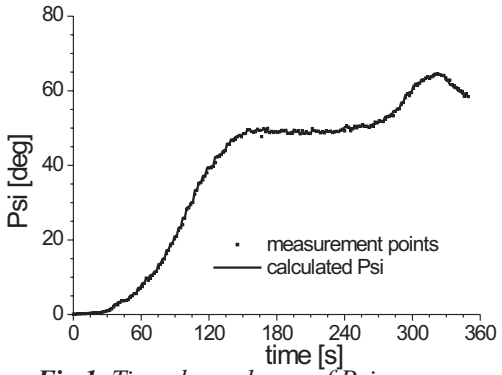

Fig 1. *Time dependence of Psi.*

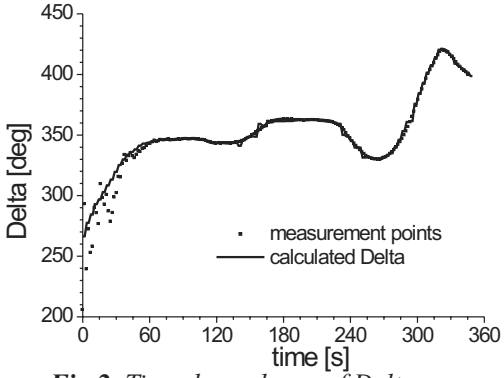

Fig 2. *Time dependence of Delta.*

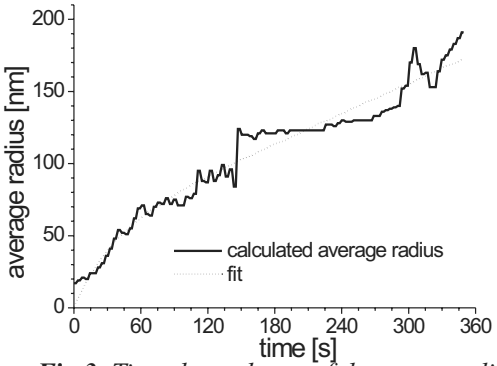

Fig 3. *Time dependence of the mean radius.*

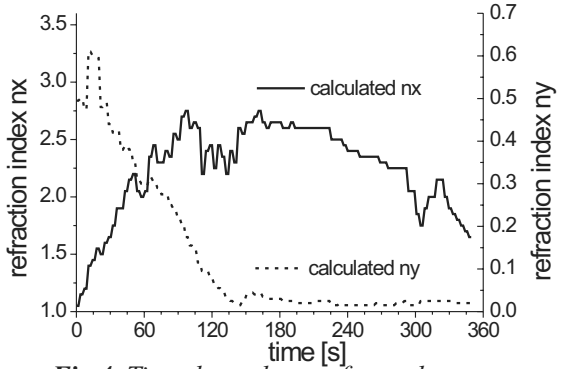

Fig 4. *Time dependence of n_x and n_y.*

The analysis of the results is based on a numerical evolution strategy [6]. The analysis [7] of the data above shows that the width of the particle distribution is small during the entire growth process with values between 2 nm and 10 nm. This is in agreement with

ex situ SEM measurements of collected particles. The time dependence of the mean particle radius and of the refractive index $n = n_x + i\, n_y$ is shown in figure 3 and 4. At very small particle radii, which occur at the beginning of the growth process, the determination of the particle size is connected with a large inaccuracy. Figure 3 suggests that the growth process can be divided essentially into two parts with different growth rates. The evaluated real part of the refractive index, which is shown in figure 4, describes three different process phases very well, which can be characterized through different polarization properties. The starting region is determined by the transition from macromolecules to particles with a size up to 80 nm. We assume that then a hydrogen reduction takes place which is coupled with a hardening and therefore with an increase of the real part of the refractive index. This hardening is probably correlated with the particle temperature, which decreases when the particle size increases under the condition of a constant applied energy density. One may expect, that a hard particle core will be generated and around this hard particle core squashier structures will be accumulated, which results in a decrease of the real part of the refractive index. The refractive index of about n_x=1.6 at the end of the growth process could be indirectly verified by ex situ ellipsometry after the particles have been applied on a surface. The high imaginary part at the beginning of the measurement could not yet be correlated with theoretical models. The value in the midrange and at the end corresponds to the expected results for a dielectric carbon particle.

CORRELATION WITH EXTERNAL DISCHARGE PARAMETERS

The growth process of the particles can be described locally with the Mie-ellipsometry as shown before. A possibility to determine the global change of the plasma parameters is the measurement of the higher harmonics of the coupled power. As can be seen from figure 5, a correlation exists between the growth process determined by the Mie-ellipsometry and the measured seventh harmonic of the applied power. The periodic variation of both measured signals is correlated with the peri-

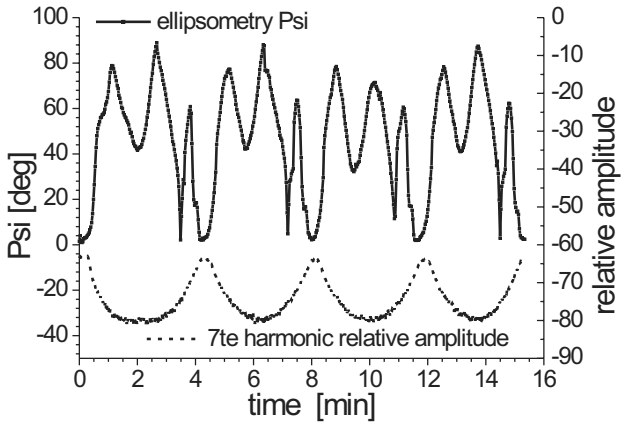

Fig. 5 *Correlation between Psi and the current amplitude of the 7th harmonics in Ar/C_2H_2.*

odic change of the growth process in the case of C_2H_2 (see also [8]). The particles grow uniformly with a small particle size distribution. When they reach a critical size, at which their weight cannot be counterbalance by the electric force, they fall onto the lower electrode. The measurements show clearly that the seventh harmonic of the coupled current is correlated with the growth process and therefore the measurement of this global plasma parameter can be used to control the growth processes in situ.

CONCLUSION

We have shown in this work that Mie-ellipsometry allows the determination of the particle characteristics during the growth process. The size-distribution of the C-nanoparticles is essentially monodisperse. This was verified by ex situ SEM-measurement. The trends of the real part of the refraction index suggest, that initially a hard particle core is generated. Around this hard particle core squashier structures are then accumulated. This would be consistent with observations made during the growth of Si-nanoparticles where a single crystalline small nucleus was identified by TEM [9]. Furthermore it was demonstrated, that a correlation exists between the growth of the particles and the 7^{th} harmonic signal of the coupled RF-power. This makes it possible to use the 7^{th} harmonic signal for process control.

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