*34th EPS Conference on Plasma Phys. Warsaw, 2 - 6 July 2007 ECA Vol.**31F**, O-3.004 (2007)*

Onionlike shell structures of plasma grown nanoparticles studied by *in situ* Rayleigh-Mie scattering ellipsometry

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Abstract

Onionlike shell structures of the nanoparticles grown in N_2-C_2H_2 plasmas are investigated systematically by means of *in situ* Rayleigh-Mie scattering ellipsometry combined with mass spectrometry. It is found that the transition from one to another shell characteristics depends strongly on both growth cycle and coupled input power. This is due to the temporal evolution of the plasma chemistry (C_2H_2 consumption pattern) after the ignition of the plasma before it reaches a steady state. After the steady state is reached, the nanoparticle formation process is rather homogeneous and isotropic in time.

INTRODUCTION

Recently, we have concluded from *in situ* Rayleigh-Mie scattering ellipsometry and from *ex situ* micro-Raman spectrometry that the nanoparticle growth at a large particle size ($\geq$50 nm in radius) is essentially the same as the surface polymerization at a surface exposed to the plasma [1], and the existence of sequential shell structures is identified [2]. These results suggest further investigations on the time evolution of nanoparticle growth process. The main aim of this paper is to address the time dependent growth process of nanoparticles formed in capacitively coupled N_2-C_2H_2 rf-plasmas by means of *in situ* Rayleigh-Mie scattering ellipsometry combined with mass spectrometry, depending on the coupled input power.

EXPERIMENTS AND DISCUSSIONS

A detailed description of the experimental setup is found in our previous publication [2]. In this experiments, a gas mixture of N_2:C_2H_2=8:1 sccm (standard cubic centimeter per minute) is

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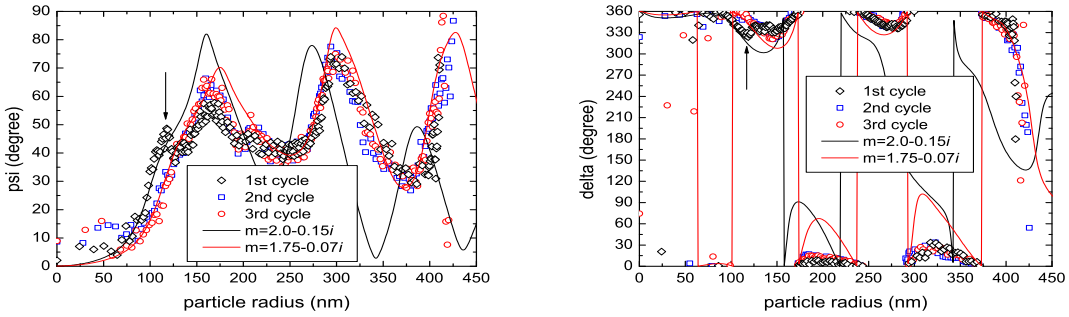
used, which results in pressures of about 2×10^{-1} mbar. The coupled input power is varied from 5 to 60 Watts. In addition to the Rayleigh-Mie scattering ellipsometry, a mass spectrometer (Balzers QMS 200) is employed to analyze residual gas components during the nanoparticle growth process.



(a) measured Ψ (b) measured Δ

Figure 1: Comparison of experimental data and theoretical fittings using two different complex refractive indices.

Fig. 1 shows measured ellipsometric angles Ψ and Δ for the nanoparticles grown in an N_2-C_2H_2 plasma with a mixture rate of 8:1 sccm at an input power level of 15 Watts (8:1 case), together with the fitting results. Open symbols represent the measurements of three sequential cycles of nanoparticle growth and the solid and dashed lines are the model calculations with complex refractive indices of $m = 2.0 - 0.15i$ and $m = 1.75 - 0.07i$, respectively. The measurements of both Ψ and Δ are well described by the theoretical calculations of the original version of the Mie theory with small deviations. This reveals that the nanoparticles are quasi spherical with narrow size distribution, isotropic, which is well known from various publications [1, 3, 4, 5]. Furthermore, the fitting with two pairs of complex refractive indices for the time evolution of Ψ and Δ clearly indicate the two sequential shell structures (r>50 nm) of the nanoparticles. The shell-shell transition occurs – in this case – at a radius of 118 nm (see arrows in Fig. 1). Series of measurements for the time evolution of Ψs and Δs at various input powers have been performed (Ψs and Δs are not shown here). Most of the nanoparticle properties can be described with the same complex refractive indices of $m = 2.0 - 0.15i$ and $m = 1.75 - 0.07i$, but the results show different shell-shell transition radii. Fig. 2 shows the shell-shell transition radius (SSTR) as a function of coupled input power. Up to 35 Watts, the SSTR decreases linearly as the coupled input power increases (label A in Fig. 2). Thereafter, the SSTR tends to saturate (label B in Fig. 2), and/or the shell-shell transition cannot be recognized or distinguished clearly from Ψ and Δ. This is not a surprising result. When the input power is coupled

to the upper electrode of the GEC cell, the increase of the power affects only slightly on the complex refractive indices of polymerlike a-C:H(:N) films deposited on a silicon wafer placed on the grounded electrode ($n \pm 0.02$ and $k \pm 0.01$ up to 40 Watts) [4]. However, the increase of the coupled input power influences the temporal evolution of the plasma chemistry, thus the growth rate of thin films increases linearly as a function of input power, until the dissociation of the precursor gas is saturated due to the power density limit [4]. The same physics holds for the nanoparticles: At a lower power density, the density of reactive species in the plasma is low, and takes longer time to be saturated. This means that the incoming flux of reactive species to nanoparticles is low (indicating the growth rate), thus the temperature of nanoparticle decreases slowly: the transition occurs at larger radii. On the other hand, at a higher power density, a faster change of the plasma chemistry and a higher growth rate lead to the rapid cooling of temperature of nanoparticles: the transition occurs at smaller radii. Thus, SSTR decreases as a function of input power before it is saturated.

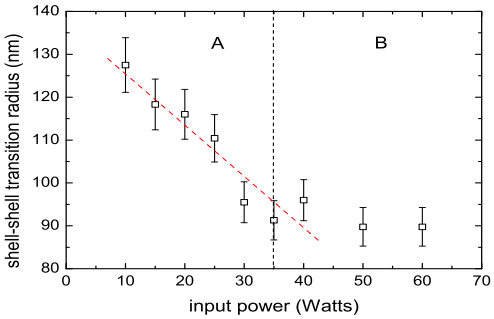


Figure 2: The shell-shell transition radius as a function of coupled input power. Dashed line is a guide to the eyes.

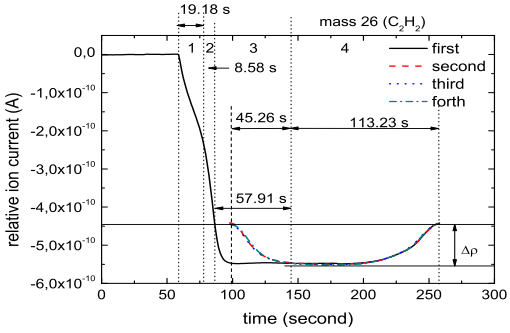


Figure 3: Mass spectrum of C_2H_2 measured during the nanoparticle formation in 8:1 case. The plasma is ignited after 60 sec.

Fig. 3 shows mass spectrum of C_2H_2 measured during the a-C:H:N nanoparticle formation in 8:1 case. The plasma is ignited after 60 sec. Note that y-axis shows relative currents of mass spectrum, which means that the background current signals (current signals without plasma) are removed. Labels 1, 2, 3, and 4 indicate different phases corresponding to the events identified in the first cycle. In the phase 1, the mass spectrum shows the decrease of the mass 26 after the plasma is ignited, indicating the consumption of C_2H_2 by dissociation. The phase 2 is defined as the stiff decrease of current level and reaches the starting level of following cycles (upper horizontal solid lines in Fig. 3). In the phase 1 and phase 2, the plasma chemistry is rapidly changing, thus it is expected that the nanoparticles have different characteristics than in other phases. The phase 3 is defined as the phase when the current level of the first cycle is in the same

zone defined by $\Delta\rho$ in Fig. 3, but shows still different C_2H_2 consumption pattern. The saturated mass spectrum of the first cycle indicates that the nanoparticle growth is homogeneous. The phase 4, the rest of the cycles, is defined as the zone where all cycles show the same C_2H_2 consumption behavior. Thus, the shells grown in this phase have the same characteristics for all cycles (see Fig. 1, r>200 nm). Total duration of the nanoparticle growth in the first cycle is about 198.9 seconds, whereas it is about 158.49 seconds in the following cycles: The first cycle needs more time than following ones. This is also seen during the construction of the time dependent radius profile for the fitting of the Rayleigh-Mie scattering ellipsometry. Note that, the change of relative current ($\Delta\rho$) for second and third cycle is about 20 % of the maximum change of the mass spectrum. Therefore, the change of the complex refractive index can be ignored (see above).

CONCLUSION

The onionlike internal shell structures are identified by the change of their complex refractive indices during the growth. The transition from one to another shell depends strongly on both the growth cycle and coupled input power: The time evolution of the plasma chemistry governs the properties of nanoparticles grown inside the plasma. At the first particle formation cycle with a coupled input power less than 35 W, the transition from a “hard” shell ($r > 50\ nm$) with $m = 2.0 - 0.15i$ to a “soft” shell with $m = 1.75 - 0.07i$ is clearly identified and the growth process is rather slow. The shell-shell transition radius decreases linearly as a function of input power due to the rapid change of the plasma chemistry in time.

Acknowledgement

This study was supported by SFB 591 and Graduiertenkolleg 1051.

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