*33rd EPS Conference on Plasma Phys. Rome, 19 - 23 June 2006 ECA Vol.**30I**, O-5.004 (2006)*

In-situ Rayleigh-Mie scattering ellipsometry on a-C:H nanoparticles: on their growth, internal structure and astrophysical meaning

Suk-Ho Hong* and Jörg Winter

Institute for Experimental Physics II, Applied Plasma Physics, Faculty for Physics and Astronomy, Ruhr-University Bochum, Universitätsstraße 150, 44780 Bochum, Germany

Abstract

We have analyzed the growth process of amorphous hydrogenated carbon nanoparticles created in capacitively coupled Ar-CH_4 and Ar-C_2H_2 plasmas by means of Rayleigh-Mie scattering ellipsometry. The complex refractive index of a-C:H nanoparticles, mean radius, and standard deviation of the particle size distribution during the particle formation process in Ar-CH_4 and Ar-C_2H_2 plasmas are determined.

Introduction

The nanoparticle formation in reactive plasmas is well known and many authors have been investigated the physics of the particle formation process in hydrocarbon plasmas [1, 2] and in Ar-Silane plasmas [3]. Because nanometer-size particles may have completely different optical/mechanical/magnetic properties from the bulk materials [4], the optical properties of nanometer-size particles are of great interest. By using Rayleigh-Mie scattering ellipsometry, particle properties such as shape, size and the dielectric properties can be extracted: it measures the change of the polarization state of scattered light by the particles in plasmas under a defined scattering angle, and the change of the polarization state of the light is analyzed by the Mie theory [5]. The original Mie theory assumes the scattering of plane electromagnetic waves from a homogeneous isotropic spherical particle. The Mie theory is enhanced to describe the particle size distribution and multi-layered particles [6]. Since it is based on a non-intrusive light scattering, the measurement itself does not affect the plasma parameters. The change of the nanoparticle characteristics can be directly determined by ellipsometric angles Ψ and Δ.

The refractive index of small a-C:H nanoparticles is of interest and has an important meaning for astrophysics, since it is directly relevant for the interpretation of the interstellar dust grains (ISD) observations. The composition of ISD grains remains still controversial, but the most important candidate materials of grains are both amorphous and crystalline silicates (SiO_x), carbonaceous particles, silicon carbide (SiC), and ice. Especially, carbon species are important,

*Email: Suk-Ho.Hong@rub.de

such that some form of graphitic carbon or polycyclic aromatic hydrocarbons (PAHs) might be responsible for a broad range of features from $\sim$2.175 μm to $\sim$11.3 μm [7]. Thus, a direct measurement of the size dependent complex refractive indices of a-C:H nanoparticles would give a useful information for the interpretation of the astrophysical observations.

In this paper, we have carefully analyzed the growth process of amorphous hydrogenated carbon (a-C:H) nanoparticles created in capacitively coupled Ar-CH_4 and Ar-C_2H_2 RF-plasmas by means of Rayleigh-Mie ellipsometry. The complex refractive index of a-C:H nanoparticles, mean radius, and standard deviation of the particle size distribution during the particle formation process in Ar-CH_4 and Ar-C_2H_2 RF-plasmas are determined.

Experiments

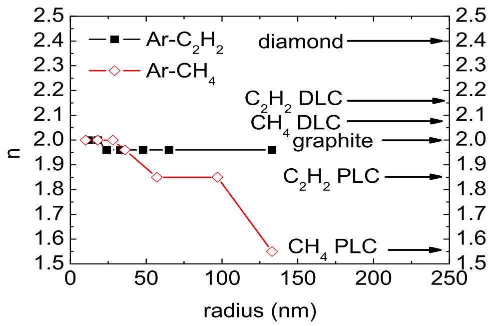
The reaction chamber is a standard GEC cell. A detailed experimental condition can be found in a previous publication [1].

For the Rayleigh-Mie ellipsometric measurements, an Ar ion laser (488 nm) is placed at a view port. A $\lambda/2$ plate right after the laser allows us to maximize the polarized laser intensity passing through the entrance polarizer. The laser beam scattered from the particles is measured under 90° relative to the primary laser beam. The polarization state of the scattered light is defined by its modulation (see references [8]). The modulation of the signal is carried out via the rotation of a $\lambda/4$ plate. The polarizer signal is then recorded by a photomultiplier. Using a Fourier analysis the polarization state of the scattered light is determined from the modulated intensity. The rotating $\lambda/4$ plate and the data acquisition are controlled by a computer. The accuracy of the polarization angles Ψ and Δ measured from the scattered light are $\pm 0.5^\circ$ [9]. The temporal resolution of the system is determined by the rotation frequency of the $\lambda/4$ plate and is 20 ms.

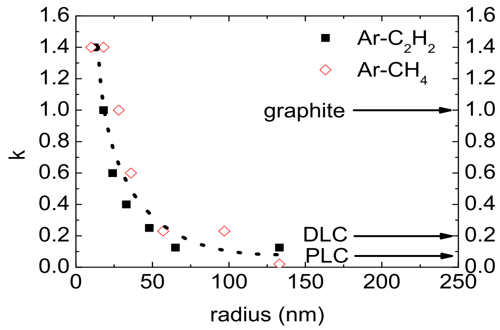
Results and Discussion

The measured Ψ and Δ are fitted by using physically meaningful refractive indices which are chosen from literatures for known a-C:H materials with a time dependent radius profile, which is a combination of a power function and a linear function. The power function is only needed to describe nonlinear growth at the early phase of the particle growth. After that, only linear functions are used.

In the case of the Ar-C_2H_2 plasma, the measured Ψ and Δ can be described by a single pair of complex refractive index $m = 1.96 - 0.125i$ except for the very early phase. This indicates that the particle growth in an Ar-C_2H_2 is homogeneous, so that the optical property of the particles is almost time-independent. On the other hand, two pairs of complex refractive index are needed to



(a) Real part of complex refractive index n as a function of particle radius.



(b) Imaginary part of complex refractive index k as a function of particle radius. Dotted line is a guide to the eye.

Figure 1: Complex refractive indices as a function of particle radius compared with that of graphite and a-C:H materials.

describe the particle formation in the Ar-CH_4 plasma. At first, the refractive index has a higher value, $m = 1.85 - 0.23i$, which is close to that of particles grown in Ar-C_2H_2 plasma, and then it decreases to a value of $m = 1.55 - 0.02i$ which is similar to that of a-C:H polymer-like film deposited at the same condition. This is due to the different initiation process [1]. The particle formation cannot be initiated when a critical density of precursors is not present in Ar-CH_4 plasma: a transient high power leading to the formation of C_2H_2 by internal plasma chemistry or direct C_2H_2 injection is needed to initiate the particle formation. Hence, at the early phase of particle formation the Ar-CH_4 plasma is in a C_2H_2-rich state. After the particle formation is initiated and when the precursors are all consumed, the particles are growing up in a CH_4-rich state. Two pairs of refractive index indicate this transition clearly. This is consistent with our ex-situ micro-Raman measurements [2].

Higher extinction coefficients are essential for particles smaller than 65 nm in both plasmas: The smaller a particle is, the higher the extinction coefficient has to be. Particles at a radius about 25 nm ($\pm$ 6 nm) have a complex refractive index of $m = 2.0 - 1.0i$ which is commonly accepted as the complex refractive index of graphite. A further increase of the extinction coefficient to $m = 2.0 - 1.4i$ is required in order to describe measured Δs for particles smaller than $\sim$ 18 nm in radius.

The interstellar dust grains, so called the organic “refractory” material in the interstellar medium is predominantly hydrocarbon in nature, possessing little nitrogen or oxygen, with carbon distributed between the aromatic and aliphatic (–CH_2– and –CH_3 groups) forms [10]. This is consistent with the growth and atomic structure models for a-C:H materials. Thus, the plasma-polymerized a-C:H nanoparticles fulfill the important criteria for interstellar dust grains (see Ref. [7]) in wide ranges of radii which makes our a-C:H nanoparticles a good candicate as an ISD analogue.

Conclusion

We have analyzed the growth as well as the internal structure of a-C:H nanoparticles in hydrocarbon plasmas. The complex refractive index, the mean particle radius and the particle size distribution of a-C:H nanoparticles during the growth process are carefully determined. It is found that the optical properties of nanoparticles grown in the Ar-C_2H_2 plasma can be described by a single pair of refractive index whereas two successive, different refractive indices are needed for the nanoparticles grown in the Ar-CH_4 plasma due to the continuous substitution of the plasma chemistry: core-shell structures are clearly identified by their size dependent complex refractive indices.

Acknowledgement

We thank Dr. Gerd Gebauer for contributing Rayleigh-Mie ellipsometric measurements and Prof. Dr. Achim von Keudell for valuable advises about developing Rayleigh-Mie ellipsometry software. This study was partially supported by SFB 591.

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