Size dependence of optical properties and internal structure of plasma grown carbonaceous nanoparticles studied by in situ Rayleigh-Mie scattering ellipsometry

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We have analyzed the growth process of a-C:H nanoparticles in Ar−C₂H₂ and Ar−CH₄ plasmas by means of in situ Rayleigh-Mie scattering ellipsometry. Complex refractive index (m=n−ki), mean particle radius (r), and particle size distribution (σ) of a-C:H nanoparticles are carefully determined and compared with those of a-C:H thin films deposited at similar conditions. It is found that, in both plasmas, small particles (r<25 nm) have graphitelike properties whereas large particles have polymerlike characteristics. These results indicate that the particles have internal structures of a hard core and soft mantles on it. The size distribution of the nanoparticles in both Ar−CH₄ and Ar−C₂H₂ plasmas is essentially monodisperse with a narrow Gaussian size distribution. A systematic comparison between the growth and atomic structure models for a-C:H materials and criteria for interstellar dust (ISD) grains known from astrophysical observations is made. Significant agreement is found in a wide range of radii, supporting earlier findings that plasma-polymerized a-C:H nanoparticles might be a good candidate as an ISD analog. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338132]

I. INTRODUCTION

Plasma based techniques are considered as one of the most important tools for the development of advanced technologies. One of the problems in plasma technologies, especially in the field of thin film processing and microprocessor fabrication, is the formation of nanoparticles. These nanoparticles are formed spontaneously during the plasma process and can grow rapidly up to a size of several hundreds of nanometers. The growth speed of the particles in the plasma volume is two to ten times faster than that of film growth on a substrate. Such particles may act as “killer particles” which are responsible for the malfunction of integrated circuits: Since there are more than 10–12 mask processes—sequential deposition and etching—for a typical device, not only detecting and monitoring but also control methods for the particle growth are highly desired. As the feature size shrinks, the request for such techniques with high sensitivity at small particle sizes is urgent.

Because nanometer-size particles may have completely different optical/mechanical/magnetic properties from the bulk materials, the controlled use of such particles may lead directly to the development of innovative functional materials, e.g., through embedding nanoparticles into a thin film and additional functional coatings of various materials on size-tailored and structure-manipulated particles.

Several authors have contributed towards understanding the basic growth mechanism of a-C:H nanoparticles and a-C:H films on a substrate. The process responsible for the thin film deposition is volume polymerization and that for the nanoparticle formation is surface polymerization. From the recent ex situ micro-Raman spectra analysis of a-C:H nanoparticles prepared in an Ar−CH₄ plasma, we have concluded that the volume polymerization at a large particle size (>100 nm in diameter) is essentially the same as the surface polymerization for polymerlike carbon (PLC) films. Large size particles act just like a surface immersed in a plasma with a floating potential of several volts. Thus, large size particles would have similar optical characteristics as PLC films deposited by similar conditions. Nevertheless, a direct measurement of the optical properties of carbonaceous nanoparticles as a function of size is of large interest, in particular, at small radii. This is of direct relevance for the research on interstellar dust (ISD) grains. Many authors have investigated IS extinction features in a wide spectral range, and graphitelike carbonaceous nanoparticles are considered as a possible candidate for the 2175 Å excitation bump. Several studies on carbonaceous materials created artificially in laboratories were performed.

Particles in a plasma are negatively charged and trapped in the sheath potential around the plasma reactor electrodes and surfaces. The equilibrium position of particles in a plasma is determined by a region, where the net force $F_e = F_{e+} + F_{i+} + F_{e-} + F_{i-} + F_D + F_G$ is zero. Here, $F_e$ is the electric force acting on the charged particle, $F_i$ the ion drag force, $F_N$ the neutral drag force, $F_D$ the force caused by thermophoresis, $F_D$ the diffusion force given by the density gradient of the particles, and $F_G$ the gravitational force. For small particles, the electric force is usually dominant, whereas gravitation is dominant for very big particles. It is known from previous studies that the particle number density is constant in time except for the very early phase and the size distribution is monodisperse. As long as the force balance is maintained, negatively charged particles are levitating in...
the plasma volume, hence particle properties can be investigated by several methods during their growth. Known particle diagnostics are (1) laser light scattering for presence and particle density,\textsuperscript{2,23} (2) \textit{in situ} Rayleigh-Mie ellipsometry for particle size, optical property, size distribution, and shape of particles,\textsuperscript{25-28} (3) \textit{in situ/ex situ} infrared absorption,\textsuperscript{29} Raman spectroscopy,\textsuperscript{1} and mass spectrometry for chemical compositions,\textsuperscript{30} (4) mass spectrometry, photodetachment for particle charge and electronegativity,\textsuperscript{31} (5) phosphorescence, blackbody radiation for particle temperature,\textsuperscript{32} and particle velocity distribution by video frame analysis,\textsuperscript{33} (6) scanning electron microscopy,\textsuperscript{1-3,23} SEM/tunneling electron microscopy (TEM), x-ray diffraction, photoluminescence for morphology and structure of the particles,\textsuperscript{23} and (7) optical spectroscopy, electrical probe measurements,\textsuperscript{3,34} mass spectrometry, and microwave diagnostics for the influence of particles on the plasmas.\textsuperscript{34-36} For our specific purpose to measure \textit{in situ} the optical properties of a-C:H nanoparticles, we have used Rayleigh-Mie scattering ellipsometry.

An ellipsometric particle diagnostic based on the Rayleigh-Mie scattering measures the change of the polarization state of light scattered by particles in plasmas under a defined scattering angle. The polarization state of light before and after the scattering is analyzed by the Mie theory\textsuperscript{37} and particle properties such as size, shape, and the dielectric properties may be extracted from the data. The Mie theory in its basic version assumes a single scattering of plane electromagnetic waves by a homogeneous isotropic spherical particle. The particle shape, size distribution, and multilayered coatings have been taken into account for the theoretical description of the results.\textsuperscript{38,39} Since the diagnostic is based on a nonintrusive light scattering, the measurement itself does not affect the plasma parameters. Thus the change of the nanoparticle characteristics in time can be directly determined by ellipsometric angles \( \Psi \) and \( \Delta \).

The main aim of this paper is to address the growth process of nanoparticles formed in capacitively coupled Ar-hydrocarbon (CH\( _4 \) and C\( _2 \)H\( _2 \)) rf plasmas by means of \textit{in situ} Rayleigh-Mie scattering ellipsometry, which would give important information for the interpretation of ISD observations. To do this, plasma polymerization processes—surface and volume polymerizations—in hydrocarbon plasmas have to be investigated systematically. For these purposes, complex refractive indices \( m=n-\kappa i \), thickness and mean radius, and the standard deviation of the particle size distribution during the nanoparticle formation process in Ar–CH\( _4 \) and Ar–C\( _2 \)H\( _2 \) rf plasmas and during the thin film formation in CH\( _4 \) and C\( _2 \)H\( _2 \) rf plasmas are carefully analyzed and compared. The criteria of ISD grain model will be compared with the growth and atomic structure models for a-C:H materials in order to show direct connection between the models.

This paper is organized as follows. We will describe the experimental setup in Sec. II and the sample \( \text{a-C:H thin films and nanoparticles} \) characterization methods in Sec. III in detail. The experimental results are then discussed in Sec. IV. Based on these results, we will analyze the growth process during the particle formation in detail in Sec. V. In Sec. VI, the growth and atomic structure models for \( \text{a-C:H nanoparticles} \) and materials and astrophysical criteria are compared: The relevance to astrophysics will be discussed. Finally, a summary and a conclusion will be given.

II. EXPERIMENTAL SETUP

Figure 1 shows a simple sketch of the experimental setup (top view). A standard gaseous electronic conference (GEC) cell is used as reaction chamber. The chamber is pumped by a rotary vane vacuum pump (Pfeiffer DUO 10 C) resulting in a pressure of about \( 10^{-4} \) mbar. Flow rates of the gases are controlled by MKS mass-flow controller. Gases are introduced through a 2\( \times \)3 in. port from a side. The plasma is generated between two parallel plate electrodes with a diameter of 10.2 cm and a separation of 3.1 cm. A 13.56 MHz rf generator (Dressler Cesar 133) is capacitively coupled to one of the electrodes through an impedance matching network. The counterelectrode is grounded.

For the formation of nanoparticles, Ar–CH\( _4 \) and Ar–C\( _2 \)H\( _2 \) gases with mixture ratios of 15:2 and 8:2 SCCM (SCCM denotes cubic centimeter per minute at STP) are used, which result in pressures of about \( 2 \times 10^{-1} \) and \( 1 \times 10^{-1} \) mbar, respectively. The coupled input power is at a constant level of 20 W, except for the ignition phase of the Ar–CH\( _4 \) plasma (\( \approx 60 \) W), in order to force the initiation of the particle formation (see Ref. 2). The discussion of the different temporal and spatial behaviors of the particle formation in different Ar-hydrocarbon plasmas can be found in Ref. 2 in detail.

An Ar ion laser (488 nm) is placed at a view port. A \( \lambda/2 \) plate right after the laser maximizes the polarized laser intensity passing through the entrance polarizer. The laser beam scattered by particles is measured under a well-defined angle, in our case under 90° relative to the primary laser beam. The polarization state of the scattered light is defined by its modulation.\textsuperscript{37,40,41} The modulation of the signal is car-
ried out via rotation of a $\lambda/4$ plate (rotating compensator). The signal is then passed through the analyzer and recorded by a photomultiplier (Hamamatsu R5929). Using the Fourier analysis, the polarization state of the scattered light is determined from the modulated light intensity. The angle of the rotating compensator and the light intensity at the photomultiplier are acquired by a personal computer. The accuracy of the polarization angle measurement ($\Psi$ and $\Delta$) was determined in a previous publication ($\pm 0.5^\circ$).28

$a$-C:H films are deposited on silicon wafers (100) placed on the lower electrode, at a pressure of about 6 \times 10^{-2} \text{ mbar} using 2 SCCM of pure CH$_4$ and C$_2$H$_2$. The deposition time was 15 min. The ion energy reaching the substrate is one of the main control parameters which determines the film characteristics: High ion energy leads to a hard diamondlike carbon (DLC) film, whereas low ion energy leads to a soft polymerlike carbon (PLC) film. Hard DLC films can be deposited with the powered lower electrode, while soft PLC films are deposited when the input power is coupled to the upper electrode of the GEC cell.3

The thickness and complex refractive index of the $a$-C:H films are characterized by in situ/ex situ spectroscopic ellipsometry (M-88, Woolam Company). During the in situ ellipsometry, the angle of incidence was fixed at 75.8° and we have used six different incident angles from 70° to 75° with a step of 1° for ex situ variable angle spectroscopic ellipsometry.

III. METHODS OF CHARACTERIZATION: ELLIPSOMETRY

A. Optical models in ellipsometry

Since a photodiode or photomultiplier is used for the detector system of an ellipsometer in general, the detector does not measure $\Psi$ and $\Delta$ directly but it measures the modulated light intensity as a function of time. Then, $\Psi$ and $\Delta$ are determined from the Fourier coefficients. Since $\Psi$ and $\Delta$ contain the characteristics of the whole optical system—polarizer, sample (layers of films and the substrate or nanoparticles), compensator, and analyzer—each of them has to be separated and characterized. In order to decouple the information, the entire electric field has to be traced from the light source to the detector before and after the reflection/scattering by using Müller or Jones matrices. For this reason, an optical model describing the unknown properties of the samples (thin film or nanoparticle) has to be specified.

It has to be stressed that there is a general difficulty in ellipsometry: Two ellipsometric angles $\Psi$ and $\Delta$ are measured at an angle of incidence as a function of wavelength at a time $t$, but there is always one more parameter to be determined, namely, complex refractive index $m(\lambda)=n(\lambda)-ik(\lambda)i$ and a size parameter—thin film thickness ($d$) or particle radius ($r$). Since the complex refractive index is a certain physical property which has to be independent of the measurement angle unless the sample under study is highly anisotropic, the information needed for the determination of the complex refractive index as a function of wavelength can be increased by using variable angle spectroscopic ellipsometry (VASE). There is still, however, always one more size parameter which has to be determined. This basic difficulty is solved by using a physically meaningful optical model system with a small number of model parameters: $\Psi$ and $\Delta$ are theoretically calculated from the given optical model and compared with measurements. If both measured and calculated $\Psi$ and $\Delta$ match within a confidential limit (usually 90%), the complex refractive index and sample size are considered as meaningful. The procedure effects two advantages: It significantly reduces the number of parameters to be determined, and the basic principle relations such as Kramers-Kronig (KK) consistency can be inherently embedded to the optical model. Otherwise, KK consistency has to be checked separately.

The difference between spectroscopic and Rayleigh-Mie ellipsometry is the sample under study: In the spectroscopic ellipsometry, the sample is a thin film on a substrate whereas it is spherical particles in the Rayleigh-Mie ellipsometry. For thin film analysis, known complex refractive indices of materials such as a SiO$_2$ layer on a silicon wafer are used for substrate in general. For unknown bulk material, oscillator models are commonly used. In such oscillator models, the complex refractive index is described by a sum of various oscillators with specific shapes, widths, and behavior as a function of wavelength which constrain physically the freedom of the parameters. In the Rayleigh-Mie ellipsometry, the interaction between linearly polarized light and particles is described by Mie theory.37

B. Spectroscopic ellipsometry

The optical model for the film-substrate system consists of three layers: silicon wafer (substrate), native oxide (about 2 nm), and $a$-C:H film. If it is necessary, a surface roughness layer is introduced in the model as top layer. The model used for $a$-C:H films is either the Cauchy dispersion relation with the Urbach absorption (CU) model or a parametric semiconductor (PS) model.42 The former is good for PLC films whereas the latter describes DLC films better. The fitting is performed iteratively until the model (calculated $\Psi$ and $\Delta$) matches the experimental data. The KK consistency was tested for the optical properties determined by the CU model, whereas the KK consistency is inherent to the PS model.

The light spot on the sample surface was an ellipse with a length of about 1 cm due to the large distance between the polarizer and the rotating analyzer during the in situ measurements. The radial thickness nonuniformity, which has to be considered in principle in such a case, is less than 5% over a radius of 3.6 cm in our case, which is negligible. Since the light spot size during the ex situ measurements is less than 5 mm, the thickness nonuniformity is not considered either. The optical band gap is obtained by the Tauc method.43

C. Rayleigh-Mie scattering ellipsometry

1. Classification of light scattering regimes

The optical model for nanoparticles grown in Ar-hydrocarbon plasmas assumes that the particles are spherical,
monodisperse, homogeneous, and isotropic and that the laser beam is scattered by a single particle as described in the Mie theory. The shape and size distribution are validated from SEM measurements, which show that the nanoparticles are spherical and, in particular, monodisperse with a narrow Gaussian size distribution [full width at half maximum (FWHM) less than 10%]. The homogeneity and isotropy are assumed as an a priori reasoning because a-C:H films deposited on a substrate by the same conditions show both homogeneity and isotropy in vertical direction (i.e., in the radial direction for nanoparticles) as long as the plasma chemistry stays in a steady state during the deposition. The single scattering of the laser beam can be verified by two different methods: The first is the measurement of the scattered light intensity with known particle density. If the scattered light intensity is doubled with doubled particle density, then the scattering is single scattering. If the particle density is unknown, the same information will be given by an extinction measurement of the laser beam. The extinction of light passing through a medium is proportional to \( e^{-\tau} \), where \( \tau \) is the optical depth of the sample (particles) along the line. If \( \tau \) is smaller than 0.1, single scattering is dominant. If 0.1 < \( \tau < 0.3 \), a correction for double scattering has to be introduced. If \( \tau > 0.3 \), complex multiple scattering becomes a factor which has to be considered. A detailed discussion about the criterion of the light scattering by bispHERIcal particle system with several interparticle distances from contact to infinite can be found in Ref. 44. In our experiment, the optical depth \( \tau \) at the maximum extinction was 0.02625 indicating that single scattering is dominant.

Figure 2 shows the scattering ratio \((\sigma = I/I_0)\) as a function of particle radius \(r\) calculated by Mie theory at a wavelength of 488 nm with a complex refractive index \(m = 2.0 - 1.0i\) (graphite). The scattering regimes are clearly divided into three regions as a function of particle size. A straight line behavior at small radii shows the Rayleigh scattering whereas an oscillating behavior thereafter indicates the Mie scattering. A constant scattering ratio at large radii \((r > 30 \mu m)\) means the beginning of the classical geometrical optics. Note that the scattering ratios calculated with (label 1) and without (label 2) the small particle approximation show different trends when the particle size is smaller than about 20 nm. In order to describe the small particle's nature correctly, asymptotic forms for Mie theory have to be used to calculate the scattering matrix. The model calculation used in this paper is based on the algorithm suggested by Wiscombe. The oscillating behavior of scattering ratio indicates the transition from Rayleigh to Mie scattering. In general, it is assumed that the transition between two scattering regimes begins slightly when the particle radius becomes larger than 10% of incident light wavelength (~50 nm at 488 nm, filled area in Fig. 2). Since the scattering ratio in Mie scattering regime is multi-valued due to the oscillation, care must be taken for the interpretation. Together with the \( \Psi \) and \( \Delta \) measurements, the particle radius can be uniquely determined.

The intensity of light at a wavelength of \(\lambda\) scattered by a single small particle with a radius of \(r (r < 0.1\lambda)\) is proportional to \(e^{-\tau}\). This size dependence of the scattered light intensity \((I_{\text{sc}})\) leads to a rapid decrease of the \(I_{\text{sc}}\) which makes the experiments difficult for small particles due to the lack of scattered photons. For example, the particle detection limit in Rayleigh scattering regime is much higher than in Mie scattering regime using the fact that the determination of \(\Psi\) and \(\Delta\) is not affected by the change of laser beam intensity during the measurements (see Refs. 26 and 41). Nevertheless, it should be emphasized that care must be taken during the interpretation of the scattering measurements in the Rayleigh scattering regime.

2. Fitting procedure in Rayleigh-Mie ellipsometry

In order to determine the optical properties of nanoparticles from \(\Psi\) and \(\Delta\) measurements, two different fitting methods are used: the “point by point” fitting and the “normal” fitting.

Point by point fitting (PBPF) finds any parameter combination with which the optical model reproduces the measured \(\Psi\) and \(\Delta\) mathematically at a given point (or time). The PBPF is repeatedly performed until the mean square error (MSE) \(\chi^2\)

\[
\chi^2 = \sum_{i}^{N} \left( \frac{\Psi_{\text{mod},i} - \Psi_{\text{meas},i}}{\Psi_{\text{meas},i}} \right)^2 + \left( \frac{\Delta_{\text{mod},i} - \Delta_{\text{meas},i}}{\Delta_{\text{meas},i}} \right)^2
\]

is less than \(10^{-12}\). During the PBPF, the complex refractive index and particle radius are varied from a coarse scale—a rough search for a local minimum \(\chi^2_{\text{local}}\) between given radii with a scale of \(-1\) nm—to a fine scale—a search around \(\chi^2_{\text{local}}\) with a scale of \(-0.1\) nm—to find the minimum of the \(\chi^2\) at a given time. Converged complex refractive index and particle radius are then used as new initial parameter set for
the PBPF of the next point. The PBPF for a given time is restricted by a maximum number of 50 iterations to prevent an endless loop. The greatest weakness of the PBPF is the strong dependency on the initial parameters given as the starting values. It finds only a local minimum regardless of physics behind: There are infinite numbers of combinations of complex refractive indices with particle radii which reproduce the measured $\Psi$ and $\Delta$ mathematically. Thus, the PBPF of the entire experimental data may lead to physically unacceptable results, e.g., sudden and discrete jump of refractive index and particle radius, or negative particle growth (i.e., etching) while particles are actually growing. For this reason, the PBPF is used only for the largest particles for an estimation of their complex refractive index at the end of the growth process: The refractive index at this phase is expected to be similar to that of $a$-$C$:$H$ films deposited on a substrate at the same condition.\(^1\)

Normal fitting (NF) means that $\Psi$ and $\Delta$ are generated by using a single physically meaningful complex refractive index at the given wavelength—either chosen from literatures for known materials or obtained by PBPF for unknown materials—with a time dependent radius profile. The reason for introducing a time dependent radius profile is as follows.

In general, $\Psi$ and $\Delta$ in Rayleigh-Mie ellipsometry are calculated as a function of radius, not as a function of time. As we have discussed in Sec. III A, three parameters—$n$, $k$, and $r$—have to be determined from two measurement quantities $\Psi$ and $\Delta$ as a function of time. In order to determine $n$ and $k$ for nanoparticles uniquely, it is necessary to know, at least qualitatively, the particle growth as a function of time. This constrains physically the ambiguity in radii. From the previous knowledge\(^2\) and \textit{ex situ} SEM measurements,\(^3,24\) the growth of the particles at the very early phase shows a strong nonlinear behavior during the nucleation and coagulation phases. As particles are growing, the growth becomes quasilinear as a function of time.\(^3,24\) The particle formation starts with a limited number of precursors (resource) and the particles grow up exponentially by consuming precursors, which leads to an exponential decrease of the resource number density in the plasma. Such a resource limited exponential growth can be described by a power function. When the precursors are all consumed, the particles are growing further linearly by accretion. Hence, we have constructed a time dependent radius profile as a combination of a power function and a linear function. In some cases, two or more linear functions are needed to describe the rest of the growth. To do this, the time steps of the measured $\Psi$ and $\Delta$ are segmented into several blocks and the linear profiles for each block are separately constructed. A block is defined when the measured $\Delta$ shows discrete jump from $0^\circ$ to $360^\circ$ (see Fig. 5). Thus, a time dependent radius profile can be written as

$$r(t) = \left[\frac{(A_1-A_2)}{1+(t/t_0)^P} + A_2 \right] + \sum_{i} (B_{1,i} + B_{2,i}t),$$

where $A_1$ and $A_2$ are the lower and the upper limits (both in nanometers) of the nonlinear growth, $t_0$ is the time (in seconds) when the radius reaches half of the sum of $A_1$ and $A_2$, i.e., \(r(t_0) = (A_1+A_2)/2\). $P$ is a power factor [see Fig. 3(a)], and $B_{1,i}$ and $B_{2,i}$ are prefactors for linear functions with the block index $i$ [see Fig. 3(b)]. The sum of both functions shown in Fig. 3(c) is the assumed radius profile as a function of time.

IV. RESULTS

A. Optical properties of $a$-$C$:$H$ thin films

Figure 4 shows complex refractive indices $n$ and $k$ of $a$-$C$:$H$ films as a function of wavelength depending on the precursor gas (CH$_4$ and C$_2$H$_2$) for two different power couplings (powered upper/lower electrodes). In both cases the gas flow rate was 2 SCCM and the input power was 20 W. The complex refractive index of the films deposited by the C$_2$H$_2$ plasma is higher than that of films deposited by the CH$_4$ plasma: Both refractive indices $n$ and $k$ at the wavelength of 488 nm [vertical line in Figs. 4(a) and 4(b)] are $m=1.57-0.01i$ for PLC and $m=2.07-0.16i$ for DLC in the case of the CH$_4$ plasma. For the films deposited in the case of the C$_2$H$_2$ plasma, $m=1.84-0.03i$ for PLC and $m=2.15-0.19i$ for DLC are obtained. The main difference of the refractive indices using the different precursor gases CH$_4$ and C$_2$H$_2$ is the different carbon to hydrogen ratio. The higher hydrogen content in the CH$_4$ molecule leads to a higher hydrogen content in the film leading to a lower refractive index.\(^3,7\)

The optical band gap energies obtained by the extinction coefficient $k$ are about 1.73 and 1.15 eV for CH$_4$ PLC and DLC films and 2.05 and 1.35 eV for C$_2$H$_2$ PLC and DLC films, respectively.

B. Optical properties of $a$-$C$:$H$ nanoparticles

Figures 5(a) and 5(b) show the measured two ellipsometric angles $\Psi$ and $\Delta$ for the nanoparticles grown in an Ar–C$_2$H$_2$ and in an Ar–CH$_4$ plasma, respectively. As the plasma operation time increases, typical trends of $\Psi$ and $\Delta$ are observed indicating the growth of nanoparticles. Since the ranges of the $\Psi$ and $\Delta$ are from $0^\circ$ to $90^\circ$ and from $0^\circ$ to $360^\circ$, the value of $\Delta$ shows discrete jump from $0^\circ$ to $360^\circ$ as a function of time, as mentioned in Sec. III C.

It should be emphasized that the particle formation in Ar-hydrocarbon plasmas shows a different behavior, namely, the periodicity of the growth cycles. In the case of the Ar–C$_2$H$_2$ plasma, particles are formed periodically with a periodicity of the growth cycles. In the case of the Ar–hydrocarbon plasmas shows a different behavior, namely, the periodicity of the growth cycles. In the case of the Ar–hydrocarbon plasmas, and it was discussed in Refs. 2 and 3. The sum of both functions shown in Fig. 3(c) is the assumed radius profile as a function of time.

Figure 6 shows the fitting results together with measured $\Psi$ and $\Delta$ for the nanoparticles grown in Ar–C$_2$H$_2$. Closed symbols are the measured $\Psi$’s and $\Delta$’s of four sequential periods and the solid line is the model calculation with a
complex refractive index of $m = 1.96 - 0.125i$. Two different growth steps are observed in Fig. 6. Labels 1 and 3 indicate the start and end of the particle formation, respectively. The Rayleigh-Mie ellipsometric angles $\Psi$ and $\Delta$ without particles, e.g., in a pure Ar plasma, are very noisy (not shown here). As soon as the particle formation is initiated and the particles start to scatter laser light, $\Psi$ and $\Delta$ start to increase from $\Psi = 0^\circ$ and $\Delta = 285^\circ - 330^\circ$ [label 1 in Fig. 6(a)]. This very early phase, when the particles are smaller than about 65 nm, cannot be described with the given complex refractive index of $m = 1.96 - 0.125i$. We will discuss about the particle properties in this phase in Sec. V in detail. At radii larger than about 65 nm (label 2 in Fig. 6), both measured $\Psi$ and $\Delta$ are well characterized by a single pair of complex refractive index of $m = 1.96 - 0.125i$ up to radii about 375 nm: Both $\Psi$ and $\Delta$, and also the phase shift of $\Delta$ are
properly described in this wide range of radii. When the particles have a mean radius larger than about 375 nm, the gravitational force overcomes the electric force. The particles are moving to the bottom of the reaction chamber and are lost from the plasma. Thus the decrease of with unphysical behavior of at the end of the growth cycle reveals that the density of the particles in the plasma volume decreases rapidly: This can be observed with naked eye. The physics in such phase cannot be described by our simple model. At label 3, a cycle of the particle formation is terminated and a new cycle begins.

Figure 7 shows measured and model calculated and for the nanoparticles grown in Ar–CH\textsubscript{4}. Symbols represent the measured and, and the solid line and dashed line indicate the model calculations with two complex refractive indices of $m=1.55-0.02i$ and $m=1.85-0.23i$, respectively. In the Ar–CH\textsubscript{4} plasma, three sequential growth steps are observed. The first growth step (label 1 in Fig. 7) is similar as described previously in the case of Ar–C\textsubscript{2}H\textsubscript{2}: After the initiation process, $\Psi$ and $\Delta$ start to increase from $\Psi=0^\circ$ and $\Delta\sim300^\circ$. The properties of particles smaller than about 65 nm in radius cannot be characterized by the given complex refractive indices (label 1 in Fig. 7). Thereafter, $\Psi$ and $\Delta$ are described by the complex refractive index of $m=1.85-0.23i$ (label 2 in Fig. 7). This complex refractive index is very close to that of a-C:H films deposited in a C\textsubscript{2}H\textsubscript{2} plasma ($m=1.84-0.03i$), but with somewhat higher extinction coefficient (see Sec. IV A). When the particles are larger than about 130 nm in radius (label 3 in Fig. 7), $\Psi$ and $\Delta$ are characterized by a lower complex refractive index of $m=1.55-0.02i$ which is very close to that of PLC films deposited in CH\textsubscript{4} plasmas [$m=1.57-0.01i$, see Sec. IV A and Fig. 4(a)]. Again, when the particles reach their critical size, they are falling down onto the bottom of the reaction chamber (label 4 in Fig. 7). A new particle formation in Ar–CH\textsubscript{4} plasma can only be initiated when an additional initiation process is applied.

Note that fittings for both particle growth in Ar–C\textsubscript{2}H\textsubscript{2} and in Ar–CH\textsubscript{4} plasmas are performed with the original assumptions of the Mie theory. Nevertheless, this simple model with one or two pairs of complex refractive indices describes the most of the growth of nanoparticles remarkably well.
V. GROWTH OF a-C:H NANOPARTICLES IN AR-HYDROCARBON PLASMAS

A. A general growth and atomic structure model of a-C:H materials

Amorphous (hydrogenated) carbon materials (a-C and a-C:H) contain a mixture of \( sp^3 \), \( sp^2 \), and sometimes a small fraction of \( sp^1 \) sites which have forms of (aromatic) rings and aliphatic chains: The peak positions and intensities of Raman and Fourier transform infrared (FTIR) spectra are varied due to the bond disorder, clustering of the \( sp^2 \) phase, presence of \( sp^2 \) rings or chains, and the \( sp^2/sp^3 \) ratio.\(^{48}\) In a-C:H materials, most \( sp^3 \) sites are bound to hydrogen,\(^{49,50}\) thus, highly \( sp^3 \) bonded a-C:H are hydrogen rich (soft, low density, and polymeric). Robertson has intensively investigated the structure of a-C(:H) materials and suggested an atomic structure model.\(^{51}\) According to his model, a-C and a-C:H materials consist of short aliphatic chains attached to one or two continuously connected aromatic ring structures in amorphous networks. In our previous \textit{ex situ} micro-Raman measurements on a-C:H nanoparticles, it is found that the “nanocrystallite” size of a-C:H nanoparticles derived from the \( I(D)/I(G) \) ratio is about 0.55–0.85 nm, which would correspond to two to four graphite rings,\(^1\) which is consistent with the Robertson model.

The growth of nanoparticles is divided into several steps.\(^{52}\) It begins with nucleation, the formation of the primary clusters from the gas. The primary clusters in hydrocarbon plasmas are \( C_xH_y \) species with a small concentration of hydrogen which would have different forms and shapes as the cluster size increases. Both experimental\(^{53–55}\) and theoretical\(^{56,57}\) results show that small linear chains of \( C_x \) with \( x<10 \) are formed; purely monocyclic rings with \( 10<x<20 \), bicyclic rings with \( 20<x<30 \), and tricyclic with \( x>30 \), and so on (polycyclic). The clusters then grow further by two different growth processes; coagulation and accretion. Due to the charge fluctuation of small plasma-suspended clusters, two small charged clusters with a radius smaller than a few nanometers, with different signs of electric charge, attract each other and stick together by collision (coagulation). The clusters then grow up further by collecting small molecules and ions (accretion).

FIG. 5. Measured \( \Psi \) and \( \Delta \) for the nanoparticles grown in an Ar–C\(_2\)H\(_2\) and in an Ar–CH\(_4\) plasma. The nanoparticle formation in an Ar–C\(_2\)H\(_2\) plasma shows periodicity (dotted vertical line with horizontal arrows indicates a single cycle) (a) Measured \( \Psi \) (solid line) and \( \Delta \) (dashed line) in an Ar–C\(_2\)H\(_2\) plasma. (b) Measured \( \Psi \) (solid square) and \( \Delta \) (open circle) in an Ar–CH\(_4\) plasma.

\[
\begin{align*}
\text{(a)} & \quad \text{single cycle} \\
\text{(b)} & \quad \text{single cycle}
\end{align*}
\]
B. Initial phase of the particle formation \((r<65 \text{ nm})\)

A critical precursor density is essential for the initiation of the particle formation in general.\(^{35,58-61}\) The production of acetylenic compounds \((\text{C}_2\text{H}_x)\) plays a very important role as a key mechanism of the particle formation in hydrocarbon plasma \((\text{CH}_4, \text{C}_2\text{H}_2, \text{and } \text{C}_2\text{H}_4)\).\(^{30}\) We assume that the precursor is \(\text{C}_2\text{H}^-\) created from \(\text{C}_2\text{H}_2\) by the reaction,

\[
\text{C}_2\text{H}_2 + e^- \rightarrow \text{C}_2\text{H}^- + \text{H}.
\]

The concentration of this precursor is critical for the particle formation in both Ar-hydrocarbon plasmas: Since the precursor is abundantly and continuously produced in the Ar–C\(_2\)H\(_2\) plasma, the particles are formed spontaneously and periodically [see Fig. 5(a), only two cycles are shown]. The existence of significant amounts of \(\text{C}_2\text{H}\) molecules in the Ar–C\(_2\)H\(_2\) plasma is directly confirmed by terahertz spectroscopy experimentally\(^{62}\) and theoretical model calculation of particle formation in a C\(_2\)H\(_2\) plasma.\(^{63}\) In Ar–CH\(_4\), however, a critical amount of C\(_2\)H\(_2\)—therefore C\(_2\)H\(^-\) precursor—has to be provided by an external initiation process: either by applying transient high power or by injecting a small amount of C\(_2\)H\(_2\). Otherwise, particle formation cannot be observed in our Ar–CH\(_4\) plasma. The role of the external initiation process for the initiation of particle growth in the Ar–CH\(_4\) plasma is described in previous publications in detail.\(^2,3\)

As described before, the particles smaller than about 65 nm in both Ar–C\(_2\)H\(_2\) and Ar–CH\(_4\) plasmas (label 1 in Figs. 6 and 7) have different complex refractive indices from that of large size particles. For such small particles in plasmas it is speculated that the particle temperature may be high. In small particles the heat of recombination of ions, the reaction enthalpy, and ion kinetic energy are distributed among a few molecules only, leading to a high effective temperature. A high particle temperature is observed during the growth of Si nanoparticles, for example, where a single crystalline small nucleus was identified by TEM.\(^{23}\) The particle temperature decreases when the particle size increases under the condition of a constant applied energy density. Similarly, one may speculate that the particle temperature at the early phase in

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**FIG. 6.** Measured and model calculated \(\Psi\) and \(\Delta\) for the nanoparticles grown in an Ar–C\(_2\)H\(_2\) plasma. Labels 1 and 3 indicate the begin/end of the particle formation for one cycle. For larger particles \((r>65 \text{ nm}, \text{label } 2)\), a single pair of complex refractive index of \(n=1.96 -0.125i\) is sufficient to describe the particle growth up to radii about 375 nm. (a) Measured and calculated \(\Psi\). (b) Measured and calculated \(\Delta\).
Ar-hydrocarbon plasma might be high enough that graphitization may take place. Graphite has a higher extinction coefficient $k = 1.0/H_2O$ than PLC $a$-$C:H$ films. The effect of the extinction coefficient on $r/H_9023$ for small particles ($r < 100 \text{ nm}$) is negligible (thus, not shown here). On the contrary, the effect on $r/H_9004$ is significant. Figure 8 shows $r/H_9004$ of the measurements and model calculations for both Ar–C$_2$H$_2$ and Ar–CH$_4$ plasmas with various complex refractive indices. Comparing measured $\Delta$ (symbols in Fig. 8) with calculated $\Delta$, higher extinction coefficients are essential for particles smaller than 65 nm: The smaller a particle is, the higher the extinction coefficient has to be. Particles at a radius about 25 nm $\pm 6 \text{ nm}$ in both plasmas have a complex refractive index $m = 2.0 - 1.0i$ which is commonly accepted value as the complex refractive index of graphite.$^{65,66}$ A further increase of the extinction coefficient to $m = 2.0 - 1.4i$ is required in order to describe measured $\Delta$’s for particles smaller than $\sim 18 \text{ nm}$ in radius.

**C. Core-shell structures of $a$-$C:H$ nanoparticles ($r > 65 \text{ nm}$)**

After the initial growth, the complex refractive indices of the particles formed in both Ar-hydrocarbon plasmas are changed as particles are growing. The change of $n$ for the particles formed in Ar–C$_2$H$_2$ plasma is negligible, but $k$ decreases practically exponentially from $k = 1.4$ to $k = 0.125$: The particles bigger than a radius of about 65 nm are described by the complex refractive index $m = 1.96 - 0.125i$. This indicates that the particles formed in Ar–C$_2$H$_2$ plasma are likely to have a hard graphitelike core of a radius smaller than about 25 nm with a soft $a$-$C:H$ shell structure on it. On the other hand, two pairs of complex refractive indices are required to describe the particle growth in the Ar–CH$_4$ plasma: a higher refractive index of $m = 1.85 - 0.23i$ for the particles with radii between about 65 and 100 nm (label 2 in Fig. 7) and then decreased values of $m = 1.55 - 0.02i$ (label 3 in Fig. 7). They are very close to that of PLC films deposited either in C$_2$H$_2$ or in CH$_4$ plasmas (see above). This indicates that the particles formed in Ar–CH$_4$ plasma may have a hard core and two sequential shells. The different growths in both Ar-hydrocarbon plasmas are due to the different initiation process and the change of the plasma chemistry in time. These results are fully consistent with our previous study of $a$-$C:H$ nanoparticles using ex situ micro-Raman spectroscopy.$^1$ Also, it supports the fact that the growth of nanoparticles is essentially the same as the growth of PLC films deposited on the surface of a silicon wafer placed on the lower electrode, when the particle radius is larger than about 50 nm.$^1$
Note that, after a certain thickness of mantle deposition, the characteristics of the inner part are unacquirable to the diagnostic because of shielding by the sequential coatings on it.

Summarizing the findings, it appears likely that the particles in the initial phase of the particle formation in both Ar-hydrocarbon plasmas are small graphitelike grains with a maximum radius of about 25 nm, deduced from ex situ micro-Raman spectroscopy: Graphitization may occur due to a high particle temperature and the associated release of hydrogen. The particles cool down as their size increases. Further growth of the particles is mainly accretion of small species (positive ions, neutral radicals) which leads to soft a-C:H mantles (shell structures) on the graphitelike core. Figure 9 shows a summary of complex refractive indices discussed above as a function of particle radius. From this figure it may speculated that the extinction also shows, in addition to the influence of structure and composition, a “finite size” effect leading to high values at small radii. It has to be considered, however, that the error of the data is large in this area due to the bad photon statistics and that care must be taken when interpreting data at such small radii ($r < 25$ nm).

VI. RELEVANCE TO ASTROPHYSICS: INTERSTELLAR DUST GRAINS

A. Interstellar dust grain model: Prerequisites

The universe is not empty but filled with stars and diffuse material between them, called interstellar medium (ISM). Interstellar dust (ISD) grains play an important role in the ISM and they shape the spectra of galaxies. Since Trumpler provided the first proof of ISD grains, authors have investigated ISD grains regarding their size, shape, and compositions. For more details, see review articles, Refs. 17 and 68.

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. Silicate materials have a strong absorption resonance at $\sim 10$ $\mu m$ due to the Si–O stretching mode which might be the origin of the $\sim 9.7$ $\mu m$ absorption feature. Some form of graphitic carbon or polycyclic aromatic hydrocarbons (PAHs) might be responsible for the absorption feature at $\sim 2.175$ $\mu m$. Other features at $\sim 3.3$ $\mu m$ (C–H stretching), $\sim 3.4$ $\mu m$ [aliphatic (chainlike) C–H stretching], $\sim 6.2$ $\mu m$ (C–C stretching),

FIG. 8. Measured and calculated $\Delta$'s for the particles grown in Ar–C$_2$H$_2$ and Ar–CH$_4$ plasmas with various extinction coefficients. Labels are the same with those in Figs. 6 and 7. (a) Measured and calculated $\Delta$ for the particles grown in Ar–C$_2$H$_2$. (b) Measured and calculated $\Delta$ for the particles grown in Ar–CH$_4$. 

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$\sim 7.7 \mu m$ (C–C stretching), $\sim 8.6 \mu m$ (C–H in-plane bending), and $\sim 11.3 \mu m$ (C–H out-of-plane bending) are also due to the PAHs.\textsuperscript{17}

From the astrophysical observations, there are certain criteria which have to be considered for ISD grain models. We will briefly summarize some criteria discussed in Refs.\textsuperscript{17} and 68.

- The 2175 Å bump is an absorption feature with no scattered component indicating ultrasmall grains (absorption dominant). It is still under doubt, but laboratory studies of UV absorption by PAH molecules, radicals, and ions indicate that 20–1000 carbon atoms are required for comparison with the observed 2175 Å profile.

- From the wavelength-dependent extinction, polarization, and near-, mid-, and far-IR emissions, grains have a size distribution from a few angstroms to a few micrometers. Thus, there must exist large size grains larger than $r > 250 \AA$ in radius heated by starlight to equilibrium temperature of $15 K < T < 25 K$ and cooled by far-IR emission to produce emission at $\lambda > 60 \mu m$ which accounts for $\sim 65\%$ of the total emitted power, and there must exist small size grains smaller than $r < 250 \AA$ in radius stochastically heated by single starlight photons to temperatures $T \gg 20 K$ and cooled by near- and mid-IR emissions to produce the emission at $\lambda < 60 \mu m$ which accounts for $\sim 35\%$ of the total emitted power.

- From the interstellar polarization, curve rises from the IR, has a maximum somewhere in the optical, and then decreases toward the UV: There must exist a population of aligned, nonspherical grains with a typical size of $r \sim 0.1 \mu m$ responsible for the peak polarization at $\lambda \sim 0.55 \mu m$.

B. Formation of PAHs and nonspherical particles

ISD grains might have mixture of both amorphous and crystalline structures of silicates, carbonaceous, and silicon carbide with various grain sizes. Pendleton and Allamandola have concluded from a detailed analysis of the 1000–4000 cm$^{-1}$ (2.5–10 $\mu m$) absorption spectra of 13 different materials produced in the laboratory that the organic “refractory” material in the ISM is predominantly hydrocarbon in nature, possessing little nitrogen or oxygen, with car-

FIG. 9. Complex refractive indices as a function of particle radius compared with that of graphite and $a$-C:H materials. (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 eyes.
bon distributed between the aromatic and aliphatic (–CH₂– and –CH₃ groups) forms.¹⁸ This is consistent with the growth and atomic structure models for a-C:H materials discussed in Sec. V A. Starting from the formation of primary clusters (C₅Hₓ), carbon clusters are growing up to polycyclic rings through formation of aliphatic chains, mono-, bi-, and tricyclic rings, etc. The particle size increases (x > 60) and smaller size rings (five- and sixfold, etc.; PAHs) appear due to the interaction among them.⁵⁷ The interactions of chains, of chain and ring, and of rings (up to χ = 90) are illustrated in Ref. 56 in detail. From the in situ Rayleigh-Mie scattering ellipsometry discussed above, a-C:H nanoparticles of a particle size smaller than ~25 nm have a complex refractive index of m = 2.0 ± 1.0i which represents graphitelike material. Calculating the size of a grain consisting of 1000 carbon atoms using the density of graphite (2.2 g/cm³), a size of ~1.3 nm in radius is obtained. These fit to the first and second criteria for ISD grain model.

At a particle size smaller than about 5 nm, the coagulation might be the dominant particle growth mechanism in reactive plasmas due to the charge fluctuation.⁵⁹ Although we might assume that small particles (r < 5 nm) in ISM somehow coagulate together and grow up further by accretion, these particles might have different size and shapes from ours: Different from the volume polymerization in reactive plasmas, there are not enough species for every particle for further homogeneous growth in ISM. Thus, the particles in ISM are probably nonspherical and polydisperse in their size. Under a certain condition in reactive plasmas, nanoparticles stick together in a particular way that they build elongated clusters consisting of linear chains of spherical a-C:H nanoparticles of a length of several hundreds of nanometers, to micrometers with sidearms and sometimes even with rings. The formation of the elongated clusters will be discussed in detail in a forthcoming publication. Similar observations are made by other authors.⁷⁰,⁷¹ These may fit to the third criterion for ISD grain model.

VII. CONCLUSION

We have analyzed the growth of a-C:H nanoparticles formed in Ar-hydrocarbon plasmas by means of in situ Rayleigh-Mie scattering ellipsometry. The Rayleigh-Mie scattering ellipsometry allows the in situ determination of the size dependent particle characteristics during the growth process: Several steps of a-C:H nanoparticle growth are clearly identified by their different optical characteristics.

The first step of particle formation in both Ar-hydrocarbon plasmas is likely to be the building of hard graphitelike cores of a size smaller than ~25 nm (or even smaller) with a complex refractive index of about m = 2.0 ± 1.0i. The extinction coefficient increases significantly with decreasing particle radius, which might be important for the interpretation of astrophysical data.

Complex refractive indices of the mantle (shell) structure of nanoparticles are essentially similar to that of a-C:H films deposited in C₂H₆ and CH₄ plasmas. Nanoparticles grown in the Ar–C₂H₆ plasma have a complex refractive index of m = 1.96 − 0.125i. In case of the Ar–CH₄ plasma, a high refractive index of m = 1.85 − 0.23i at radii between 65 and 100 nm, which is similar to that of C₂H₂ PLC films, reveals that a “carbon-rich” shell is generated in this phase and a more soft “hydrogen-rich” shell is accumulated with a low refractive index of m = 1.55 − 0.02i at large radii, which is also similar to that of CH₄ PLC films. This is due to the external initiation process for the particle formation in the Ar–CH₄ plasma which leads to the change of the plasma chemistry in time.

For larger particles (r > 100 nm) in both Ar-hydrocarbon plasmas, it is shown that the growth is homogeneous and isotropic in time.

The criteria of interstellar dust grains are compared with the growth and atomic structure models for a-C:H materials. It is found that the plasma-polymerized a-C:H nanoparticles fulfill the important criteria for ISD grain model in wide ranges of radii which makes our a-C:H nanoparticles a good candidate as an ISD analog.

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