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Treatment of dust particles in an RF plasma monitored by Mie scattering rotating compensator ellipsometry

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Abstract: Micrometer size particles can be processed by trapping them in a low pressure radio-frequency (RF) plasma. Their size can be influenced by etching or deposition. Mie scattering ellipsometry has been applied to monitor the particle properties during the plasma processing. Using this diagnostic, in which the polarization of light is modulated by means of a rotating compensator, the size and the size distribution of a cloud of particles are measured. The 5 μm particles, made of melamine-formaldehyde (MF) have been etched in an oxygen plasma. The experimental data have been fitted with a numerical model. The results indicate that the average size of the particles decreases and that the etching rate is 1.1 Ås^{-1}. At the same time, the dispersion of the particle size increases.

INTRODUCTION

Particles formed in RF plasmas have received a lot of attention in the last decade. Controlling the formation and trapping of dust particles in plasmas is important for the industry. Particles produced in semiconductor processing plasmas were seen as a dangerous source of surface contamination and the main reason for defects in the fabricated components. Thus, an extensive research effort was undertaken to avoid or to reduce the particle growth. Recently, another line of investigation has been introduced, after it was established that dust particles produced in the plasma can also have some important applications. The unique qualities of plasma produced particles, like their easy to control physical properties, small sizes, mono-disperse size distributions and regular shapes, have opened new possibilities in ceramic industry, catalysis, deposition, and many other areas.

Besides powder formation in plasmas also the injection of particles into the plasma has received some attention (refs. 1-3). As the particles in the plasma acquire a charge, in some cases the interactions between them leads to spatial arrangement of the particles into regular patterns, called Coulomb crystals. This effect was theoretically predicted by Ikezi (ref. 4) and observed experimentally by many research teams (ref.1,2). A Coulomb crystal can be formed when the ratio of the Coulomb energy to the kinetic energy of the particles exceeds a certain critical value. The formation and structure of the crystal depends on plasma parameters like RF power, gas pressure and gas flow rate, but also on particle parameters like size and size distribution. Analogies between the Coulomb crystal and a solid state crystal make the former a very promising model system to study solid state processes, like phase transitions and crystal lattice dynamics. In addition to its fundamental impacts, a Coulomb crystal provides good trapping of particles in the discharge, which facilitates plasma processing. In (ref. 2) Coulomb crystals in an RF discharge were studied by injecting 60 nm particles, which grew up to 2 μm by plasma deposition. This work illustrates the possibility of surface treatment of particles immersed in plasmas.

A good plasma diagnostics is indispensable for *in situ* monitoring of particles in the plasma. Tachibana *et al.* (ref. 5) have developed Mie scattering ellipsometry, an optical diagnostic for studying the particle growth in plasmas. With this diagnostic, based on a rotating analyzer ellipsometer, they could infer size, size distribution, density, and refractive index of the growing particles. In our laboratory we have built a rotating compensator ellipsometer to monitor the treatment of particles immersed in an RF plasma. The particles can be treated in several ways. Particle properties can be changed by deposition of layers (ref. 3); this process has found many applications, e.g. in catalysis. Alternatively, the particle surface can be smoothed or roughened. In this paper we present preliminary results of particle etching in an oxygen plasma.

EXPERIMENTAL

Our experimental set-up has been described elsewhere (ref. 3). We inject mono-disperse spherical melamine-formaldehyde (MF) particles (Microparticles GMBH, Berlin) into an oxygen RF plasma. The particles have a diameter $2r = 4.79 \pm 0.08$ μm, a density $\rho = 1.51$ gcm^{-3}, and a real refractive index $m = 1.68 \pm 0.05$ at $\lambda = 488$ nm. Typical operating conditions are: a pressure of 1.3 mbar, a gas flow rate of 20 sccm, and an RF power input of 36 W. We have used a rotating compensator ellipsometer (RCE) as our main diagnostics to monitor the etching of the particles. A LEXEL 85 argon ion laser operating at a wavelength of 488 nm and an output power of 300 mW has been used as a light source. The laser light is linearly polarized with an azimuth of 45° with respect to the scattering plane (*i.e.* the plane formed by the incoming and the reflected/scattered beam) by a Glan-laser prism polarizer. The light, scattered by the particles suspended in the plasma, is detected under 90° with respect to the incident laser beam. The detection system consists of a rotating compensator, a sheet polarizer, and a photomultiplier (Thorn EMI). Diaphragms and lenses are used to image the scattering volume on the photomultiplier and to limit the detection angle.

The rotating compensator system consists of a quarter-wavelength plate that is mounted on an encoder. The encoder is motor driven and rotates with a frequency of 37.5 Hz, thereby giving one index pulse and 2500 clock pulses every rotation. The signal is modulated by the rotation of the quarter-wavelength plate. Acquiring one single signal takes 1/37.5 s; analysis and storage takes 2 s. The rotating compensator is used to measure a complex quantity ρ which is defined as

$$\rho \equiv \tan\Psi \exp(j\Delta) \equiv S_2(\theta,\varphi) \big/ S_1(\theta,\varphi) \qquad (1)$$

where Ψ represents the relative amplitude attenuation of the two orthogonal polarizations ($0° \leq \Psi \leq 90°$) and Δ represents the phase difference between the two orthogonal polarizations of the light ($0° \leq \Delta \leq 360°$). The scattering amplitude functions $S_1(\theta,\varphi)$ and $S_2(\theta,\varphi)$ depend on the azimuth φ of the light and the scattering angle θ. These two scattering amplitude functions are furthermore dependent on the wavelength of the light and on the particle size and refractive index. These functions can be determined using Mie theory. A good reference for the Mie theory is (ref. 6), in which a thorough derivation can be found. The rotating compensator offers several clear advantages compared to other ellipsometric systems, one of them is the unambiguous determination of Δ.

RESULTS AND DISCUSSION

In fig. 1 a typical Mie scattering RCE measurement is shown.

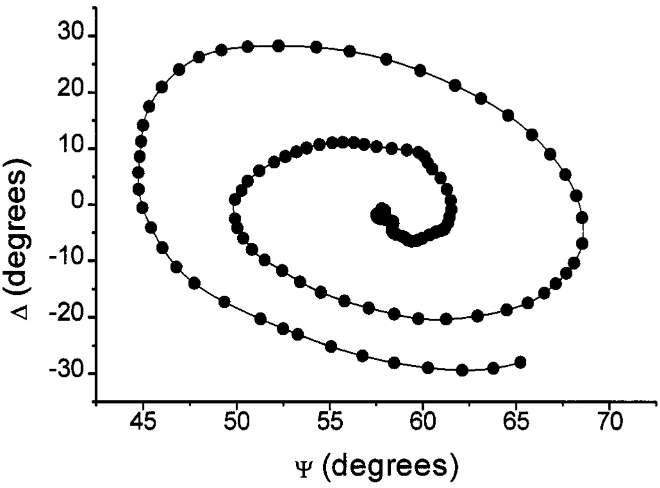

Fig. 1 A typical etching measurement of MF particles trapped in an oxygen RF plasma. The solid line shows the smoothed overall behavior and the dots represent single measurements. For clarity only one out of ten measurement points is shown. The RF plasma is operated at 1.3 mbar, 20 sccm, and 36 W, the used MF particles have a diameter $2r = 4.79 \pm 0.08$ µm.

The MF particles are injected in an oxygen plasma which is operated at 36 W, 1.3 mbar, and 20 sccm. The signal is recorded 58 s after the injection of the particles. This time is needed to open the slit protecting the photomultiplier and to adjust the operating voltage of the photomultiplier. In the plasma the particles acquire a negative charge, which results in their trapping at the plasma-sheath boundary. The particles are arranged in a solid-like structure, which does not change much during the measurement. This has been observed visually. The different layers of the solid were clearly visible, due to the light scattering by individual particles. Also the vertical stacking of the layers, mentioned by other authors (ref. 7) could be observed. No estimation of the number of particles in the scattering volume could be made. In the plasma the particles are oxidized and the changes in their scattering properties are monitored. The ellipsometric angles at the beginning of the measurement are $\Psi = 65°$ and $\Delta = -25°$, where Δ is made negative to obtain a smooth curve (normally Δ ranges from 0° to 360°). The measurement curve is an asymmetric helix, which converges clockwise to $\Psi = 57°$ and $\Delta = 0°$. The intensity changes are detected by the photomultiplier, while the compensator rotates. After one full rotation of the compensator the signal is analyzed; this takes 2 s. In fig. 1 only 10 % of the measurement data is shown (dots). The time interval between the consecutive points is approximately 20 s. The measurement has been stopped at $t = 2600$ s after it has been observed visually that the particles start to leak out of the plasma. In order to find the relation between the ellipsometric angles and the particle size it is necessary to perform simulations using Mie theory. In the simulation we have assumed that the particles remain homogeneous, spherical, mono-disperse in size, and that the particle modification in the plasma does not alter their refractive index. Based on the Mie theory $S_1(\theta,\varphi)$ and $S_2(\theta,\varphi)$ can be calculated for various radii, complex refractive indices, wavelengths, scattering angles and azimuth angles of the light. We have taken the refractive index $m = 1.68$, $\lambda = 488$ nm, $\theta = 90°$ and $\varphi = 45°$, and we have varied the particle size $2r$ from 4.70 to 4.90 µm. Using equation (1) we can link $S_1(\theta,\varphi)$ and $S_2(\theta,\varphi)$ to the ellipsometric angles. These calculations show the necessity to use size distribution functions to relate calculated ellipsometric angles to measured ones because of the large number of particles present in the scattering volume in the experimental situation. Therefore a first attempt is made by assuming a gaussian distribution of the particles with a constant standard deviation of 2% and a decreasing mean size during the etching process; this is shown in fig. 2.

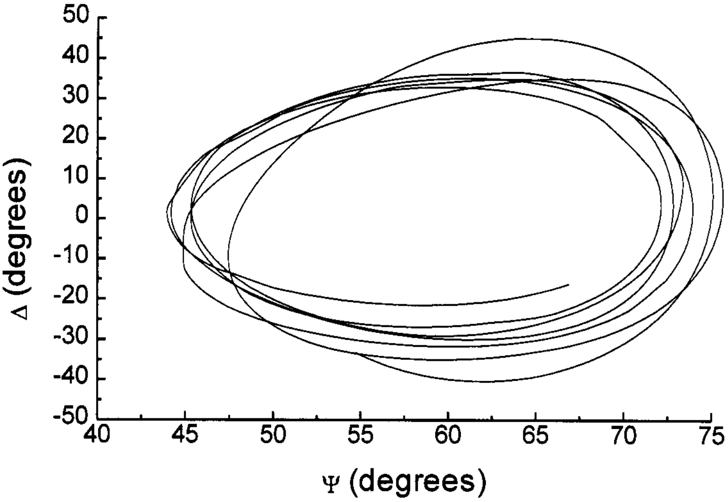

Fig. 2 Simulation of the ellipsometric angles taking the size dispersion of the particles into account. A gaussian distribution is assumed with a constant standard deviation of 2% and a decreasing mean size. The simulation starts at Ψ = 67° and Δ = -20 ° and ends at Ψ = 55° and Δ = -30 °.

The beginning at Ψ = 67° and Δ = -20° is in a good agreement with the experimental situation, however a larger particle size $2r = 4.88$ μm has to be assumed. According to the supplier the particles have a diameter $2r = 4.79$ μm. The simulation does not show the same behavior like the measurement; the typical helix-like structure is missing. This leads to the conclusion that not only the size but also the size dispersion should be varied. This has been done in several simulations. We have assumed a linearly increasing standard deviation in size and the results have been improved. Finally, we have introduced a translation operated log normal distribution, similar to the one used by Hayashi (ref. 8). We have applied this distribution in the simulation of the etching process of particles and the curve shown in fig. 3 has been obtained.

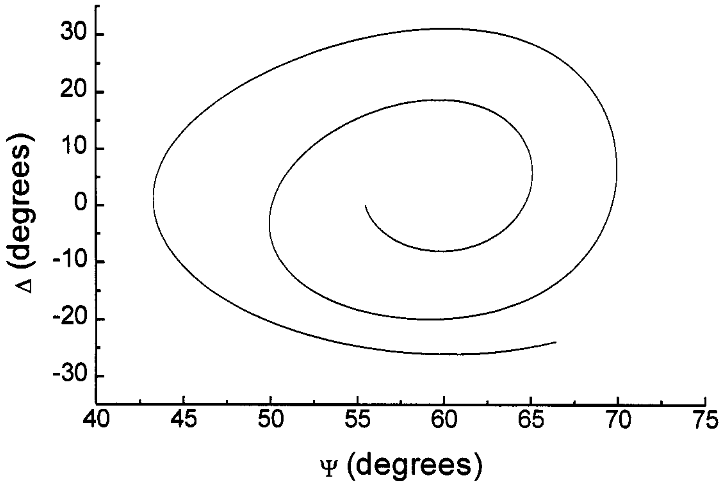

Fig. 3 Simulation of the measurement assuming a translation operated log normal size distribution. The geometric standard deviation increased from $\sigma = 0.078$ at the start to $\sigma = 0.19$ at the end of the measurement. The radius of the particle is $r = 2.44$ μm at the start and $r = 2.16$ μm at the end. The simulation shows the typical helix-like structure but misses the asymmetric form.

In the simulation an initial particle size of $2r = 4.88$ µm has been taken in order to find ellipsometric angles comparable to the measurement. The geometric standard deviation is found to be $\sigma = 0.078$ at the beginning of the measurement and it increases linearly to $\sigma = 0.19$ at the end. The change in the particle size is $\delta r = 0.28$ µm. The necessity to increase the geometric standard deviation indicates that the oxidation rate is not the same for all the particles trapped in the detection volume. An explanation for this non-uniform oxidation can be the creation of a wake and an ion focusing region (ref. 9). These tow regions are created due to the focusing of ions by the negatively charged particles. The simulation clearly shows a helix-like structure, but still misses the asymmetric behavior shown in the measurement.

Besides the increase of the size dispersion other explanation can be provided for the measured behavior. The surface of the particle can be changed due to chemical reactions. In this case a particle acquires a layer and the description of its scattering properties has to be modified. Several authors (ref. 10, 11) performed this and an attempt was made to simulate the resulting ellipsometric behavior. This did not lead to satisfying results because the algorithm was not stable. Changing the surface in a drastic way can also result in layers with different refractive indices. Assuming a different refractive index for a particle has a large impact on the simulation results. For a complex refractive index the simulations run anti-clockwise. Also Ψ and Δ change dramatically in value; Ψ becomes smaller than 45° and the value of Δ is no longer around 0° and 360° but is close to 180°. Simulations clearly show helix-like structures, but the curve runs anti-clockwise. Another effect, which can influence the experimental Ψ-Δ curve, might be due to a change of the particle shape during oxidation. However, we suppose that the particles are spinning and that the oxidation is homogeneous enough to preserve their spherical shape.

The measurement and the simulation intersect at some points; the simulation has been optimized for intersection points. Plotting the size obtained from the simulation against of the time obtained from the experiment at these intersection points results in the time dependence of the particle size, displayed in fig. 4. It can be seen that the particle radius decreases linearly with time. The slope of this line, which indicates the etch rate, is not sensitive to experimental errors in the ellipsometric parameters.

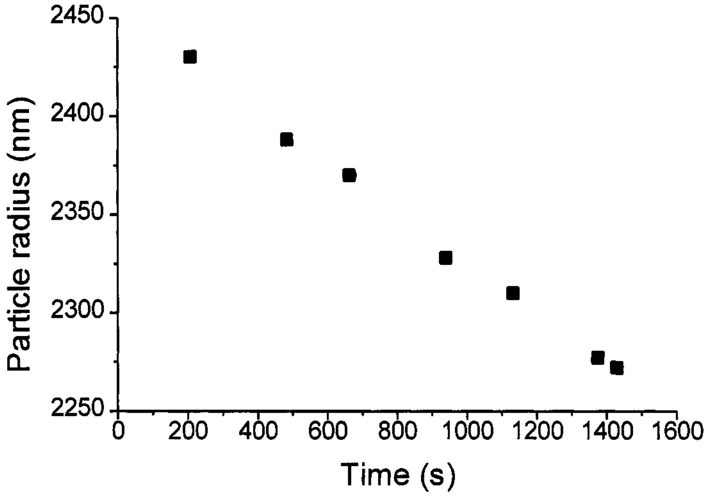

Fig. 4 Comparing the simulation to the measurement the particle radius of the simulation is shown as a function of the time of the measurement at the intersection points. The resulting etch rate is 1.1 Ås^{-1}.

An etch rate of 1.1 Ås^{-1} has been determined. Comparing the etching of particles to etching of surfaces this etch rate is low. This can be understood, as in ion-assisted etching the energy of incident ions is an important parameter. The particles, suspended in the plasma, remain at the floating potential, which is in the order of several volts. This is much lower than the plasma sheath voltage (several hundreds of volts), so the energy of positive ions at the particle surface is substantially lower than at the electrode surface and consequently lower etch rates for particles can be expected.

CONCLUSIONS

We have presented the preliminary results obtained with Mie scattering rotating compensator ellipsometry. This in-situ technique has been used to monitor the oxidation process of polymer particles in an RF plasma. The measurements have been fitted with the simulation data, based on the Mie scattering theory, in order to determine the time dependent particle size. The experimental behavior of the ellipsometric parameters can be explained if a change in the size distribution of the particles during oxidation process is taken into account. The measurement is best fitted assuming a translation operated log normal size distribution with increasing size dispersion. The size of the particles decreases linearly with time and an etch rate of 1.1 $\text{Å}s^{-1}$ has been determined.

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