Fluorination of silicon in fluorocarbon rf discharges studied by *in situ* high-speed infrared ellipsometry

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Abstract

During the etching process a layer of partly damaged and fluorinated silicon is formed on top of the substrate. Through this layer fluorine is transported to the underlying silicon and reaction products such as SiF_2 and SiF_4 are formed and transported to the gas phase. Up till now the structure and composition of this active layer has been studied mainly by *ex situ* X-ray photoelectron spectroscopy (XPS), which means that no information on the dynamics in the begin stages of the process can be obtained. Moreover with this technique it is difficult to obtain quantitative results on densities and layer thickness since the electron escape depth is in general not known accurately. Therefore an effort is being made to implement a high-speed infrared ellipsometer system that uses a tunable diode laser as a light source and a photo-elastic modulator to modulate the polarization state of the light. With this system it is possible to study the formation of SiF_x-bonds (x=1..4) on the surface during the begin stages of the plasma with submillisecond time resolution and a high signal-to-noise ratio. For the identification of the different SiF_x-bonds a broad-band FT-IR Rotating-compensator ellipsometer will be used before and after plasma exposure. Preliminary measurements in the visible region have shown that a small part of the reactive layer is removed in the afterglow of the plasma after plasma switch-off.

Introduction

Halocarbon rf discharges, in particular using fluorocarbons as a feed gas, are used widely for dry etching of silicon and silicon oxide. Though these plasmas are used widely by the industry, many of the fundamental processes that take place in these plasmas are not clear yet. Especially the plasma-surface interaction is still not well understood. Several groups have performed *ex situ* chemical analysis of the surface using UHV-compatible techniques like XPS [1,2]. Moreover, some studies have been performed using internal-reflection FT-IR. Furthermore, some work has been performed using *in* situ single-wavelength ellipsometry on the dynamics of the etching process in the begin stages after plasma excitation[4]. However, there is hardly any data on the dynamics of different bonds on the surface in the begin stage of the process, where much could be learned about the plasma-surface interaction. For this reason an effort is

underway in our group to implement a high-speed infrared ellipsometer system. The system uses an infrared diode laser as a light source, which basically makes it a single-wavelength apparatus. However, by tuning the temperature of the laser diode, the wavelength can be tuned enough to cover the typical width of an absorption band of a certain bond. In this way it will be possible to follow the number of bonds on the surface as a function of time after the plasma has been excited or extinguished. For the identification of the position of different absorption bands a broad-band FT-IR based Rotating Compensator Ellipsometer (which also has been developed in our group) can be used.

Experimental

The fast ellipsometer setup is built around a small parallel-plate rf reactor driven at 13.56 MHz (see Fig. 1).

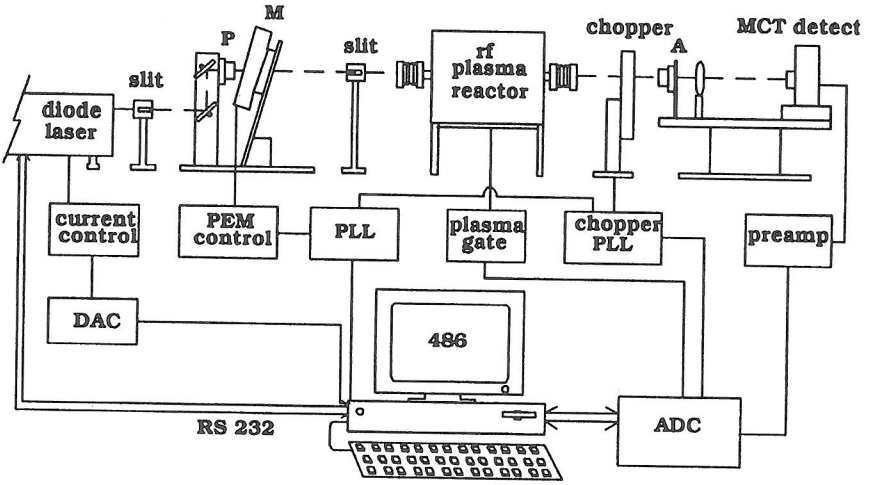

Figure 1: Experimental setup of the fast infrared ellipsometer. The infrared light reflects inside the reactor at an angle of 30-70° with respect to the normal of the sample, which is mounted on the rf electrode. P, M and A are the polarizer, photo-elastic modulator and analyzer, respectively.

The measurement system consists of a Polarization Modulation Ellipsometer (PME) which uses a tunable diode laser (TDL) as a light source. The wavelength of the light being used can be tuned by changing the temperature of the laser. Though this allows for changes of only 5-10 % of the central wavelength, this is enough to cover the width of a typical solid state absorption band. For measurements in the visible region the alignment laser of the TDL, a 632.8 nm HeNe laser, is used. The light that comes out of the TDL system first enters a polarizer then a ZnSe photo-elastic modulator. After this the light reflects on the surface and subsequently passes a second polarizer. The modulation of the polarization state of the light is performed by the photo-elastic modulator (PEM),

which modulates the phase difference between the parallel and perpendicular parts of the light at a frequency of 31.1 kHz (i.e. the resonance frequency of the crystal). Since in principle one modulation cycle suffices to determine the optical properties of the surface under study, the maximum measurement frequency that can be achieved is 31.1 kHz. In the infrared region this cannot always be done in practice, since in most cases the d.c. part of the signal must be measured also. Due the drift of the infrared detector, it is therefore necessary to chop the light beam using a mechanical chopper. In the present setup this limits the measurement frequency to 2.6 kHz. The chopping frequency is regulated such that it has a constant phase relation with the PEM. As is indicated in Fig. 1 the modulator head is tilted with respect to the beam direction. This has been done to eliminate any multiple reflections that take place inside the modulator and therefore give rise to unwanted interference effects. The ellipsometric signal is measured using a 12-bits 8 MHz A/D converter that has been developed within the university. The intensity as a function of time is given by [5]

$$I(t) = I_0[1 + I_c \cos(\delta(t)) + I_s \sin(\delta(t))]$$

where I_0, I_s, I_c are respectively the dc-term, the sinusoidal part and the cosine term of the signal. Fourier expansion of the detected intensity is necessary to relate the measured harmonics to I_c and I_s.:

$$\sin(\delta(t)) = \sin(B\sin\omega t) = \sum_{n=0}^{\infty} J_{2k+1}(B)\sin((2k+1)\omega t)$$

$$\cos(\delta(t)) = \cos(B\cos\omega t) = J_0(B) + \sum_{n=0}^{\infty} J_{2k}(B)\cos(2k\omega t)$$

Inserting the expansions we get:

$$I = I_0[(1 + J_0(B)) + I_s(2J_1(B)\sin(\omega t)+\ldots) + I_c(2J_2(B)\cos(2\omega t)+\ldots)]$$

The values of I_s and I_c can therefore be calculated from the measured d.c. part and the first two harmonics of the modulation angular frequency ω. How I_s and I_c are related to the ellipsometric parameters Δ and Ψ depends on the angular settings of the polarizer, modulator and analyzer. For instance at (P=45°, M=0°, A=45°) it can be derived that [5]:

$$I_s / I_0 = \sin 2\Psi \sin\Delta$$
$$I_c / I_0 = -\cos 2\Psi$$

A key parameter in the measurement of Δ and Ψ is the modulation amplitude B. The value of it can be set by the PEM controller, but may not always be stable in time. Therefore it is obtained from the measurement signal itself by taking the ratio of the first and third harmonic in the signal given by

$$I(3\omega) / I(\omega) = J_3(B) / J_1(B)$$

Since this is a monotonous increasing function of B, this directly yields the modulation amplitude B.

Preliminary measurements

Since most interesting materials like Si and GaAs are transparent in the mid-infrared where the interesting absorption band are located, classical external reflection ellipsometry suffers from multiple reflections inside the sample, which makes the measurement very sensitive to temperature changes of the sample and hence makes the interpretation difficult. Therefore we have chosen to combine ellipsometry with attenuated total reflection (ATR) spectroscopy, where the light is guided through the wafer like a waveguide, having many (total) reflections before leaving the material again. Since the preparations for this are still under way, it has been decide to start off in the visible region using external reflection ellipsometry. In fig. 2 shows the changes in Δ and Ψ that occur in a modulated plasma as a function of the flow rate in a CF_4 plasma etching silicon. It is obvious that the effects that occur are complementary in Δ and Ψ. Since for thin layers on top of silicon the change in Ψ mostly relates to a change in the damaged part of the top layer [6], this indicates that the amount of damage in the top layer is reduced when the plasma is switched off and increases again when the plasma is switched on. The reason for this is probably etching of silicon atoms that have dangling bonds on the surface. The fact that this effect decreases at low flow rates may indicate that the species involved in the etching process (fluorine) become less abundant at conditions of low flow, which may be due to the loading effect. In the change in Δ, which is caused by adsorption/desorption of a transparent layer the behavior is quite the opposite. This indicates that the species that adsorbs on the surface when the plasma is switched off becomes more abundant at conditions of low flow. In a CF_4 plasma this species could be CF_x radicals. If the density of fluorine is reduced at low flow rates due to the loading effect, the gas phase loss of CF_x radicals is reduced and therefore they may become more abundant in the plasma. To clarify what exactly happens, measurements in the infrared region should yield definite answers.

Also the size of the effects shown here is interesting to know. Since the effects in Δ and Ψ point to thickness changes in the order of 0.1-0.2 Å, this indicates that the surface of a silicon sample does not appear to change much after switch-off of the plasma. This indicates that post-plasma diagnostics that require UHV, such as XPS and Auger, should yield results that are more or less representative for the situation that exists during plasma operation.

In the near future we will investigate these effects in more detail in the infrared region. For broad-band steady-state IR ellipsometric measurements a rotating-compensator ellipsometer will be used. With this apparatus the correct wavelength region where we should measure can be obtained. The fast ellipsometer described here will subsequently be used to measure the time evolution of absorption bands of interest.

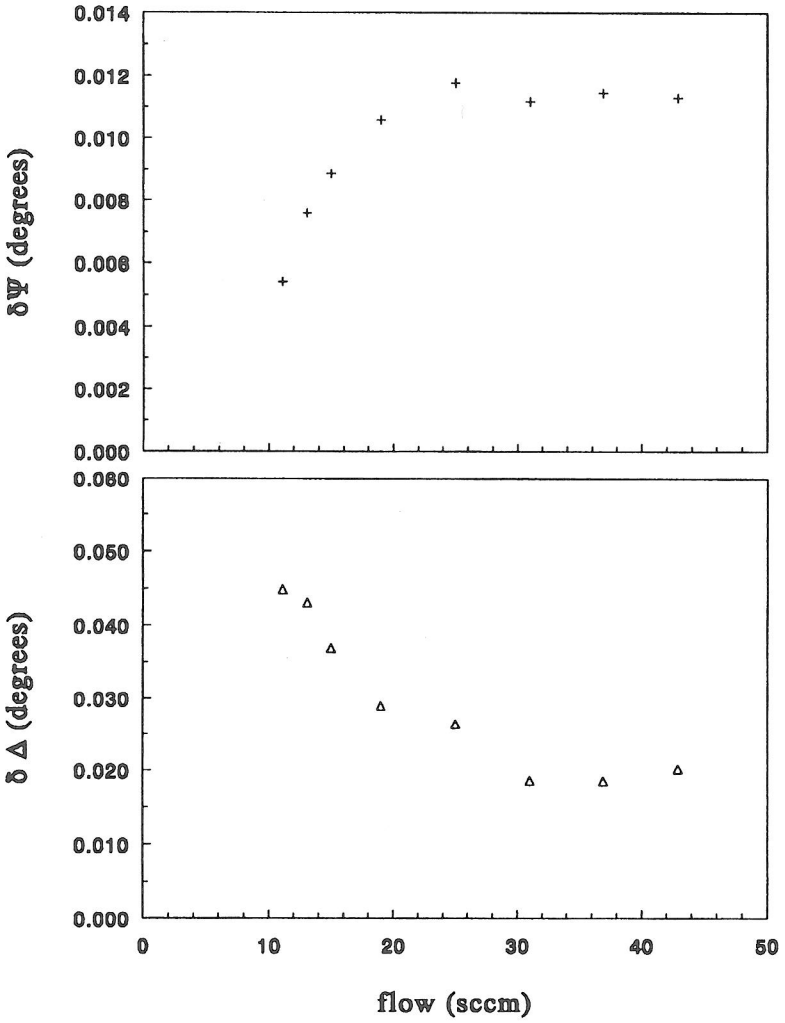

Figure 2: Measurement of the changes in Δ and Ψ in a modulated plasma. $\delta\Delta$ and $\delta\Psi$ are defined as $\Delta_{\text{plasma on}} - \Delta_{\text{plasma off}}$ and $\Psi_{\text{plasma on}} - \Psi_{\text{plasma off}}$. The change in Ψ results from etching of part of the damaged layer on top of the surface by radicals in the afterglow. The change in Δ results from adsorption of (other) radicals in the afterglow.

Acknowledgments

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