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In situ ellipsometry during plasma etching of SiO₂ films on Si

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The etching of SiO₂ films on a Si substrate in an rf plasma in CF₄ has been studied with *in situ* ellipsometry. The etch rate was measured as a function of flow, rf power and pressure. An accurate analysis of the experimental data using numerical simulations based on multilayer models has yielded information both on the refractive index of the etched SiO₂ film and on the existence of a top layer. It could be established that a layer is present on top of the SiO₂ during etching, which is probably caused by roughening of the SiO₂ layer. Furthermore at high pressures (> 8 Pa) it was demonstrated that after the complete removal of the SiO₂ film a polymer layer starts growing on the Si substrate.

I. INTRODUCTION

Various methods are being used to determine the etch rate of plasma etching processes. They can be classified roughly into two groups: real time *in situ* methods which continuously monitor the effect of the plasma on the etching process and stylus methods where the effect of the plasma on the wafer is only observed after completion of the etching process. Within the first group, in addition to the use of an oscillating quartz crystal,^{1,2} several optical methods have been developed: determination of the change in reflected intensity of a laser beam that is diffracted at a lithographed grating on the wafer,^{3,4} reflectometry,^{5,6} and ellipsometry.⁶⁻¹⁰

Each method has its own major advantages and disadvantages, but only the *in situ* methods are capable of end point detection. The quartz crystal microbalance is very accurate, but is difficult to implement. The diffraction method is specifically suited for end point detection. Reflectometry is easy to implement but the refractive index of the material to be etched must be known to be able to use this method. Ellipsometry requires a computer system and special adaptations of the vacuum system to avoid unwanted contributions to the polarization of the light beam. Ellipsometry however is the only of the mentioned methods that yields accurate information on the layer thickness as well as on the refractive index of the material.¹¹ Therefore it is a good tool to study the physics of the etching process. In this paper we report the ellipsometric monitoring of etching of a 1.0- μ m-thick SiO₂ film on a silicon substrate. Not only the etch rate was measured, but also a layer on top of the SiO₂ was seen. This result was obtained using a simulation model of the ellipsometric effects of a number of layers on a substrate.

II. EXPERIMENT

The single-wafer plasma etch reactor used in this experiment is designed to carry one 2-inch wafer. The vacuum vessel has a height of 0.2 m and a diam of 0.5 m, and holds a number of ports and windows to allow the execution of various diagnostics,^{11,12} like e.g., mass spectroscopy, microwave spectroscopy, and ellipsometry. The pumping system consists of a Pfeiffer WKP 250 rootsblower combined with a Pfeiffer DUO 030 A primary pump. The absolute gas pres-

sure is measured with a MKS 370 HS-10 Baratron pressure gauge. The gas (CF₄) is fed through a Tylan FC 260 mass flow controller. The gas flow and the pressure can be varied independently by changing the pumping speed with a Balzers IB 063 throttle valve. The rf excitation voltage is provided by a combination of a Hewlett Packard 8116A function generator and a ENI 3100 LA rf power amplifier. The rf power is fed into the reactor through an inductively coupled matching network. One of the two parallel, cylindrically shaped electrodes is rf powered, the other one is electrically isolated from the vacuum system which is grounded, so its voltage can be controlled. The wafer can be mounted on either one of the electrodes. By selecting the appropriate conditions the reactor can operate in the plasma etching as well as in the reactive ion etching (RIE) mode. The wafers investigated in this study consist of a silicon (100) surface covered with an ~ 1.0 μ m thick layer of SiO₂ which was formed by thermal oxidation. Typical experimental conditions are given in Table I.

The rotating analyzer ellipsometer (RAE) used for the experiments described has the standard polarizer sample analyzer (PSA) configuration. This type of ellipsometer has been discussed extensively by Aspnes and Studna.¹³ The light source is a stabilized He-Ne laser¹⁴ which produces linearly polarized light. The beam is circularly polarized by a quarter wave plate (to have enough light intensity at all settings of the polarizer angle). After this the beam passes through a fixed polarizer. The now linearly polarized beam is incident on the sample at an angle of 69.8 deg. The angle of

TABLE I. Experimental conditions in the single-wafer etch reactor.

Gas used	CF ₄
Gas flow	0-50 sccm
Absolute pressure	1.5-20 Pa
rf power	5-30 W
Wafer diam	2 in.
Electrode diam	80 mm
Electrode spacing	20 mm
rf frequency	13.6 MHz

incidence was measured using a geometrical method. The reflected beam passes an analyzer which rotates with a frequency of 50 Hz and impinges on the detector, an EG&G SGD 100A pin diode. The detector signal is sampled by a 12 bits ADC which is triggered 128 times every revolution of the analyzer by pulses produced by an optical encoder mounted on the analyzer. The data thus produced are processed by a microcomputer system based on the Motorola M68000 microprocessor. With this setup it is possible to measure a value of Δ and ψ (see Analysis of Data) each second. The relative accuracy of Δ and ψ is then within 0.01 deg in the region where Δ is around 90 deg. A schematic view of the reactor is given in Fig. 1.

III. ANALYSIS OF DATA

If the complex ratio ρ of the reflection coefficients R_p and R_s of light polarized respectively parallel and perpendicular to the plane of incidence on the sample is expressed in the two real angles ψ and Δ by

$$\rho = R_p/R_s = \tan \psi \exp(i\Delta), \quad (1)$$

the intensity at the detector can be calculated to be

$$I(t) = g[a \cos 2A(t) + b \sin 2A(t) + 1], \quad (2)$$

where

$$a = \frac{\cos 2P - \cos 2\psi}{1 - \cos 2P \cos 2\psi}, \quad (3)$$

$$b = \frac{\sin 2\psi \cos \Delta \sin 2P}{1 - \cos 2P \cos 2\psi}, \quad (4)$$

$$g = F(R_s^2 + R_p^2)(1 - \cos 2P \cos 2\psi). \quad (5)$$

Here F represents the amplification of the system which does not depend on the sample, P is the polarizer angle and $A(t)$ the analyzer angle as a function of time. In our case the polarizer angle P is chosen to be 45 deg and the analyzer angle A is a linear function of time, so the coefficients a and b and the angles Δ and ψ can be obtained from Fourier analysis of the detector signal. The polarizer and analyzer angles were calibrated using the residue method.¹³ The birefringence of the vacuum windows was not measured but was accounted for in the data analysis.

FIG. 1. Experimental setup for the measurement of the etch rate using ellipsometry. A: rotating analyzer, C: $\lambda/4$ plate, C1, C2: matching capacitors, D: detector (Si photodiode), L: matching inductor, La: light source (He-Ne laser), M: hollow axis motor, MC: flow controller, P: polarizer, Pa: power amplifier, and Pu: pump flange.

Using the Fresnel equations,¹⁵ the relation between the ellipsometric angles Δ and ψ and the various experimental parameters can be calculated for a single gas-solid interface from

$$n_1 = n_0 \tan \varphi_0 \left(1 - \frac{4\rho}{(1+\rho)^2} \sin^2 \varphi_0 \right)^{1/2}, \quad (6)$$

where n_1 and n_0 are the complex refractive indices of the solid and the gas respectively, φ_0 is the angle of incidence and ρ is the complex number defined in Eq. (1). If the solid is covered by a thin film with refractive index n_2 and thickness d one obtains¹⁶

$$\rho = \frac{A + Bx + Cx^2}{D + Ex + Fx^2}, \quad (7)$$

$$\text{with } x = \exp \left[-4\pi i \left(\frac{d}{\lambda} \right) (n_2^2 - n_0^2 \sin^2 \varphi_0)^{1/2} \right]. \quad (8)$$

Here λ represents the wavelength of the incident light, and A , B , C , D , E , and F are functions of the Fresnel coefficients of the two interfaces (see Azzam and Bashara¹⁶). If the refractive indices and the layer thickness are known the complex number ρ can be calculated. If a second layer is placed on top of the first one, one first calculates ρ for the substrate and the first layer with Eqs. (7) and (8). Then the system of substrate and first layer is treated as a new semiinfinite substrate of which the effective refractive index can be evaluated from Eq. (6). Applying Eqs. (7) and (8) and using both the calculated effective refractive index and the parameters of the top layer the angles Δ and ψ for the complete system can be calculated. By repeating this procedure it is possible to calculate the ellipsometric parameters of a system with an arbitrary number of layers. If the refractive index is a continuous function of the distance from the substrate the system may be treated as a large number of very thin, but homogeneous films.¹⁷

The common way to represent ellipsometric data of an evolving system is to plot the measured points in the Δ - ψ plane. In our case this yields an egg shaped curve in the Δ - ψ plane. The shape of this curve gives information on the refractive index profile of the layer. An alternative way to represent the data is to plot the measured points in the a - b plane. With this representation the effect of several parameters (like the real and imaginary part of the refractive index of the SiO₂ layer, the thickness and refractive index of the top layer, and window errors) can be more or less distinguished. Therefore the values of these parameters can be estimated through use of a trial and error fitting procedure. Once the evolution of the refractive index profile is known the etch rate can be accurately deduced from the time dependence of Δ and ψ or a and b .

IV. Δ - ψ CURVES

In Fig. 2 and 3 typical examples of Δ - ψ curves are shown as they are measured during etching in the RIE mode (see Table I for experimental conditions). The contours have a good resemblance to the model contour obtained through use of a numerical simulation model that calculates the ellipsometric effects of a substrate with a homogeneous layer.

FIG. 2. Measured Δ - ψ contour, $p = 20$ Pa, flow = 20 std cm³/min (sccm), $P_{rf} = 31$ W. Each full revolution of the egg-shaped curve corresponds to an etched thickness of ~ 280 nm. At the end of the process (see insert) a deviation of the ideal curve is observed caused by deposition of a fluorocarbon layer.

The most important results of this simulation are listed in Table II.

In the case of a CF₄ plasma and pressures below 8 Pa, the curve stops at $\Delta = 180$, and $\psi = 12$ deg, showing that only a Si substrate remains, with possibly an undetectably thin fluorocarbon film on top of this.¹⁸ Since no change of Δ and ψ is observed after this, roughening of the Si surface does not occur significantly. Above 8 Pa, the curves do not reach the point where $\Delta \approx 180$ deg but inverse in direction and proceed in a different direction in the Δ - ψ plane. This indicates that a thick polymer layer with a refractive index of ~ 1.50 is deposited on the Si surface. The refractive index of this layer agrees fairly well with the value of 1.48 obtained by Oehrelein *et al.*¹⁰ The polymer composition will be probably Teflon-like, in correspondence with the results of Thomas *et al.*¹⁹ The position on the ellipsometric "egg" where the curve starts to deviate depends on the pressure. This behavior can be explained if we take into account that the SiO₂ layer is roughened during etching (see Sec. V). Therefore the thickness of the SiO₂ layer is not constant over the surface. Thus

FIG. 3. Measured Δ - ψ contour, $p = 5$ Pa, flow = 20 sccm, $P_{rf} = 31$ W. In this case the curve does not reverse direction after the endpoint (see insert). This indicates that no thick polymer film starts growing at lower pressures ($p < 8$ Pa).

TABLE II. Results of numerical simulation of the Δ - ψ curve described during RIE etching.

Total layer thickness	1 μ m
Etch rate	1.5 nm/s (at 8 Pa)
Refractive index Si	3.88-0.059i
Refractive index SiO ₂	1.45-0.001i
Thickness of polymer layer	15-20 nm (at 20 Pa)
Refractive index polymer layer	1.50
Thickness of top layer	20-25 nm (at all pressures)
Refractive index top layer	1.2

at the endpoint of the etching process some parts of the SiO₂ will already be etched completely, while other parts are still being etched. At higher pressures a fluorocarbon layer starts to deposit on the etched parts. Therefore the effective layer thickness will not reach zero at a high pressure. Since the ion bombardment is less effective²⁰ at higher pressures, the etch rate is decreased in this situation (see etch rates). Thus the point where the effective layer thickness starts to increase, causing the curve to reverse direction, gives information about the roughness of the SiO₂ layer during etching. Our measurements yielded a value of 15-20 nm for the highest pressure used.

V. *a-b* CURVES

Representation of the data in the *a-b* plane offers the possibility to obtain more information about the layer on top of the SiO₂. To study the ellipsometric effects due to this layer, we have used a model in which the layer is simulated by a thin homogeneous layer. Furthermore we have included a simulation of the birefringence of the vacuum windows, since this was not measured during the experiments (Fig 4). The effects of the top layer and windows in the *a-b* plane are shown in Fig. 5.

For the top layer two different refractive indices can make the simulations fit with the experimental data. The first one yields a refractive index of 1.2 and a thickness of ~ 250 Å. The second yields a refractive index of 2.0 with possibly a small imaginary part and a layer thickness of ~ 35 Å. The first possibility points to a SiO₂ layer with a roughened top layer of ~ 250 Å, which compares well with the value found from the endpoint behavior. The thickness of the top layer

FIG. 4. Simulation model used to calculate the ellipsometric effects of *a-b* layer on top of the SiO₂.

FIG. 5. Demonstration of the ellipsometric effects in the a - b plane of a top layer and a layer between SiO₂ and Si, and comparison with an observed a - b curve. The curves are offset for clarity. I: Observed curve ($p = 1.6$ Pa, flow = 20 sccm, $P_{rf} = 31$ W). II: Calculated curve without any transition layer. The slight loop in this curve is caused by the imaginary part of n_{Si} . III: Calculated curve with a window error in Δ of 1.0 deg. IV: Calculated curve with a window error in Δ of 1.0 deg and a layer between SiO₂ and the vacuum (200 Å, $n = 1.2$).

was almost constant during the etching process. This suggests that the morphology of the top layer is changed by the CF₄ plasma, as already known from transmission electron microscopy (TEM) and reflection high-energy electron dif-

FIG. 6. (a) Etch rate of SiO₂ in CF₄ as a function of pressure (flow = 20 sccm, rf power = 31 W). Also included is the electron density as a function of pressure. (b) Total flux of positive ions as a function of pressure, as measured by Bisschops (Ref. 20).

FIG. 7. (a) Etch rate of SiO₂ in CF₄ as a function of rf power ($p = 8$ Pa, flow = 20 sccm). (b) Total flux of positive ions as a function of RF power, as measured by Bisschops (Ref. 20).

fraction (RHEED) studies.^{21,22} Small amounts of electrode material which are sputtered by the ion bombardment may well be responsible for this.^{23,24} The second possibility suggests that a thin fluorocarbon layer with a large carbon-to-fluorine ratio (comparable to layers found on Si^{18,25}) and therefore a high refractive index is present on top of the SiO₂ during etching. The thickness is much higher than the one

FIG. 8. Etch rate of SiO₂ in CF₄ as a function of flow ($p = 8$ Pa, rf power = 31 W).

found by Oehrlein *et al.*¹⁸ who used x-ray photoelectron spectroscopy (XPS) after partly etching of SiO₂ in a CF₄/40% H₂ plasma. The second model is therefore not very likely.

VI. ETCH RATES

The etch rate has been determined as a function of gas pressure, flow, and rf power (Figs. 6(a)–8) and appears to be at best 1.5 nm/s, which is a standard value for the type of reactor used. Also included are values of the average electron density, as measured with microwave techniques in the same reactor.²⁰ The results indicate that the etch rate increases as a function of flow and rf-power, and decreases as a function of pressure above 8 Pa. These results can be related to the total flux of positive ions. The ion flux bombarding the grounded electrode has been measured by Bisschops,²⁰ discriminated on both mass and energy of the ions. Results of these measurements are given in Figs. 6(b)–7(b).

If the trends of the ion flux on the grounded electrode as a function of pressure and rf power are compared with the etch rates, we can see that a strong correlation exists between the two. At low power levels, the etch rate and the ion flux decrease dramatically. The increase in the etch rate with flow may be caused by a decreasing recombination of positive and negative ions. To study this, densities of negative ions as a function of flow are needed. An attempt to determine these densities will be carried out in future.

VII. CONCLUSIONS

It has been shown that *in situ* ellipsometry can provide for an excellent monitor of the etching process during single wafer etching of an SiO₂ film on a Si substrate. Not only an accurate determination of the etch rate is possible but also the refractive index of the SiO₂ film and thickness of a top layer or an emerging polymer layer can be obtained. The top layer is caused by roughening of the SiO₂ layer and its thickness is estimated to be 200 Å. Under the conditions used in this study, the etch rate is found to be at best 1.5 Å/s, which is a typical value for these conditions. The refractive index of the SiO₂ film was 1.45, and was constant over the entire depth. The imaginary part of the refractive index of the SiO₂ layer was $\sim 10^{-3}$. The strong correlation between the etch rate and the total ion flux as a function of pressure, and rf

power indicates once more that positive ions play an important role in the etch reaction.

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