Study of the SiO_2-to-Si_3N_4 etch selectivity mechanism in inductively coupled fluorocarbon plasmas and a comparison with the SiO_2-to-Si mechanism

M. Schaepkens, T. E. F. M. Standaert, N. R. Rueger, P. G. M. Sebel,[a] and G. S. Oehrlein[b]
Department of Physics, University at Albany, State University of New York, Albany, New York 12222

J. M. Cook
Lam Research Corporation, Fremont, California 94538-6470

(Received 21 July 1998; accepted 2 October 1998)

The mechanisms underlying selective etching of a SiO_2 layer over a Si or Si_3N_4 underlayer, a process of vital importance to modern integrated circuit fabrication technology, has been studied. Selective etching of SiO_2-to-Si_3N_4 in various inductively coupled fluorocarbon plasmas (CHF_3, C_2F_6/C_3F_6, and C_3F_6/H_2) was performed, and the results compared to selective SiO_2-to-Si etching. A fluorocarbon film is present on the surfaces of all investigated substrate materials during steady state etching conditions. A general trend is that the substrate etch rate is inversely proportional to the thickness of this fluorocarbon film. Oxide substrates are covered with a thin fluorocarbon film (<1.5 nm) during steady-state etching and at sufficiently high self-bias voltages, the oxide etch rates are found to be roughly independent of the feedgas chemistry. The fluorocarbon film thicknesses on silicon, on the other hand, are strongly dependent on the feedgas chemistry and range from ~2 to ~7 nm in the investigated process regime. The fluorocarbon film thickness on nitride is found to be intermediate between the oxide and silicon cases. The fluorocarbon film thicknesses on nitride range from ~1 to ~4 nm and the etch rates appear to be dependent on the feedgas chemistry only for specific conditions. The differences in etching behavior of SiO_2, Si_3N_4, and Si are suggested to be related to a substrate-specific ability to consume carbon during etching reactions. Carbon consumption affects the balance between fluorocarbon deposition and fluorocarbon etching, which controls the fluorocarbon steady-state thickness and ultimately the substrate etching. © *1999 American Vacuum Society.* [S0734-2101(99)03201-7]

I. INTRODUCTION

Etching of via or contact holes into SiO_2 to make electrical contact with an underlayer is an indispensable process in modern integrated circuit fabrication technology. High SiO_2 etch rate and selectivity of SiO_2-to-Si are important requirements for etch processes to be commercially viable in manufacturing. Etch processes employing fluorocarbon discharges are typically able to meet these demands, as first reported by Heinecke[1] and an extensive number of subsequent studies.[2–12]

It is believed that the primary mechanism for highly selective SiO_2-to-Si etching using fluorocarbon plasmas is the selective formation of a relatively thick passivating film on the Si surface during steady-state etching conditions. The Si etch rate in that situation is limited by the arrival of atomic fluorine that needs to diffuse through the film to the Si surface, where it chemically reacts.[13–16] For the same process conditions SiO_2 surfaces stay clean of fluorocarbon material, and are etched directly through a mechanism of chemical sputtering.[6,17,18]

The ability to achieve selective etching of SiO_2 over Si_3N_4 is becoming an increasingly important requirement. Silicon nitride is used as a passivating layer that protects circuits from mechanical and chemical attack, or as an etch stop layer, enabling the fabrication of certain damascene and self-aligned contact (SAC) structures. Selective SiO_2-to-Si_3N_4 etching has been demonstrated in several systems.[19–24] Correlations between the Si_3N_4 etch rate and the amount of fluorocarbon material present on the surface during etching suggest a SiO_2-to-Si_3N_4 selectivity mechanism that is analogous to the SiO_2-to-Si etching mechanism. A detailed comparison between the two mechanisms, however, is lacking.

This work summarizes results obtained in a study where SiO_2, Si_3N_4 and Si were processed in an inductively coupled plasma source fed with various fluorocarbon feedgas chemistries (CHF_3, C_2F_6/C_3F_6 and C_3F_6/H_2). Etch rates of SiO_2, Si_3N_4, and poly-Si samples and surface modifications of crystalline Si samples were measured using *in situ* ellipsometry. The surface chemistry of processed SiO_2 and Si_3N_4 samples was examined using postplasma *in situ* x-ray photoelectron spectroscopy (XPS). The experimental results allow a direct comparison of SiO_2, Si_3N_4, and Si etch mechanisms and therefore a comparison of the SiO_2-to-Si_3N_4 and SiO_2-to-Si etch sele[...] son it can be underst[...] give SiO_2-to-Si sele[...]

[a]On leave from Eindhoven University of Technology.

IP Bridge Exhibit 2226
TSMC v. Godo Kaisha IP Bridge 1
IPR2017-01843

DOCKET ALARM
Find authenticated court documents without watermarks at docketalarm.com.

Study of the SiO_2-to-Si_3N_4 etch selectivity mechanism in inductively coupled fluorocarbon plasmas and a comparison with the SiO_2-to-Si mechanism

M. Schaepkens, T. E. F. M. Standaert, N. R. Rueger, P. G. M. Sebel,[a)]
and G. S. Oehrlein[b)]
Department of Physics, University at Albany, State University of New York, Albany, New York 12222

J. M. Cook
Lam Research Corporation, Fremont, California 94538-6470

(Received 21 July 1998; accepted 2 October 1998)

The mechanisms underlying selective etching of a SiO_2 layer over a Si or Si_3N_4 underlayer, a process of vital importance to modern integrated circuit fabrication technology, has been studied. Selective etching of SiO_2-to-Si_3N_4 in various inductively coupled fluorocarbon plasmas (CHF_3, C_2F_6/C_3F_6, and C_3F_6/H_2) was performed, and the results compared to selective SiO_2-to-Si etching. A fluorocarbon film is present on the surfaces of all investigated substrate materials during steady state etching conditions. A general trend is that the substrate etch rate is inversely proportional to the thickness of this fluorocarbon film. Oxide substrates are covered with a thin fluorocarbon film ($<$1.5 nm) during steady-state etching and at sufficiently high self-bias voltages, the oxide etch rates are found to be roughly independent of the feedgas chemistry. The fluorocarbon film thicknesses on silicon, on the other hand, are strongly dependent on the feedgas chemistry and range from $\sim$2 to $\sim$7 nm in the investigated process regime. The fluorocarbon film thickness on nitride is found to be intermediate between the oxide and silicon cases. The fluorocarbon film thicknesses on nitride range from $\sim$1 to $\sim$4 nm and the etch rates appear to be dependent on the feedgas chemistry only for specific conditions. The differences in etching behavior of SiO_2, Si_3N_4, and Si are suggested to be related to a substrate-specific ability to consume carbon during etching reactions. Carbon consumption affects the balance between fluorocarbon deposition and fluorocarbon etching, which controls the fluorocarbon steady-state thickness and ultimately the substrate etching. © *1999 American Vacuum Society.* [S0734-2101(99)03201-7]

I. INTRODUCTION

Etching of via or contact holes into SiO_2 to make electrical contact with an underlayer is an indispensable process in modern integrated circuit fabrication technology. High SiO_2 etch rate and selectivity of SiO_2-to-Si are important requirements for etch processes to be commercially viable in manufacturing. Etch processes employing fluorocarbon discharges are typically able to meet these demands, as first reported by Heinecke[1] and an extensive number of subsequent studies.[2–12]

It is believed that the primary mechanism for highly selective SiO_2-to-Si etching using fluorocarbon plasmas is the selective formation of a relatively thick passivating film on the Si surface during steady-state etching conditions. The Si etch rate in that situation is limited by the arrival of atomic fluorine that needs to diffuse through the film to the Si surface, where it chemically reacts.[13–16] For the same process conditions SiO_2 surfaces stay clean of fluorocarbon material, and are etched directly through a mechanism of chemical sputtering.[6,17,18]

The ability to achieve selective etching of SiO_2 over Si_3N_4 is becoming an increasingly important requirement. Silicon nitride is used as a passivating layer that protects circuits from mechanical and chemical attack, or as an etch stop layer, enabling the fabrication of certain damascene and self-aligned contact (SAC) structures. Selective SiO_2-to-Si_3N_4 etching has been demonstrated in several systems.[19–24] Correlations between the Si_3N_4 etch rate and the amount of fluorocarbon material present on the surface during etching suggest a SiO_2-to-Si_3N_4 selectivity mechanism that is analogous to the SiO_2-to-Si etching mechanism. A detailed comparison between the two mechanisms, however, is lacking.

This work summarizes results obtained in a study where SiO_2, Si_3N_4 and Si were processed in an inductively coupled plasma source fed with various fluorocarbon feedgas chemistries (CHF_3, C_2F_6/C_3F_6 and C_3F_6/H_2). Etch rates of SiO_2, Si_3N_4, and poly-Si samples and surface modifications of crystalline Si samples were measured using *in situ* ellipsometry. The surface chemistry of processed SiO_2 and Si_3N_4 samples was examined using postplasma *in situ* x-ray photoelectron spectroscopy (XPS). The experimental results allow a direct comparison of SiO_2, Si_3N_4, and Si etch mechanisms and therefore a comparison of the SiO_2-to-Si_3N_4 and SiO_2-to-Si etch selectivity mechanisms. From this comparison it can be understood why certain feedgas chemistries that give SiO_2-to-Si selectivity do not necessarily give SiO_2-to-Si_3N_4 selectivity. However, it has been found that SiO_2-to-

[a)]On leave from Eindhoven University of Technology.
[b)]Electronic mail: oehrlein@csc.albany.edu

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

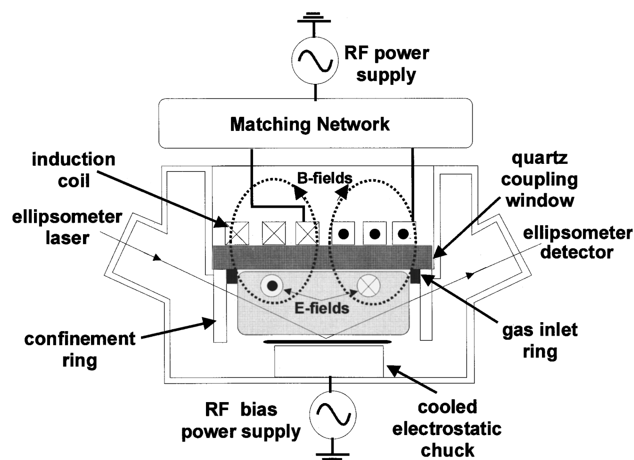

FIG. 1. Schematic outline of the experimental setup of the used ICP source.

Si_3N_4 selectivity in an etching process also provides SiO_2-to-Si selectivity. More importantly, a trend in the etch rate behavior of the different materials has been identified allowing a general description of fluorocarbon plasma etching to be formulated.

II. EXPERIMENTAL SETUP

The high-density plasma source used in this work is a radio-frequency inductively coupled plasma (ICP) source of planar coil design. This plasma source has also been referred to in the literature as transformer coupled plasma (TCP)[25] and radio frequency induction (RFI)[26] source. A schematic outline of the used ICP reactor is shown in Fig. 1. It is similar to the one described by Keller *et al.*[27]

The apparatus consists of an ultrahigh vacuum (UHV) compatible processing chamber in which the plasma source and a wafer holding electrostatic chuck are located. The center part of the ICP source is a planar, 160-mm-diam induction coil that is separated from the process chamber by a 19.6-mm-thick, 230-mm-diam quartz window. The coil is powered through a matching network by a 13.56 MHz, 0–2000 W power supply.

Wafers with a diameter of 125 mm can be placed on a bipolar electrostatic chuck during processing. The chuck is located at a distance of 7 cm downstream from the ICP source and allows the wafer to be rf biased and cooled during processing. A helium pressure of 5 Torr is applied to the backside of the wafer during the experiment to achieve good thermal conduction between the wafer and the chuck.[28] The chuck is cooled by circulation of a cooling liquid.

Samples placed at the center of a wafer can be monitored by an *in situ* He–Ne (632.8 nm) rotating compensator ellipsometer (RCE) in a polarizer-compensator-sample-analyzer (PCSA) configuration. Plasma diagnostics like a retractable Langmuir probe and optical emission spectroscopy (OES) can be used for plasma gas-phase characterization. With the retractable Langmuir probe it is possible to make a scan of the ion current density over 70% of the wafer at a distance of 2 cm above the wafer surface.

A variable frequency rf power supply (500 kHz–40 MHz, 0–300 W) is used to bias the wafer for etching experiments. The experiments reported in this work were all performed at 3.4 MHz. In the process regime investigated, no significant influence of rf biasing on the ion current density measured with the Langmuir probe was observed. The ion energy and the ion flux to the surfaces can thus be varied independently.

The process chamber is pumped using a 450 l/s turbomolecular pump backed by a roughing pumpstack, consisting of a roots blower and a mechanical pump. The process gases are admitted into the reactor through a gas inlet ring located just under the quartz window. The pressure is measured with a capacitance manometer. Pressure control is achieved by an automatic throttle valve in the pump line.

In order to remove deposited fluorocarbon films from the walls of the process chamber, the chamber is cleaned with an O_2 plasma after each experiment. The cleaning process is monitored by taking real time OES data. The absence of optical emission of fluorocarbon related gas phase species is a measure for the cleanliness of the chamber.

The ICP apparatus is connected to a wafer handling cluster system. Processed samples were transported under UHV conditions to a Vacuum Generators ESCA Mk II surface analysis chamber for x-ray photoelectron spectroscopy (XPS) analysis using a polychromatic Mg $K\alpha$ x-ray source (1253.6 eV). Photoelectron spectra were obtained at photoemission angles of 90° and 15° with respect to the sample surface.

III. EXPERIMENTAL RESULTS

A. Fluorocarbon deposition and etch rates

In fluorocarbon plasma processing, deposition and etching occur simultaneously. Deposition and etching processes have different dependencies on the energy of the ions that bombard the surface on which they occur. By varying the ion bombardment energy one can therefore switch from fluorocarbon deposition to etching of earlier deposited fluorocarbon material or other substrate materials, such as SiO_2, Si_3N_4, or Si.

At low self-bias voltages, i.e., low ion bombardment energy, these processes produce net fluorocarbon deposition. The deposition characteristics are strongly dependent on the feedgas chemistry. Figure 2(a) shows the fluorocarbon deposition rates obtained as a function of feedgas (CHF_3, C_2F_6, C_3F_6, and C_3F_6/H_2) in discharges at 6 mTorr operating pressure, 1400 W inductive power, and no rf bias power applied to the surface. The deposition rate in CHF_3 and C_2F_6 is significantly lower than in C_3F_6 or C_3F_6/H_2. The highly polymerizing character of C_3F_6 or C_3F_6/H_2 discharges may be related to the size and chemical structure of the fluorocarbon parent molecules.[2,24]

Figure 2(b) shows the refractive index of the deposited fluorocarbon films using the different gases. The refractive index of the fluorocarbon deposited using C_2F_6 and C_3F_6 are found to be lower than if CHF_3 or C_3F_6/H_2 is used. Crystalline Si samples on which 150 nm fluorocarbon material was deposited were analyzed by XPS. It was found that the

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

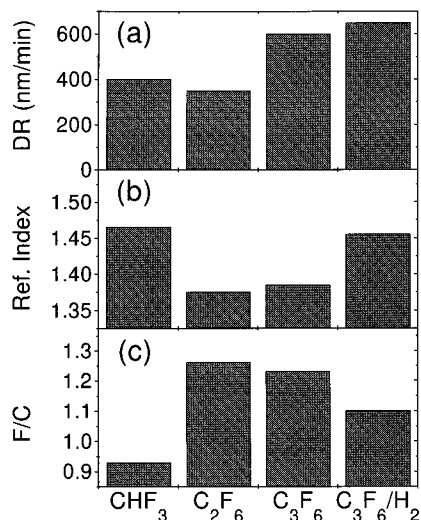

FIG. 2. (a) Deposition rates, (b) refractive index, and (c) fluorine-to-carbon ratio determined from XPS analysis of fluorocarbon material deposited at 6 mTorr operating pressure in discharges fed with 40 sccm of CHF_3, C_2F_6, C_3F_6, or C_3F_6/H_2 (27%). The fluorine-to-carbon ratios determined under 15° electron escape angle are slightly higher than the ratio determined under 90°. The values in (c) are averages of the two values.

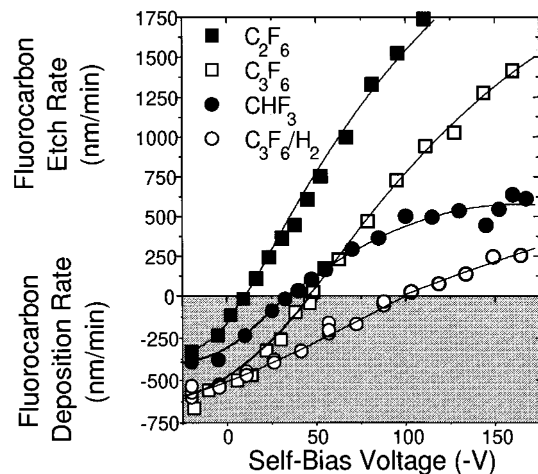

FIG. 3. Fluorocarbon etch rates as a function of self-bias voltage, measured with respect to ground, at 6 mTorr operating pressure in discharges fed with 40 sccm of CHF_3, C_2F_6, C_3F_6, or C_3F_6/H_2 (27%). The fluorocarbon substrate was deposited at 0 W rf bias power at the same process condition where the etch rates were determined. The plasma potential at these conditions typically varies between 20 and 30 V. This potential needs to be added to the self-bias voltage in order to estimate the actual average ion bombardment energy.

fluorine-to-carbon ratio of the fluorocarbon material, see Fig. 2(c), is inversely proportional to the refractive index. Further, the fluorine-to-carbon ratio of the deposited fluorocarbon material is lower if hydrogen is present in the feedgas chemistry. This trend can be explained by the fluorine scavenging effect of hydrogen in the gas phase,[2] or more likely at these operating pressures fluorine reduction as a result of hydrogen–fluorine recombination at the reactor walls. Also, fluorine abstraction by hydrogen from a fluorocarbon surface could explain the observations.[29]

The fluorocarbon films that deposit if no bias is applied to the substrate, can be etched off the thin film substrate at self-bias voltages above a certain threshold value. The etch rates of the fluorocarbon films deposited at unbiased conditions have been measured as a function of self-bias voltage by *in situ* ellipsometry in discharges of CHF_3, C_2F_6, C_3F_6, and C_3F_6/H_2 at 6 mTorr operating pressure and 1400 W inductive power. The fluorocarbon etch rates are plotted as positive values in Fig. 3. Also included in Fig. 3 are the fluorocarbon deposition rates (negative values) measured by *in situ* ellipsometry at self-bias voltages below the threshold for etching. It shows that the fluorocarbon deposition rate decreases as the self-bias voltage increases.

The fluorocarbon etch rates are found to be strongly dependent on the feedgas chemistry. First, the fluorocarbon etch rate is relatively low at conditions where hydrogen is present in the feedgas mixture, e.g., compare CHF_3 to C_2F_6 processing and C_3F_6 to C_3F_6/H_2 processing. This observation can be attributed to the fact that fluorine is a precursor for etching of fluorocarbon material.[3] The presence of hydrogen in the feedgas chemistry namely results in (a) a reduction of fluorine in the plasma gas phase (observed when comparing optical emission spectra from 40 sccm CF_4 and 40 sccm CHF_3 plasmas at identical conditions), and (b) a more fluorine depleted fluorocarbon substrate (the fluorine-to-carbon ratio of fluorocarbon is reduced, see Fig. 2). A second observation is that the higher the fluorocarbon deposition rate at 0 W bias power, the lower the fluorocarbon etch rate under biased conditions, e.g., compare C_2F_6 to C_3F_6 processing and CHF_3 to C_3F_6/H_2 processing. Net fluorocarbon etching apparently benefits from a reduction in fluorocarbon deposition.

The position of the threshold voltage for net etching is consistent with the above observations. If hydrogen is present in the feedgas chemistry or if the fluorocarbon deposition rate at 0 W bias power is high, the threshold voltage is relatively high, and vice versa.

B. SiO_2, Si_3N_4, and Si etch rates

At conditions where net fluorocarbon etching takes place, other substrate materials, such as SiO_2, Si_3N_4, and Si, can also be etched. Figure 4 shows the SiO_2, Si_3N_4, and Si etch rates measured on blanket samples by *in situ* ellipsometry as a function of self-bias voltage in discharges of CHF_3, C_2F_6, C_3F_6, and C_3F_6/H_2 at 6 mTorr operating pressure and 1400 W inductive power.

At sufficiently high self-bias voltage, SiO_2 etching of the blanket samples occurs at a relatively high rate, which is roughly independent of the feedgas chemistry. This is consistent with Langmuir probe measurements performed for the different discharges. The Langmuir probe data showed that the ion current density does not vary significantly with feedgas chemistry. Since SiO_2 etching has been suggested to occur through a chemical sputtering mechanism in which the ion flux is the limiting factor,[18] the SiO_2 etch rate is expected to be relatively independent of the feedgas chemistry. (Note: this is the case if the average composition of the fluorocar-

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

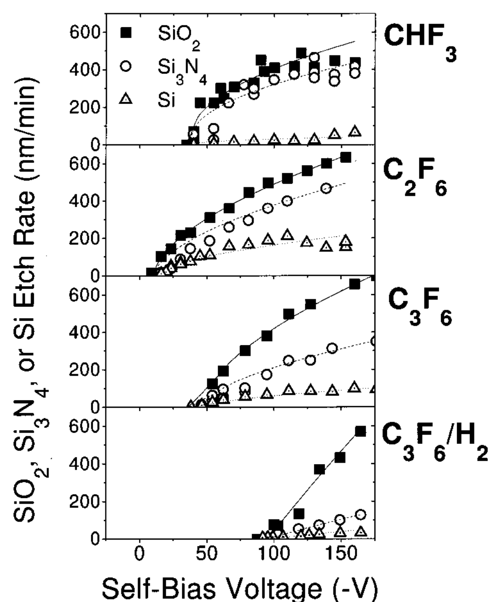

FIG. 4. Etch rates of SiO_2, Si_3N_4, and Si substrates as a function of self-bias voltage at 6 mTorr operating pressure in discharges fed with 40 sccm of CHF_3, C_2F_6, C_3F_6, or C_3F_6/H_2 (27%).

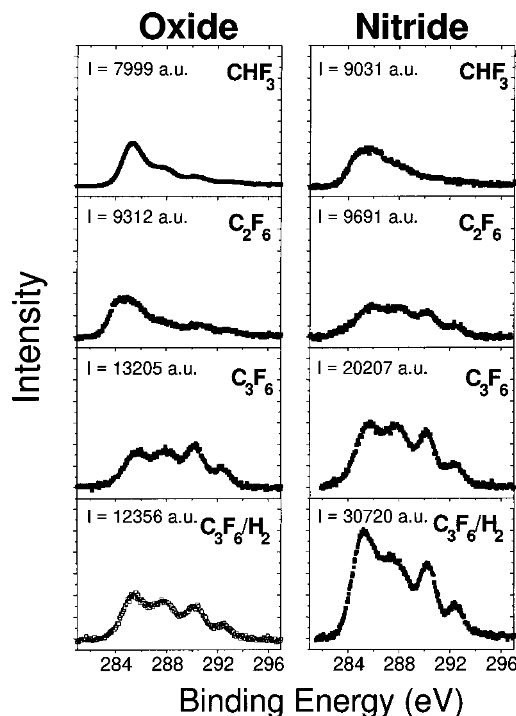

FIG. 5. C(1*s*) spectra obtained by XPS surface analysis under 90° emission angle on SiO_2 and Si_3N_4 samples processed in CHF_3 (40 sccm), C_2F_6 (40 sccm), C_3F_6 (40 sccm), and C_3F_6/H_2 (20 sccm/15 sccm) discharges at 6 mTorr and a self-bias voltage of −100 V. The C (1*s*) intensity is a measure for the amount of fluorocarbon material present on the surfaces during steady-state etching conditions.

bon ion flux that bombards the SiO_2 surface does not change significantly with the various conditions. If the average composition of the ion flux changes, e.g., from CF_2^+ to CF^+, the average SiO_2 sputter yield possibly changes as well.)

The blanket Si etch rates for the above conditions are significantly lower than the SiO_2 etch rates. The etch rates of silicon show a strong dependence on feedgas chemistry. The dependence is similar to that observed for fluorocarbon etching, suggesting that the effects due to hydrogen addition and fluorocarbon deposition rate ultimately are also responsible for the etch rate behavior of Si.

Etching of Si_3N_4 is intermediate between SiO_2 and Si, both in etch rate and dependence on the feedgas chemistry. For chemistries that result in a low fluorocarbon deposition rate, the Si_3N_4 etch rate is relatively independent of the feedgas, similar to SiO_2 etching. For chemistries resulting in a high fluorocarbon deposition rate, the Si_3N_4 etch rate dependence is similar to that observed for Si and fluorocarbon etching. In other words, hydrogen addition only helps to suppress Si_3N_4 etching at conditions where the fluorocarbon deposition rate is sufficiently high.

C. Surface analysis: Steady-state fluorocarbon films

The surface chemistry of processed SiO_2 and Si_3N_4 samples was investigated by XPS as a function feedgas chemistry in discharges at 6 and 20 mTorr operating pressure. The feedgas chemistries used were CHF_3, C_2F_6, C_3F_6, and mixtures of C_2F_6/C_3F_6 and C_3F_6/H_2. At the same conditions the surface modifications of crystalline Si samples were measured by *in situ* ellipsometry.[30]

Figure 5 shows high-resolution C (1*s*) photoemission spectra obtained from SiO_2 and Si_3N_4 surfaces etched at −100 V self-bias voltage at 6 mTorr operating pressure in discharges fed with CHF_3, C_2F_6, C_3F_6, and C_3F_6 /H_2. The binding energies were corrected for charging of the dielectric substrate materials. The integrated intensity of the C (1*s*) spectrum, plotted in the upper left corner of each graph in Fig. 5, is a measure for the amount of fluorocarbon material present on the sample surface. It shows that the C (1*s*) intensity from processed SiO_2 surfaces is typically lower than the intensities measured on Si_3N_4 samples processed under the same process conditions, and compared to processed Si_3N_4 samples relatively independent of the feedgas chemistry. The intensity of the C (1*s*) spectrum from processed Si_3N_4 depends significantly on the feedgas chemistry. It clearly shows that the amount of fluorocarbon material on the Si_3N_4 surface shown in Fig. 5, is inversely proportional to the corresponding etch rate at −100 V self-bias from Fig. 4.

The C (1*s*) intensity measured on the processed surfaces can be expressed as a fluorocarbon film thickness. This thickness can be calculated from photoemission intensities, due to the exponential decay of the XPS signal with depth. A method that uses angular resolved intensities from substrate elements is described by Rueger *et al.*[18] Standaert *et al.*[16] describe a method of quantifying the fluorocarbon film thickness by comparing the C (1*s*) intensity from a processed sample to the C (1*s*) intensity of a semi-infinitely thick fluorocarbon film (e.g., a fluorocarbon film deposited at 0 W). A comparison of the two methods showed that at low C (1*s*) intensities, both methods give very similar values for the fluorocarbon thickness. At high C (1*s*) intensities, slightly

DOCKET ALARM Find authenticated court documents without watermarks at docketalarm.com.

DOCKET ALARM

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts

Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research

With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips

Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.

WHAT WILL YOU BUILD? | sales@docketalarm.com | 1-866-77-FASTCASE

fastcase® Smarter legal research.