SIGNIFICANCE OF THE O TO F ATOMIC CONCENTRATION RATIO IN RF PLASMAS FOR ETCHING ORGANIC MATERIALS

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ABSTRACT

Plasma etch rate behavior of polymers is compared with data from optical emission spectroscopy and XPS. For a given [O] in the plasma, there is an optimum [O]/[F] required to achieve a maximum etch rate for a given polymer. Rate behavior with variations in gas composition (using CF₄ or SF₆ in O₂), rf power and load size is explained based on deviations from this optimum [O]/[F].

1. INTRODUCTION

In plasmas generated from mixtures of O₂ and a fluorine-containing gas, the primary etch species for organic materials appear to be atomic oxygen and atomic fluorine [1-4]. Fluorine atoms in small concentrations enhance etch rates through reactions at the surface which can weaken or break existing bonds. Fluorine present in excess, however, inhibits etching through competition with O atoms for sites, leading to the formation of fluorocarbon compounds on the surface [5,6,7]. Hence, for a given amount of atomic oxygen in the plasma, there is an optimum amount of atomic fluorine required to achieve a maximum etch rate [7].

2. EXPERIMENTAL

Complete descriptions of the etching system, optical emission equipment, X-ray photoelectron spectroscopy (XPS) instrumentation and experimental techniques used are given in references 4 and 7. The planar diode etching system is shown schematically in Figure 1. Polymer films on 82 mm diameter silicon wafers were prepared by applying either spin or spray coatings and curing at appropriate temperatures. Samples to be etched were placed on the RF cathode which has a diameter of 29.2 centimeters. When elimination of the effects of energetic ions was desired, samples were separated from the plasma using a quartz plate placed above the wafer and within the sheath at the cathode (as discussed in reference 4). Feed gas composition and surface area of etchable material were varied while total gas flow rate was fixed at 70 SCCM; chamber pressure and rf power were fixed at 350 mTorr and 300 Watts, respectively. When variations in rf power were made, 30% CF₄ in O₂ at 70 SCCM total gas flow rate and
350 mTorr chamber pressure were used. Intensities of emission spectral
lines of neutral atomic oxygen (0I 845 nm) and neutral atomic fluorine (FI
704 nm) were monitored. A small amount of argon was added as an
actinometer [8], using ArI 750 nm. Polymer etch rates were measured using
a laser interferometer.

3. RESULTS AND DISCUSSION

Etch rate behavior of polyimide and the intensities of emission spectral
lines of atomic oxygen and atomic fluorine are shown in Figure 2a for
various concentrations of CF₄ in O₂. It is clear that the etch rate
behavior of polyimide is not solely a function of the concentrations of
atomic oxygen or atomic fluorine in the plasma [4,9]. In fact, for a
given amount of atomic oxygen, a local maximum in etch rates is achieved
at a specific ratio of concentrations of atomic oxygen and fluorine,
measured experimentally as (0I 845 nm)/(FI 704 nm). This ratio is related
to the O to F atomic concentration ratio. The relationship between these
two ratios is not simple. However, the ArI 750 nm line can be used in
actinometry with both 0I 845 nm [10] and FI 704 nm [8]. At values of
[O]/[F] greater than the optimum for a given material, fluorine enhances
etching; at lower values, the excess fluorine inhibits etching.

Preferentially removing fluorine from the plasma results in a shift of the
maximum etch rate toward higher concentrations of CF₄. This has been
demonstrated by positioning uncoated silicon wafers adjacent to a
polyimide coated wafer during etching. The etching of silicon results in
a discriminate consumption of atomic fluorine. The resulting shift is
shown in Figure 2b, curves 1 and 2.

Curve 3 of Figure 2b plots the polyimide etch rate as a function of SF₆
concentration in O₂. Although the three maxima of Figure 2b occur at
different gas compositions, each occurs at roughly the same ratio of
concentrations, [O]/[F], as indicated in Figure 3.

Figure 4a shows the etch rate of polyimide as a function of rf power.
Etching was done using the quartz shield described above to eliminate the
effect of energetic ions. The etch rate decreases for increasing power
levels between 100 watts and 250 Watts, an intuitively unexpected result
(a similar finding is reported in reference 9). However, as the rf power
is varied, the number densities of atomic oxygen and atomic fluorine
change at different rates. The ratio 0I/FI is plotted in Figure 4b. The
dashed line represents the value of 0I/FI for which maximum etch rates are
achieved, obtained from gas composition data. Clearly, as 0I/FI
approaches the optimum value, etch rates increase. As the deviation from
the optimum value 0I/FI increases, etch rates decrease.

The [O]/[F] ratio at which maximum etch rates are achieved is,
understandably, a function of the material being etched. Figure 5a
comparing the etch rate behavior of polyimide and an oxirane-based
copolymer in O₂–CF₄ plasmas. Figure 5b shows the same data plotted as a
function of the ratio 0I/FI. Apparently, relatively more fluorine is
required to attain optimum etching conditions for the oxirane-based
copolymer. Abstraction of hydrogen has been proposed as a means by which
atomic fluorine can enhance organic etch rates [2]. The oxirane-based
copolymer used in this experiment has a H:C ratio which is about twice
that of the polyimide. One might anticipate, therefore, that a higher
concentration of CF₄ (more fluorine) would be required to achieve the maximum etch rate. The fluorine content on polyimide surfaces treated in plasmas of O₂–CF₄ and O₂–SF₆ and the surface of the oxirane-based copolymer treated in a plasma of O₂–CF₄ are compared in Figure 6. For polyimide, about 10% surface coverage by fluorine exists under conditions for which maximum etch rates are achieved (22.5% CF₄ or 5% SF₆ in O₂) while about twice the fluorine surface coverage is present on the oxirane-based copolymer after exposure to a plasma at 35% CF₄ in O₂, where maximum etch rate is achieved.

Figure 7 shows how the ratio [O]/[F] changes during the etching of the oxirane-based copolymer. It appears that the etching process drives the ratio [O]/[F] toward the fluorine-deficient regime. Etching more of this polymer will result in larger changes. The etch rates for various surface areas exposed to the plasma are plotted in Figure 8a. As expected, as the surface area is increased, more CF₄ must be added to O₂ to achieve the maximum etch rate. When plotted as a function of O₁/F₁ obtained during etching, the maxima become aligned at the same value. Furthermore, it seems that an "inverse loading" effect appears at the higher concentrations of CF₄ in Figure 8a. For example, at 50% CF₄ in O₂, a load of 160 square centimeters etches at a greater rate than a load of 53 square centimeters. When viewed with respect to the ratio of [O]/[F] as in Figure 8b, this seemingly anomalous effect is no longer present. An inverse relationship between load size and etch rate for kapton was also reported in reference 3.

4. CONCLUSIONS

It has been observed that the etch rate of organic polymers in gas plasmas containing oxygen and fluorine depends on the ratio of their emission intensities, O₁ 845 nm, and F₁ 704 nm, a quantity related to the O to F atomic concentration ratio. The [O]/[F] ratio at which maximum etch rates are achieved is, understandably, a function of the polymer being etched. This ratio has been shown to be lower for an oxirane-based copolymer than for polyimide, the latter containing half as much hydrogen per carbon atom in the untreated film. These results are consistent with XPS analyses of plasma-treated surfaces. Seemingly anomalous etch rate behavior with respect to variations in rf power and load size can be explained based on deviations from the optimum value of [O]/[F].

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REFERENCES


Figure 1. Schematic diagram of planar diode etching system.

Figure 2a. Intensities of emission spectral lines of OI 845 nm and FI 704 nm (nonetching) compared with the etch rate of polyimide for various concentrations of CF₄ in O₂.

Figure 2b. Polyimide etch rate behavior with and without silicon loading for O₂-CF₄ plasmas and without silicon loading for O₂-SF₆ plasmas.

Figure 3. Etch rate data of Figure 2a plotted as a function of OI/FI obtained during polyimide etching.

Figure 4a. Polyimide etch rate vs. rf power.

Figure 4b. OI/FI vs. rf power.
Figure 5a. Comparison of the etch rate behavior of polyimide and an oxirane-based copolymer in O₂-CF₄ plasmas.

Figure 5b. Etch rate data of Figure 5a plotted as a function of OI/FI obtained during etching.

Figure 6. Comparison of fluorine content on O₂-CF₄ and O₂-SF₆ plasma treated surfaces of polyimide and O₂-CF₄ plasma treated surfaces of an oxirane-based copolymer.

Figure 7. Comparison of OI/FI with and without the etching of polymer films.

Figure 8a. Etch rate as a function of gas feed composition for varying amounts of exposed surface area of etchable material.

Figure 8b. Etch rate data of Figure 8a plotted as a function of OI/FI measured during etching.