MATRIX ISOLATION AND CHARACTERIZATION
OF
PLASMA ETCHING INTERMEDIATES

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ABSTRACT

Silicon and SiO₂ surfaces have been etched in low pressure RF and microwave-excited plasmas containing fluorocarbon etchants. The dominant plasma species were trapped in solid argon matrices at 10⁰K for subsequent spectroscopic examination. A separate series of windowless VUV-photolysis experiments had examined the fragmentation pathways and products of molecules exposed to the entire radiation envelope of the plasma.

INTRODUCTION

A technique which seems especially suited to the isolation and characterization of plasma etching products and intermediates, particularly in highly energetic reaction sequences, is Matrix Isolation Spectroscopy (MIS). Reactive gas phase molecules are generated and trapped in an inert, transparent matrix at cryogenic temperatures (<10⁰K) for examination by conventional spectroscopic techniques (FTIR, Raman ....). In such an environment, the matrix-isolated species will exhibit molecular constants similar to those in the gas phase since the inert gas atoms of the matrix (usually argon) prevent species association and/or reaction. Moreover, since all vibrational transitions in matrix spectra originate from the ground state and free molecular rotation is unlikely, spectra are considerably simplified and more readily yield fundamental information concerning structure and bonding.
EXPERIMENTAL

For the plasma-matrix experiments, a specially designed parallel plate plasma reactor was constructed from a modified X-band microwave directional waveguide fabricated from 316-stainless steel with provisions made for water-cooling both the cathode and grounded anode. The areas of the parallel-spaced cathode and grounded anode were ca. 9.58 and 11.34 sq. cm., respectively, although in practice the relevant anode area was significantly larger due to the grounded stainless side walls. The inter-electrode spacing was ca. 25 mm. and the entire reaction zone was confined to a cylindrical volume estimated at ca. 30 cc. Etchant gases, appropriately diluted in argon, were fed into the plasma zone from a stainless/teflon gas handling manifold by way of an electrically isolated 3 mm. dia. orifice. After reaction with the substrate of interest (Si, SiO₂ wafers), all reaction gases exited through a 3 mm. stainless orifice and were condensed onto a cold (<10⁶ K) cesium iodide window (18 mm. dia. x 2 mm. thick) for subsequent infrared transmission measurements. In order to maintain a suitable vacuum (<10⁻³ torr) in the matrix chamber and sustain the high etchant flow rates, a high capacity turbomolecular pump (Leybold-Heraeus Turbvac 150) was situated in close proximity to the cryogenic window. With this arrangement, pressures of the order of 1 torr could be achieved in the plasma reactor while maintaining an adequate vacuum in the main chamber which housed the trapping window. An ENI Plasmaloc 1-HF oscillator/amplifier, tunable over the 90-460kHz range was used to excite the RF plasmas while a Burdick Model MW 200 Diathermy Unit (2.45 GHz, 80W) was used for microwave excitation. A Digilab Model FTS-15C FTIR spectrometer covering the range of 400-4000 cm⁻¹ at 0.5 cm⁻¹ resolution was used to examine the trapped products. Samples were deposited at 2-4 mmoles per hour for several hours before taking spectra.

RESULTS AND DISCUSSION

Figure 1 illustrates one such series of FTIR absorption spectra of the matrix-isolated products of the plasma etching of silicon (Si) and silica (SiO₂) by a dilute (0.2%) mixture of the fluorocarbon etchant CHF₃ in argon. Relevant plasma parameters were 100kHz, 10W, 0.5 torr total pressure, 3 cc/min. flow rate for 2-4 hrs. The "blank" experiment where the plasma was in contact with only the stainless steel housing and a remote quartz viewing port produced new absorptions attributable to unreacted CHF₃ and the product bands of HF, CF₄, COF₂, C₂F₄, and SiF₄. Traces of the atmospheric impurities H₂O and CO₂ were observed in addition to CO which was presumably produced by the plasma. When a silica (SiO₂) sample was placed directly into the plasma in a second run, the HF and COF₂ absorption intensities were an order of magnitude lower even though the CHF₃ destruction efficiency was somewhat increased and the
Fig. 1. Matrix infrared absorptions in the C-F and Si-F stretching regions produced by the condensed (10⁶K) effluent gases from the plasma etching reactor. P=parent CHF₃, W=window bands.
SiF$_4$ absorption doubled. The differences in product yield were also observed in an experiment performed after inserting a Si(100) single crystal wafer into the plasma. An even greater yield of SiF$_4$ was produced, accompanied by further decreases in the starting compound and HF. The intensity of the CO$_2$ bands was greatest in the SiO$_2$ experiments and significantly less (ca. 50%) with no sample or with Si present. This suggests a complex mechanism involving both HF and the CF$_2$ radical in the SiO$_2$ reaction. Traces of both the CF$_2$ and CF$_2^+$ radicals were seen in the final matrix deposits. CO$_2$ is suppressed in the Si experiment, consistent with the lower oxygen concentration available. However, the fate of the carbon atoms in that process is, as yet, uncertain. Further work involving isotopic substitution at the carbon atom of the etchant molecule should clarify this point. These results demonstrate the qualitative and semi-quantitative diagnostic aspects of matrix isolation in plasma chemical processes.

**PLASMA RADIATION EFFECTS**

A second series of experiments was conducted in order to examine the effects of plasma radiation on the etchant molecule of interest. With this in mind, an argon discharge was excited in a quartz tube (19 mm. o.d., 17 mm. i.d.) which was situated in an Evenson-Broida microwave cavity (2.45 GHz, 80W) modified to accommodate the larger quartz tube. The center of the discharge (ca. 8 cm. long) was located ca. 30 cm. from the 10°K CsI window (18 mm. dia.) and some 12 cm. from a coaxial capillary array which consisted of a series of parallel 4 cm. sections of Pyrex capillary tubing (1.7 mm. o.d., 1.4 mm. i.d.) held together by an outer band of heat-shrinkable Teflon tubing. The axial transmittance of this array was measured at 31% at 220 nm. The purpose of this capillary array was to de-excite any argon metastables via wall-collisions after exiting the electronically "hot" plasma zone. In this "windowless" fashion, only the plasma radiation envelope and ground state argon atoms were normally incident to the 10°K deposition window. Simultaneously with this radiation, various argon-diluted etchants (CHF$_3$, SF$_6$, CF$_4$,...) were deposited through a section of 6 mm i.d. stainless tubing situated at a 45° angle to the cold window. Infrared absorption spectra were recorded over the 200-4000 cm$^{-1}$ region on a Beckman IR-12 filter-grating spectrometer. Extensive fragmentation was observed in the case of CHF$_3$ and SF$_6$, and none in the case of CF$_4$. This is illustrated in Figure 2 for the case of CHF$_3$. 

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Fig. 2. Matrix infrared absorptions in the C-F stretching region produced before (left) and after (right) windowless argon plasma photolysis of equivalent Ar-CHF$_3$ samples; 17 micromoles CHF$_3$.

As a check to ensure that fragmentation was due to radiation effects, equivalent amounts of SF$_6$ were photolyzed both with and without the capillary array. From an analysis of the normalized ratios of product formation (ca. 30%) which precisely paralleled the transmittance of the capillary array (31%), we concluded that fragmentation in this configuration was proceeding primarily via plasma radiolysis. Subsequent experiments with the open argon discharge tube front-ended into an NRL-modified Baird VUV spectrometer recorded the intense Ar resonance doublet at 1048, 1067A as well as major Ar$^+$ ion contributions at 920 and 932A in the low pressure (< 60 millitorr) cases. For the open tube with an 18 millitorr argon inlet pressure, the Ar$^+$ resonance doublet at 920, 932A was 23% as intense as the Ar atom resonance doublet while the higher energy Ar$^+$ lines at 662-762A and 806-894A gave 9.6% and 4.6% of the intensity at 1048, 1067A, respectively.
CONCLUSIONS

Matrix Isolation Spectroscopy is well suited to examine the effluent gas phase reaction products and chemical intermediates found in a conventional RF-excited plasma-etching reactor. Except for the lighter rare gases (He, Ne) and hydrogen (H₂), all gas phase species/radicals can be trapped and immobilized in a 10⁶K argon matrix for subsequent examination. For Si and SiO₂ plasma etching by CHF₃, the dominant product found is SiF₄ with lesser contributions from CF₄, COF₂, CO and CO₂. The amount of SiF₄ produced in parametrically-equivalent Si and SiO₂ etching studies is in direct agreement with the preferential etch rate of SiO₂ vis-a-vis Si by plasma-discharged fluoroform, CHF₃.

The photochemical effects of plasma radiation, heretofore largely unexamined, have been shown to be significant. CHF₃ and SF₆ etchants undergo fragmentation when exposed to the entire radiation envelope of a nonequilibrium argon plasma. Although not as extensive as that which occurs in the active plasma zone, etchant decomposition is appreciable nonetheless. CF₄, SF₆, SF₅ and other reaction products as well as the fluorine-containing CF₃, CF₂, CHF₂, SF₅ and SF₆ radical fragments have been isolated and characterized. In addition to the strong argon resonance lines near 12eV (1048, 1067Å), the higher energy (13-19eV) Ar⁺ ion lines assume increasing importance at the lower plasma pressures. It is suggested that such a less invasive "windowless" high energy photolysis route might serve as the basis for alternative etching schemes whereby the damaging effects of particle bombardment can be avoided.