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Measurements of dioxygen fluoride (O_2F) in an atmospheric pressure plasma jet

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When etching tantalum with a coaxial-cylinder-type atmospheric pressure plasma jet (APPJ) in a $\text{He}/\text{CF}_4/\text{O}_2$ gas mixture, we found that the etch rates vary little with the distance between the plasma region and the substrate. Etch rates decrease by less than a factor of 3 when the distance increases from 0.3 to 20.3 cm in a closed tube that carries the APPJ effluent. These results indicate that reactive species may last up to 40 ms in the effluent. Ultraviolet absorption spectroscopy was employed to measure possible reactive species, specifically dioxygen fluoride (O_2F) and ozone (O_3), in a parallel-plate type APPJ. O_2F was found to be a significantly long-lived species, lasting up to 10 ms in the effluent with a constant density of about 10^{15} cm^{-3} . Using a measured O_3 density profile, the concentration of atomic fluorine (F) was estimated to be about 10^{13} cm^{-3} , which is two orders of magnitude lower than that of O_2F at a distance of 1 cm away from the APPJ exit. In summary, F atoms produced inside the APPJ combine with O_2 molecules, producing O_2F molecules, which can live long enough to reach and possibly etch metal surfaces. © 2005 American Institute of Physics. [DOI: 10.1063/1.1968420]

Over the past several years, Los Alamos National Laboratory has developed a nonthermal plasma source, called an “Atmospheric Pressure Plasma Jet (APPJ),” which uses a capacitively coupled electrode configuration and operates with rf power at 13.56 MHz.¹ The primary feed gas in the APPJ is helium, to which small concentrations of reactive gases [e.g., oxygen (O_2), carbon tetrafluoride (CF_4)] are added to generate a high flux of chemically active species. Discharge characteristics of the APPJ have been determined by electrical and optical measurements to be $\sim 1 \text{ kV/cm}$ breakdown field, 10^{10} – 10^{11} cm^{-3} electron density, and 2–4 eV electron temperature.^{2,3} For operation with a He/O_2 gas mixture, reactive species concentrations [O , $\text{O}_2(^1\Delta_g)$, $\text{O}_2(^1\Sigma_g^+)$, O_3 , etc.] have been determined using ultraviolet emission and absorption spectroscopy.⁴ The He/O_2 -based APPJ has been used to decontaminate surfaces exposed to chemical and biological warfare agents (e.g., anthrax surrogate, VX).⁵

Recently, we have demonstrated that a $\text{He}/\text{CF}_4/\text{O}_2$ -based APPJ can volatilize (or etch) plutonium (Pu), which is an actinide material.⁶ The APPJ generates reactive chemical “intermediates,” which may react with an actinide-contaminated surface to form a volatile gaseous product, such as plutonium hexafluoride (PuF_6).⁶ At low-pressure plasma conditions, $\text{He}/\text{CF}_4/\text{O}_2$ gas mixtures have been widely used in semiconductor etching processes.⁷ However, at atmospheric pressure, reaction chemistry is altered by frequent collisions and few studies have been carried out for $\text{He}/\text{CF}_4/\text{O}_2$ plasmas. In relation to this work, collaborating with a team at UCLA, we studied He/O_2 plasmas at atmospheric pressure in 2000.⁴ For a He/CF_4 plasma, the UCLA team measured atomic fluorine (F) concentrations in 2003.⁸ The interactions between CF_4 , O_2 , and their byprod-

ucts are not well-known at atmospheric pressure. There have been some studies of a few of the possible reactions,^{9,10} but not under plasma conditions. Therefore, it is of vital importance to identify reactive chemical intermediates in $\text{He}/\text{CF}_4/\text{O}_2$ and to correlate observed etch rates with the measured concentrations of reactive species to improve understanding of the etching mechanism.

Tantalum (Ta) etching experiments, in which tantalum serves as a surrogate metal for the actinide material, were carried out with a coaxial-cylinder-type APPJ, which is a typical prototype for a decontamination process. As shown in Fig. 1(a), the APPJ consisted of an inner electrode, which was coupled to a rf power source at 13.56 MHz, and a water-cooled grounded outer electrode. A $\text{He}/\text{CF}_4/\text{O}_2$ gas mixture was fed into the annular space of thickness 1.6 mm between the two electrodes at a flow rate of 25 slpm. Collimators (stainless-steel tubes with 1.5 cm inner diameter) of different lengths were attached at the exit of the plasma jet to lengthen the distance to the substrate from 0.3 to 20.3 cm. The tanta-

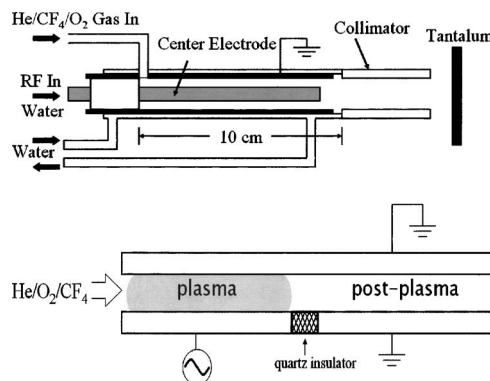


FIG. 1. (Top) Schematic of a coaxial-cylinder-type APPJ, which was designed for tantalum etching. (Bottom) Schematic of a parallel-plate-type APPJ, used for spatially resolved UV absorption spectroscopy.

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lum substrate was placed at a distance of 0.3 cm from the end of the collimator. A collimator enables reactive species to reach a substrate without diverging or being diluted by ambient air. Tantalum foil of 25 μm thickness was attached to a heating plate using a conductive silver paste. The temperature of the Ta substrate was varied between 200–350 $^{\circ}\text{C}$.

For spectroscopic measurements of reactive species concentrations inside and outside of the plasma, a parallel-plate-type APPJ was employed. As shown in Fig. 1(b), this consisted of two parallel-plate electrodes made of stainless steel and separated by a 0.2 cm gap. The grounded upper electrode, measuring 5 cm wide by 10 cm long, was water cooled. The lower plate was divided into two parts by a quartz spacer. A rf power source was coupled to the upstream part of the lower plate. The downstream part of the lower plate acted as a collimator. Quartz windows were used to cover the sides of the electrodes parallel to the flow so that spectroscopic measurements could be made inside and outside the plasma. UV absorption spectroscopy was used to measure the O_2F and O_3 concentrations. A deuterium lamp (Optronic Laboratories, OL UV-40) was mounted on one side of the APPJ, while an optical fiber captured light on the other side. Pinholes, approximately 1 mm in diameter, were made in front of the lamp and fiber bundle to eliminate any stray light. UV light passed through the plasma and post-plasma regions along the collimator and entered a monochromator (Jobin Yvon, THR 640) equipped with a liquid-nitrogen-cooled CCD detector (Princeton Instruments, Inc.). In the absence of a plasma, we measured an optical intensity I_o between 200 and 400 nm. After the plasma was turned on, the optical intensity I was measured again, which was lower than I_o . Ozone is known to absorb UV light around 254 nm with a cross section $\sigma(\text{O}_3)$ of $1.41 \times 10^{-17} \text{ cm}^2$,¹¹ while O_2F absorbs UV light at 215 nm with a cross section $\sigma(\text{O}_2\text{F})$ of $1.26 \times 10^{-17} \text{ cm}^2$.¹⁰ $[\text{O}_3]$ and $[\text{O}_2\text{F}]$ were derived using the Beer-Lambert law,¹¹ $\ln(I/I_o) = -\sigma(X)l[X]$, where X represents O_3 or O_2F and the effective absorption length l is 5 cm in this work.

Figure 2(a) shows the Ta etch rates obtained by varying the collimator length from 0 to 20 cm in the coaxial-cylinder APPJ. The operational parameters were an input power of 300 W (47 W/cm³), a 25 slpm He flow, a 0.5 slpm CF_4 flow (2% of He flow), a 0.25 slpm O_2 flow (1% of He flow), and a 300 $^{\circ}\text{C}$ substrate temperature. The average flow velocity was about 5 m/s and the time required for species to transport from APPJ exit to substrate is displayed in Fig. 2(a). For the no-collimator case, high etch rates of up to 5 mg/min ($\sim 2.5 \mu\text{m}/\text{min}$) were obtained. Significantly, the etch rate varies a little with the collimator length. The etch rate decreased by less than a factor of 3 when the collimator length was increased from 0 to 20 cm. This result indicates that the reactive species involved in etching tantalum may last up to 40 ms in the APPJ effluent.

The activation energy for tantalum etching was obtained in order to determine the etching mechanism and compare it for different collimator lengths. The temperature dependence of the chemical reaction rates for the etching agents and the surface to be etched is described by the Arrhenius relation, $R(T_{\text{sub}}) \propto \exp(-E_a/kT_{\text{sub}})$, where R is the chemical rate constant, T_{sub} is the substrate temperature, and E_a is the activation energy for the chemical reaction, which characteristi-

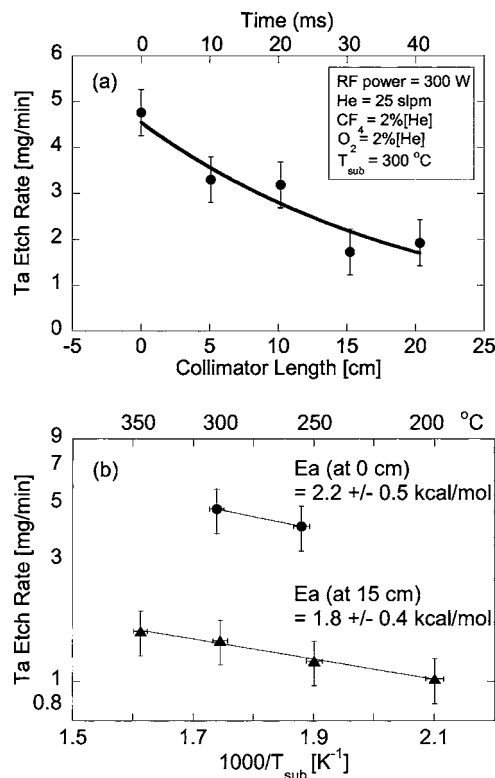


FIG. 2. (a) Tantalum etch rates obtained as a function of collimator length. (b) Tantalum etch rates obtained as a function of substrate temperature.

cally lies between 0.1 and 1 eV.⁷ Figure 2(b) shows Ta etch rates obtained for varying substrate temperatures, ranging from 200 to 350 $^{\circ}\text{C}$, at two different collimator lengths. E_a was determined to be $0.096 \pm 0.022 \text{ eV}$ ($2.2 \pm 0.5 \text{ kcal/mol}$) at 0 cm and $0.079 \pm 0.017 \text{ eV}$ ($1.8 \pm 0.4 \text{ kcal/mol}$) at 15 cm. It can be seen that the activation energies for Ta etching weakly depend on the collimator length. That is, the composition of reactive species may be similar at 0 cm and at 15 cm. Since one of probable tantalum etch reactions is $\text{Ta} + 5\text{F} \rightarrow \text{TaF}_5$, and TaF_5 (tantalum pentafluoride) is volatile at atmospheric pressure,¹² two possible conjectures can be made from Fig. 2. The first is that although atomic fluorine is known to have a relatively short lifetime ($< 1 \text{ ms}$) at atmospheric pressure,¹³ there may be unknown atomic fluorine production reactions that would allow the species to maintain a high population for at least 40 ms in these experiments. The other possibility is that there may be other reactive species that live long enough to reach and etch the tantalum.

To test these conjectures, UV absorption spectroscopy was carried out with the parallel-plate APPJ, with which we can increase an optical absorption length up to 5 cm and measure reactive species inside and outside the plasma. Figure 3 shows $[\text{O}_2\text{F}]$ and $[\text{O}_3]$ measured at various locations inside and outside the parallel-plate APPJ. Measurements were carried out in the APPJ discharge using an input power of 200 W (40 W/cm³), a 20 slpm He flow, a 0.4 slpm CF_4 (2% of He flow), and a 0.2 lpm O_2 (1% of He flow). The average flow velocity was about 5 m/s and the time required for species to transport from APPJ exit to measuring location is displayed in Fig. 3. Inside the plasma, we measured an O_2F concentration of $4.5 \times 10^{14} \text{ cm}^{-3}$, that likely resulted from reactions between atomic fluorine and molecular oxygen in the presence of helium ($\text{F} + \text{O}_2 + \text{He} \rightarrow \text{O}_2\text{F} + \text{He}$) and was destroyed mostly by atomic oxygen ($\text{O} + \text{O}_2\text{F} \rightarrow \text{OF}$

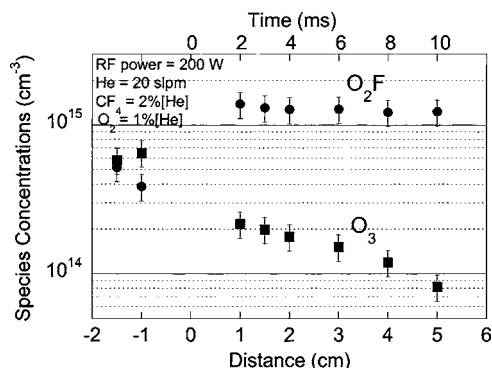


FIG. 3. The dependence of $[O_2F]$ and $[O_3]$ on distance and time operated at 200 W, $He/CF_4/O_2=20/0.4/0.2$ slpm, and gas temperature of 30–60 °C.

$+O_2$).¹³ Outside the discharge region the concentration of O_2F rapidly increased, rising to $1.3 \times 10^{15} \text{ cm}^{-3}$ at a distance of 1 cm, then remaining constant up to a distance of 5 cm. O_2F is therefore considered a fairly long-lived species (at least 10 ms in the present measurement), and could be one of species reacting with the metal surfaces. A possible reaction is $Ta + O_2F \rightarrow TaF + O_2$. In other words, O_2F could be a carrier of atomic fluorine in the $CF_4/O_2/He$ postplasma region. The square symbols in Fig. 3 show $[O_3]$ obtained. $[O_3]$ was $4.5 \times 10^{14} \text{ cm}^{-3}$ inside the plasma and decreased with distance outside the plasma. Since ozone is easy to decompose thermally, we checked the gas temperature outside the plasma with a thermocouple. The gas temperature ranged over 30–60 °C. Thermal decomposition of ozone can be negligible in this case. Ozone depletion is mainly caused by reactions with atomic fluorine, $O_3 + F \rightarrow OF + O_2$, in a $He/CF_4/O_2$ gas mixture.¹³ The concentration of the atomic fluorine at 1 cm away from the APPJ exit ($[F]_1$) was estimated to be $7.35 \times 10^{12} \text{ cm}^{-3}$ using the rate equation $\Delta[F]/\Delta t = \Delta[O_3]/\Delta t = k[O_3]_1[F]_1$, where $\Delta[O_3]$ was $1.2 \times 10^{14} \text{ cm}^{-3}$ between 1 and 5 cm, the reaction rate k is $1.02 \times 10^{-11} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}$, $[O_3]_1 = 2 \times 10^{14} \text{ cm}^{-3}$, and

Δt is 8 ms. This means that atomic fluorine may decay quickly and be two orders of magnitude lower in concentration than O_2F at a distance of 1 cm away from the APPJ exit.

In summary, the concentration of O_2F was measured in a $He/CF_4/O_2$ APPJ. Inside the plasma it was $4.5 \times 10^{14} \text{ cm}^{-3}$, rising rapidly in the effluent to $1.3 \times 10^{15} \text{ cm}^{-3}$ at a distance of 1 cm. It remained constant out to 5 cm (10 ms) from the APPJ. It is believed that fluorine (F) atoms produced inside the APPJ combine with oxygen (O_2) molecules to produce O_2F molecules. These molecules can live long enough to react with and etch metal surfaces. These measurements of reactive species were carried out under near room temperature conditions (30–60 °C). Practical APPJ applications may require a higher temperature operation (up to 300 °C). Therefore, the present work will be extended to higher temperature conditions for a $He/CF_4/O_2$ atmospheric plasma in the future.

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