

FINAL REPORT

U.S. Department of Energy

Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces

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Executive Summary

The purpose of this project was to develop a low-cost, environmentally benign technology for the decontamination and decommissioning of transuranic waste. This goal has been achieved with the invention of the atmospheric-pressure plasma jet. This device selectively etches heavy metals from surfaces, rendering objects radiation free and suitable for decommissioning. The volatile reaction products are captured on filters, which yields a tremendous reduction in the volume of the waste. Studies on tantalum, a surrogate material for plutonium, have shown that etch rates of 6.0 microns per minute can be achieved under mild conditions (i.e., at temperatures below 250 °C). Over the past three years, we have made numerous improvements in the design of the plasma jet. It may now be operated for hundreds of hours and not undergo any degradation in performance. Furthermore, small compact units have been developed, which are easily deployed in the field.

We have made important advances in plasma science and its application to the environmental management of nuclear materials. It has been demonstrated that by addition of helium and by altering the electrode design, a plasma may be generated at atmospheric pressure that is weakly ionized with a neutral temperature of 75 to 125 °C. The electrons in this plasma are not in equilibrium with the rest of the gas: their energy is 2 to 3 electron volts, or more than 20,000 °C. The electrons are present in very low concentration. Nevertheless, they cause the dissociation of a significant fraction of the molecules present. For example, at an applied power of 24.4 Watts/cm³ and 10 Torr O₂ in the feed, the plasma dissociates about 1% of the oxygen molecules into atoms (a concentration of $\sim 10^{16}$ cm⁻³). We found that by adding a few Torr of carbon tetrafluoride with the oxygen, the plasma generates a large flux of fluorine atoms. These fluorine atoms etch tantalum and other metals at several microns per minute. A detailed examination of the surface chemistry has revealed that the etching rate is limited by desorption of volatile metal fluorides, and not by the flux of fluorine atoms from the plasma.

This project involved a successful collaboration between the University of California, Los Angeles, and Los Alamos National Laboratory. By working as a team, the University and laboratory scientists were able to tackle the complex physics, chemistry, materials processing, and environmental issues encountered in the development of this technology. Three graduate students and two postdoctoral scholars participated in the project. A Ph.D. and an M.S. dissertation were completed during the grant period, and they are attached to the Appendix. We have published seven papers in scholarly journals, obtained one U.S. patent, filed four patent applications, and presented thirteen talks at scientific meetings. The papers and presentations have generated a lot of interest, particularly the article published in Discover Magazine (Oct. 1997), which highlighted the decontamination application. In 1999, the UCLA and LANL research team was awarded an R&D 100 Award for the development of the plasma jet. Currently, several companies have expressed an interest in acquiring patent rights and commercializing the plasma jet technology.

The science undertaken through this project has addressed a critical need within the U.S. Department of Energy. The decontamination and decommissioning of buildings, structures and materials within the nuclear weapons complex is one of the most expensive and challenging components of the environmental restoration effort. The atmospheric-pressure plasma jet shows real promise as a cost-effective and environmentally benign method of removing radioactive contamination. The research funded by the Environmental Management Sciences Program has put this technology on a firm scientific foundation, and has laid the groundwork for transfer into practice. Although much progress has been made, much work remains to be done. The physics and chemistry of fluorine-containing plasmas needs to be characterized, as well as the interactions of the fluorine atoms with the surface to be etched. Studies of the plasma etching of uranium should be undertaken, and the metal-fluoride etching products should be carefully identified. Through the continued support of the Department of Energy, this exciting science will yield new technologies that significantly reduce costs and accelerate the cleanup effort.

Research Objectives

The objectives of this program are to understand the scientific principles of operating the atmospheric-pressure plasma jet, and to apply this technology to converting transuranic waste (TRU) into low-level radioactive waste (LLW). The Department of Energy has an interest in developing cost-effective, cleaning technologies, because of the need for decontaminating weapons production facilities. Decommissioning buildings and materials contaminated with thin layers of transuranic elements is one of the most challenging and costly undertakings that DOE faces in cleaning up the nuclear weapons complex [1]. Currently, solvent scrubbing and mechanical blasting of surfaces is used for this purpose. These methods generate large quantities of waste and present a serious risk of exposure to the workers. Plasmas, on the other hand, may be used to selectively remove the radioactive elements via a gas-phase process that produces a small volume of highly concentrated waste on filters. Moreover, because this process proceeds at low temperature and without adding large quantities of chemicals, it does not jeopardize the health and safety of DOE personnel [2]. In short, the plasma jet is an environmentally safe and easy-to-use alternative to cleaning techniques now in use.

There are many types of atmospheric-pressure plasmas used in materials processing [3]. Traditional sources include transferred arcs, plasma torches, corona discharges and dielectric barrier discharges. In arcs and torches, the electron and neutral temperatures exceed 5000 °C and the densities of charge species range from 10^{16} to 10^{19} cm⁻³ [4-6]. Due to the high gas temperature, these plasmas are used primarily in metallurgy. Corona and dielectric barrier discharges produce non-equilibrium plasmas with gas temperatures between 50 and 400 °C, and densities of charged species between 10^{10} and 10^{15} cm⁻³ [7-9]. However, since these discharges are non-uniform, their use in materials processing is limited. The atmospheric-pressure plasma jet exhibits many characteristics of a conventional, low-pressure glow discharge [8,10-13]. In the jet, the gas temperature ranges from 25 to 200 °C, charged-particle densities are $\sim 10^{11}$ cm⁻³, and reactive species are present in high concentrations, i.e., 10 to 100 ppm. Since this source does not have to be operated in a vacuum chamber, it can be applied to a much wider range of applications.

The atmospheric-pressure plasma jet has generated substantial interest from other organizations. We have received funding from DuPont, Beta Squared Inc, and several University of California organizations, including the SMART program, the LANL/UC Directed Research and Development program, the Center for Environmental Risk Reduction, and the Toxic Substances Research and Training Program. Some of the support we have received is for the development of environmentally benign cleaning technologies. Other support was in the form of fellowships to support graduate student research. At the present time, these projects have been concluded and no further funds are being received. We do, however, have a grant with the National Science Foundation for the plasma-enhanced chemical vapor deposition of silicon dioxide and nitride films using the atmospheric-pressure plasma source. We are actively seeking further support for the application of the plasma jet to decontamination and decommissioning of nuclear waste.

Methods and Results

Plasma Source Physics

Shown in Fig. 1 is a picture of the atmospheric pressure plasma jet. A schematic of the initial design of the source is shown in Fig. 2. It consists of two concentric electrodes separated by a gap of 1 to 3 mm. The inner electrode is driven with 50 to 500 W of radio frequency power at 13.56 MHz, while the outer electrode is grounded. Feed gas, containing helium and up to 5 vol% of other gases, flows between the electrodes and is ionized. The gas emerges from the nozzle and impinges on a substrate placed 2 to 10 mm downstream, whereby cleaning or etching of the material takes place [10]. For example, tantalum foil placed 5 mm downstream of the plasma source is etched at rates up to 6 $\mu\text{m}/\text{min}$ with a feed gas composed of 97.5% helium, 2.0% carbon tetrafluoride, and 0.5% oxygen [11,12]. In this case, the plasma is driven with 400 W RF power and the metal sample is heated to 250 $^{\circ}\text{C}$. Thus far, we have developed several source designs that are scalable to large areas and can treat a variety of objects, including glove boxes and building walls.

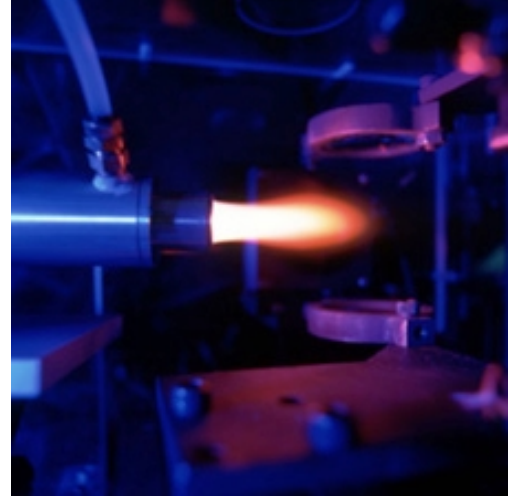


Fig. 1. The atmospheric-pressure plasma jet.

High-speed imaging of the plasma reveals a uniform, arc-free gas discharge. Shown in Fig. 3 are time-resolved measurements of the plasma voltage and current. One sees a smooth sinusoidal variation with the current preceding the voltage in time. This behavior is characteristic of a capacitive discharge. It is not at all like a plasma torch, or a dielectric barrier discharge, where arcing is the principle mode of gas ionization. Nor is it like a corona, where breakdown occurs across the high electric field generated about a sharp point. On the other hand, this plasma is similar to a parallel-plate discharge that is generated at low gas pressure.

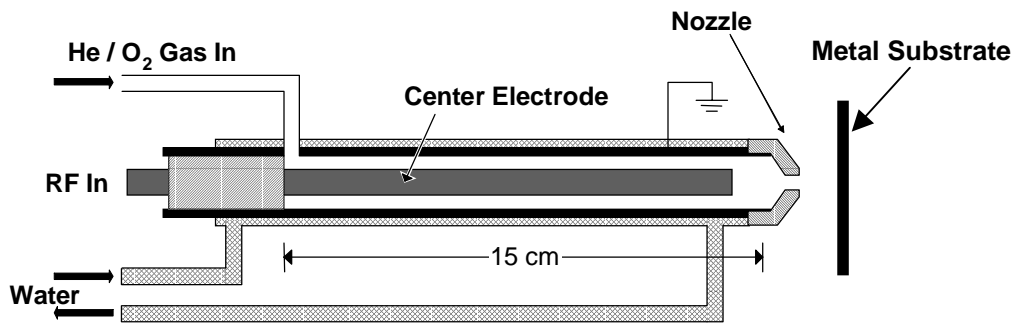


Fig. 2. Schematic of the atmospheric-pressure plasma jet.

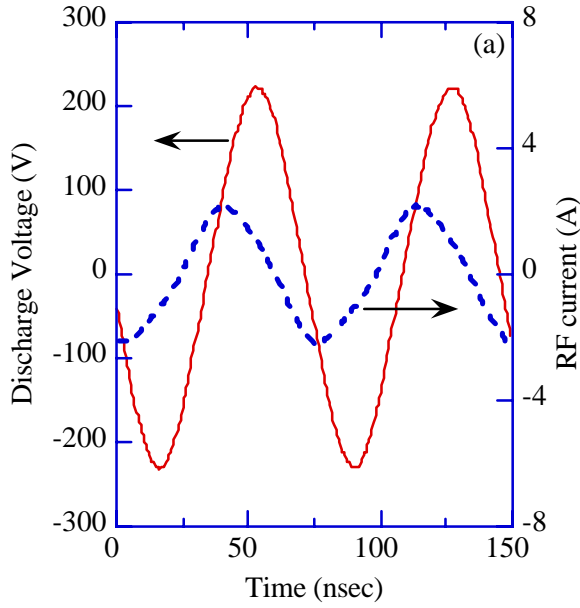


Fig. 3. Time-resolved measurements of the plasma voltage and current.

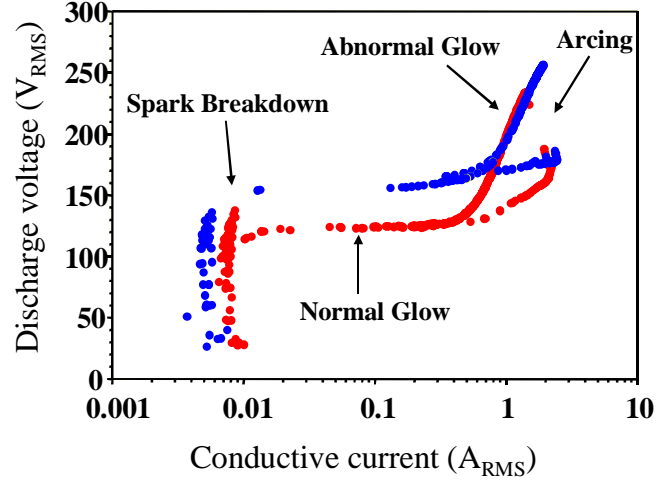


Fig. 4. Time-averaged current-voltage characteristics of the atmospheric-pressure plasma with helium gas.

Presented in Fig. 4 is the dependence of the voltage upon the current during steady-state operation of the plasma source. The red and blue lines are for electrodes with two different gap spacings. Initially, a Townsend dark region is observed, in which the voltage rapidly rises with the current. This appears as a vertical line in the figure because the meter used in the experiment could not detect currents below 0.007 A. At about 0.01 A, spark breakdown occurs and the discharge is ignited. This is followed by a normal-glow region, in which the voltage remains constant with increasing current, and an abnormal-glow region, in which the voltage rises monotonically with the current. Finally, arcing occurs and there is a rapid drop in the voltage with a further rise in current.

The behavior depicted in Fig. 4 is the same as that observed in a DC discharge at low pressure [14,15]. Notice that a low breakdown voltage is required to ignite the plasma, only 150 V. This may be contrasted with other atmospheric-pressure discharges, such as arcs, torches and coronas, where voltages of 1,000 to 50,000 V are required for breakdown. Based on an analysis of the continuum emission from plasma [12], we have determined that the electron density is $3 \times 10^{11} \text{ cm}^{-3}$ and the electron temperature (T_e) is about 2.0 eV. On the other hand, the neutral gas temperature (T_n) ranges from 50 to 150 °C. This is typical of weakly ionized, non-equilibrium plasmas, such as those generated at low pressure. By contrast, an arc or torch at ambient pressure exhibits a T_e of 5-10 eV and a T_n of 0.5-2.0 eV ($\sim 3,000$ to $20,000$ °C) [3].

Plasma Chemistry

Decontamination of transuranic waste using the plasma jet depends critically on the production of reactive species for metal etching. Accordingly, we have undertaken a careful study of the reaction chemistry in the plasma jet, using ultraviolet absorption spectroscopy, optical emission spectroscopy and numerical modeling [13]. So far, our work has focussed on oxygen and helium plasmas, since they are somewhat easier to characterize. However, soon we hope to study plasma jets that contain carbon tetrafluoride, oxygen and helium.

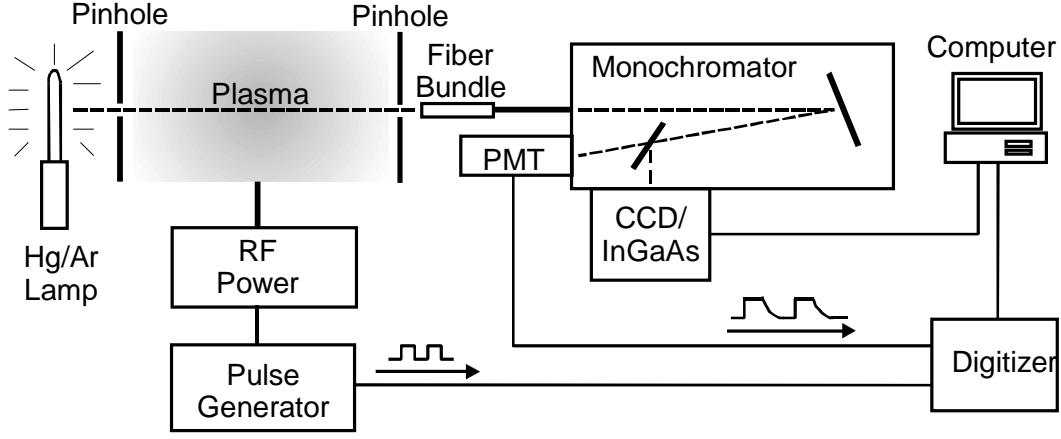


Fig. 5. Schematic of the experimental setup for optical measurements.

For these experiments, we modified our plasma source to consist of two parallel-plate electrodes made of aluminum, and separated by a gap 2 mm in height. The upper electrode is 10.2 cm wide by 5.5 cm long and is driven by RF power at 13.56 MHz, while the lower electrode is 10.2 cm wide by 20.4 cm long and is grounded. Just downstream of the lower electrode is an aluminum oxide plate that allows the gas to flow undisturbed pass the region of ionization. The sides of the duct parallel to the flow direction are sealed with quartz windows so that spectroscopic measurements of the gas may be made.

The optical setup for time-resolved ultraviolet absorption and optical emission spectroscopy is illustrated in Fig. 5. A calibrated mercury/argon lamp is mounted on one side of the plasma, while a quartz fiber-optic bundle is placed on the other side. Light passes through a pinhole into the fiber-optic bundle, then into a monochromator, and is detected by either a charged-coupled device (CCD), or a photomultiplier tube (PMT). Ultraviolet absorption at 253.7 nm is used to measure the concentration of ozone in the plasma, while the metastable states of oxygen, $O_2(^1\Sigma_g^+)$ and $(^1\Delta_g)$, are recorded by visible and infrared emission at 760 and 1269 nm, respectively, shown in Fig. 6 [16,17]. In these experiments, the plasma is pulsed at 0.5 Hz with a 50% duty cycle, and the transient signal from the PMT is collected at 500 kHz using a high-speed digitizer. The time resolution of the measurements is 2 μ s.

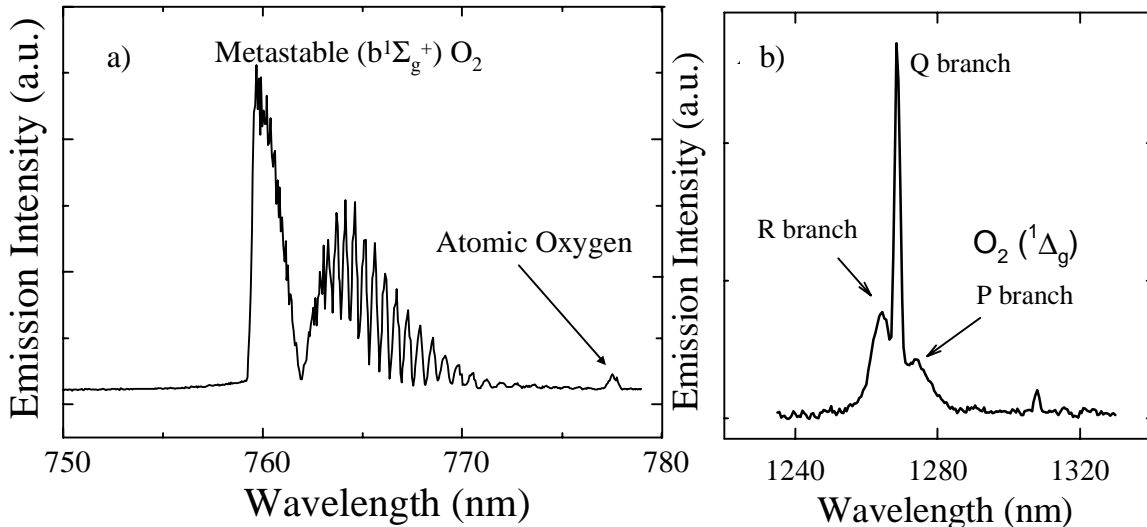


Fig. 6. Gas-phase emission spectra of a) $O_2(^1\Sigma_g^+)$ at 760 nm and b) $O_2(^1\Delta_g)$ at 1269 nm

We have developed a numerical model to simulate the gas-phase chemical kinetics that occurs after the RF power to the plasma is turned off, i.e., in the afterglow regime. This model provides a means of accurately calculating the concentration of oxygen atoms and the other species as they evolved in time, or distance downstream of the source. In addition, at zero time, we obtain the concentrations of the reactive species within the plasma for a given operating condition. The reaction mechanism includes the following species: helium, oxygen molecules ($^3\Sigma_g^-$), two metastable oxygen molecules ($^1\Delta_g$ and $^1\Sigma_g^+$), ground-state oxygen atoms (3P), and ozone. The excited states of helium (3S) and oxygen atoms (1D) are neglected, because their lifetimes are too short to influence the chemistry ($\tau_{O^*} = 3$ ns) [18]. The numerical model solves the simultaneous set of material balances for the six species in the gas. For a given component, the material balance is:

$$\frac{d[X]}{dt} = \sum_i R_i, \quad (1)$$

where $[X]$ is the concentration of species X , and R_i is the rate of reaction i that either produces or consumes X . Fifteen reactions are included in the model and their rate constants may all be obtained from the literature.

Presented in Fig. 7 is the evolution of the oxygen atoms, metastable oxygen molecules and ozone with time after turning off the power to the electrode. Distance is plotted on the upper x axis so that one can also examine how the reaction evolves as the gas travels downstream in the afterglow region. The curves are the concentrations predicted from the numerical model, whereas the symbols are the experimental data. Excellent agreement is achieved between the theory and the experiment. At time zero, which corresponds to the conditions with the plasma on, the concentrations of the five oxygen species are $1.3 \times 10^{17} \text{ cm}^{-3}$ ground state O_2 , $6.0 \times 10^{15} \text{ cm}^{-3}$ O atoms, $5.0 \times 10^{15} \text{ cm}^{-3}$ $O_2(^1\Delta_g)$, $1.0 \times 10^{15} \text{ cm}^{-3}$ $O_2(^1\Sigma_g^+)$ and $2.5 \times 10^{15} \text{ cm}^{-3}$ O_3 . In other words, at an applied power of 24.4 W/cm^3 (400 W), the plasma converts 2% and 3.5% of the oxygen fed into O atoms and $O_2(^1\Delta_g)$ molecules, respectively.

After the discharge has been extinguished, the oxygen atoms rapidly recombine with oxygen molecules to produce ozone. The ozone concentration climbs to a constant value of $5 \times 10^{15} \text{ cm}^{-3}$ after about 3 ms, and does not change further. Thereafter, the oxygen atoms rapidly decay with time. The two metastable oxygen molecules, ($^1\Delta_g$) and ($^1\Sigma_g^+$), exhibit dramatically different decay rates. The singlet-delta state persists out to about 100 ms, whereas the singlet-

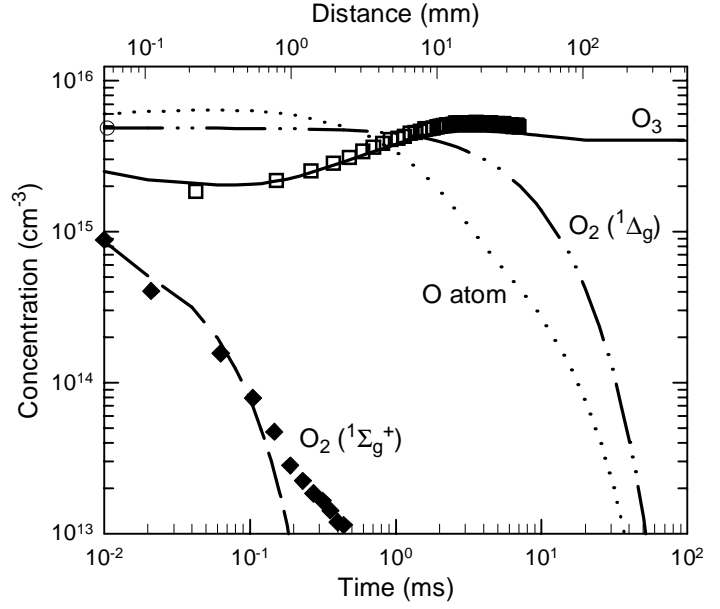


Fig. 7. The dependence of the O , $O_2(^1\Delta_g)$, $O_2(^1\Sigma_g^+)$ and O_3 concentrations on time and distance for plasma operation at 24.4 W/cm^3 , 6.0 Torr O_2 and 120°C .

sigma state is essentially extinguished by 500 μ s. The consumption rate of both of these species is governed by their reaction with ozone.

The atmospheric-pressure plasma source produces a relatively high concentration of oxygen atoms, $\sim 10^{16}$ cm⁻³, at a low gas temperature, ~ 125 °C. This plasma also makes large quantities of ozone and metastable oxygen molecules. The reactive gases generated by the plasma jet are well suited for carrying out materials processes that have normally been performed in low-pressure plasmas [19]. For example, organic films, such as polyimide, may be stripped from silicon wafers at rates of 1 to 5 μ m/min at 100 to 200 °C [20].

Surface Chemistry of Metal Etching

We have investigated the plasma etching of tantalum at atmospheric pressure using a gas mixture containing carbon tetrafluoride, oxygen and helium [11]. Tantalum was studied because it exhibits reaction chemistry similar to that of plutonium and may be used as a surrogate material for the actinide metals [2,21-24]. Although it should be noted that the etching rate of plutonium is about ten times slower than that observed for tantalum under the same conditions [2,21]. With the atmospheric-pressure plasma, we obtain a maximum etching rate of 6 μ m/min at 14.8 Torr oxygen, 22.4 Torr carbon tetrafluoride, 720 ± 5 Torr helium, 500 W RF power, and a film temperature of 300 °C. The etching rate increases with applied power, carbon tetrafluoride pressure, oxygen pressure, and residence time of the gas between the electrodes. This dependence on the plasma reaction conditions suggests that the rate is proportional to the flux of fluorine atoms to the metal surface.

Shown in Fig. 8 are x-ray photoemission spectra of the Ta 4f_{5/2} and 4f_{7/2} states before and after etching a tantalum foil with the CF₄/O₂/He plasma. These data have been obtained *in situ* by mounting the source in a chamber that is attached to our XPS system (see Fig. 13 below). The spectra contain a series of overlapping bands due to the presence of different tantalum oxidation states. The binding energy scale has been fixed by referencing the 4f_{7/2} peak for metallic tantalum, Ta⁰, to 20.9 eV [22,25]. Deconvolution of the bands was performed using a Gaussian-Lorentzian model to fit the peak shapes [26]. Each individual chemical state yields a doublet split corresponding to the 4f_{7/2} and 4f_{5/2} lines. These lines are separated by 1.8 eV and exhibit a fixed area ratio of A(4f_{7/2})/A(4f_{5/2}) = 4/3.

Before etching (Fig. 8(a)), three doublets are observed due to Ta⁰, Ta⁺¹ sub-oxide, and Ta⁺⁵ oxide [22,25,27,28]. The tantalum 4f_{7/2} binding energies for these three states are 20.9, 21.7 and 26.2 eV, respectively. The Ta⁺¹ designation is provided to distinguish this feature from Ta⁰, and is not meant to indicate the formal valence on the atom. This band most likely arises from adsorbed oxygen or fluorine on the metal surface, as distinguished from the bulk metal [27]. By integrating the area under the 4f_{7/2} bands, one obtains the following distribution among the different chemical states: 5% Ta⁰, 8% Ta⁺¹, and 87% Ta₂O₅. These results are consistent with previously published data on tantalum foils exposed to air [22,23,28].

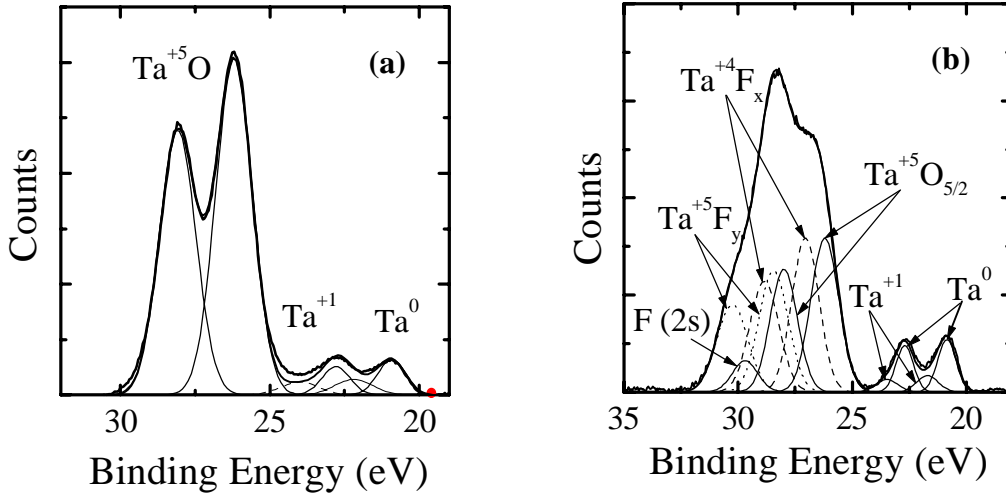


Fig. 8. Tantalum $4f_{5/2}$ and $4f_{7/2}$ photoemission spectra (a) before etching and (b) after etching.

After etching (Fig. 8(b)), two new Ta $4f_{7/2}$ peaks are observed at 27.0 and 28.5 eV. These features are obviously due to fluorinated tantalum, and are assigned to metal fluorides or oxyfluorides in the +4 and +5 valence states [25,29]. From the areas of the $4f_{7/2}$ bands, the tantalum surface layer is distributed among the different species as follows: 8% Ta^0 , 3% Ta^{+1} , 32% Ta_2O_5 , 31% $Ta^{+4}F_x$, and 26% $Ta^{+5}F_y$. Tantalum fluorides and/or oxyfluorides comprise 57% of the material sampled. The Ta-F states appearing at binding energies above that of Ta_2O_5 have not been observed in previous studies of plasma etching of tantalum [22,28]. Evidently, this is due to the much higher flux of fluorine atoms to the metal surface in the atmospheric-pressure plasma.

Based on the results of our study, we propose that etching occurs through a gas-surface, or surface-surface collision between fluorine atoms and adsorbed tantalum fluoride, e.g., TaF_{4s} [11]. In the former case, an Eley-Rideal mechanism is obeyed in which F atoms react directly with TaF_{4s} and desorb volatile TaF_5 molecules. In the latter case, a Langmuir-Hinshelwood mechanism is followed: the F atoms adsorb onto the surface, diffuse to the reaction site, and react with TaF_{4s} to desorb TaF_5 . Many aspects of the surface chemistry remain to be determined. In particular, we are inferring that fluorine atoms are the principal reactive species in the plasma. Yet we have taken few spectroscopic measurements of the discharge, and have no direct evidence of their formation. Moreover, we have not detected the production of TaF_5 molecules, nor have we made any measurements of the desorption kinetics of tantalum fluorides from the metal surface. Clearly, much more research is needed to understand the plasma-surface interactions.

The above discussion highlights what we have learned so far about the atmospheric-pressure plasma etching of heavy metals. The plasma source exhibits unusual discharge physics that is not well understood at this point. Our study of the oxygen/helium plasma reveals that extremely high concentrations of reactive species are produced, e.g., $6 \times 10^{15} \text{ cm}^{-3}$ O atoms. In fluorine-containing plasmas, tantalum may be etched at rates between 1 and 6 $\mu\text{m}/\text{min}$ without any ion bombardment. The reactive species responsible for this reaction and the mechanism involved remain to be determined.

Relevance, Impact and Technology Transfer

- a) ***Focus on new scientific knowledge required for DOE Environmental management problems:*** One of the most formidable obstacles facing the Department of Energy is the cleanup of nuclear weapons facilities [1]. Hundreds of buildings and thousands of pieces of equipment have been coated with thin layers of transuranic elements. New scientific knowledge is needed to address the removal and re-concentration of these highly radioactive layers. Today, wet chemical solvents and mechanical blasting is used to clean contaminated surfaces. These methods not only generate large quantities of toxic waste, but also present a serious exposure risk to workers. We have developed a novel approach to surface decontamination: The atmospheric-pressure plasma jet selectively removes thin layers of transuranic elements by converting them into volatile metal fluorides. The metal fluorides are then captured and re-concentrated on inorganic filters. This results in a tremendous reduction in the volume of waste to be treated, and allows the buildings and equipment to be safely decommissioned. Our research has provided evidence that the plasma jet is a viable and potentially superior alternative to current cleanup technologies. Further scientific knowledge is required on plasma physics and chemistry, on surface chemistry of actinide metal etching, and on adsorption of metal fluoride vapors.
- b) ***How the new scientific knowledge will improve DOE compliance and cleanup approaches:*** The atmospheric-pressure plasma jet produces a high flux of reactive fluorine species that etch heavy metals at rates much higher than in low-pressure plasmas. The plutonium and other actinide elements are converted into volatile fluorides, e.g., PuF_5 , which are trapped by adsorption and filtration. This process is environmentally benign, because only a small volume of oxygen and carbon tetrafluoride are needed to remove the surface contamination, and the small quantity of gaseous byproducts is safely captured and concentrated on solid adsorbents. The plasma jet should also provide a low-cost solution. Since it operates at ambient pressure, there is no need for expensive vacuum equipment, or for dismantling and breaking up the contaminated materials to fit in a process chamber. This invention is simple in design, making it easy to produce and repair. Furthermore, the plasma jet may be configured as a portable unit for rapid deployment in the field.
- c) ***How the program has helped bridge the gap between fundamental research and technology applications:*** The support provided by the Environmental Management Sciences Program has made it possible for us to understand the discharge physics and chemistry of the atmospheric-pressure plasma jet. This understanding has led to many improvements in materials of construction, electrode design, and plasma operation, so that now this technology may be considered for demonstration of D&D applications. In particular, we identified the optimum process conditions for etching tantalum (a plutonium surrogate), and discovered that removal rates can be ten times faster than that achieved in low-pressure plasmas. In addition, we have developed innovative jet designs for treating areas larger than 1 ft^2 and at much higher applied powers. Applying these results to plutonium etching would bring us to the point where we could test the plasma jet for decommissioning and decontamination purposes.

- d) ***How the project has impacted individuals, laboratories and institutions:*** This EMSP project fostered a valuable collaboration between the University of California, Los Angeles, and the Los Alamos National Laboratory. It resulted in the development of a new technology for cleaning and decontaminating surfaces. This technology has generated a lot of interest in the scientific community as well as in the commercial sector, as evidenced by the selection of the atmospheric-pressure plasma jet for a 1999 R&D 100 Award. The invention is currently in the process of being licensed for commercial applications. In addition, the EMSP project provided funding for the education of 2 postdoctoral scholars (Jaeyoung Park and Andreas Schütze) and 3 graduate students (James Jeong, Steve Babayan and Vincent Tu). Many publications, patents and presentations resulted from this work as well (see below).
- e) ***Are larger scale trials warranted? What expertise has been developed:*** Larger scale trials are needed to demonstrate and deploy the plasma jet for decontamination of TRU wastes. In particular, it is essential that we extend our “bench-top” results on tantalum (an actinide surrogate) to uranium and plutonium thin films. Through this project, we have developed a fundamental understanding of the discharge physics of the atmospheric pressure plasma. In addition, we have characterized the gas-phase reaction chemistry of oxygen/helium plasmas, and have demonstrated the capability of the jet for heavy metal etching. Although much more work remains to be done, our research has significantly advanced the science of atmospheric-pressure plasmas and their use in materials processing. The expertise gained in this study will be essential for further research on plasma etching of uranium and plutonium.
- f) ***Improvement in the capabilities of the collaborating scientists:*** The collaboration between UCLA Chemical Engineering and LANL Plasma Physics has given us the opportunity to develop strong fundamental studies of the atmospheric-pressure plasma jet. At LANL, the basic physics of the plasma jet has been studied extensively, while at UCLA, research focused on the surface chemistry and engineering of metal etching. Working together as a team, we completed an experimental and theoretical study of the reaction chemistry in the plasma afterglow. This work, which involved a series of elegant time-resolved measurements of the reactive species, has provided us with key insights into the physical and chemical mechanisms governing the operation of the atmospheric-pressure plasma.
- g) ***How the research has advanced our understanding in the area:*** This research has led to a fundamental understanding of high-pressure plasmas and their interaction with metal surfaces. We have characterized the plasma physics of an exciting new discharge that operates at atmospheric pressure. At the same time, we have identified the gas-phase chemical reactions occurring in oxygen-containing plasmas, and determined the surface kinetics of etching metals with plasmas. In addition to significantly advancing plasma and materials science, this research project should lead to new applications of plasmas in the ambient pressure regime. The most significant application is the decommissioning and decontamination of nuclear wastes. Our technology could provide the U.S. Department of Energy with a cost-effective solution for cleaning hundreds of contaminated buildings and structures throughout the nuclear weapons complex. Nevertheless, the plasma science is exciting in its own right, and the knowledge gained from this work should stimulate many important advances in the field.

Additional scientific and other hurdles to be overcome: We have a number of scientific and technological hurdles to overcome. The scientific hurdles include understanding (1) the physics of fluorine-containing plasmas used in etching, (2) the gas-phase reaction chemistry of fluorine-containing plasmas, and (3) the surface reaction mechanism of metal etching. We also need to demonstrate the etching of uranium and plutonium with the atmospheric-pressure plasma jet. This research is described in detail in the Future Work section below. Studies of the discharge physics and chemistry will focus on plasmas that contain carbon tetrafluoride, nitrogen trifluoride and sulfur hexafluoride. These latter compounds will be investigated because they may provide a more efficient source of reactive fluorine species.

In addition to understanding the plasma science, we must consider how to transform the atmospheric-pressure plasma jet into a serviceable tool for decontamination and decommissioning applications. The atmospheric-pressure plasma jet etches metals by creating fluorine species that react with the surface and form volatile metal fluorides. These latter compounds have to be captured by solid adsorbents, such as by carbon black or by silica-alumina molecular sieves. To develop this process, we must first identify the volatile compounds by mass spectrometry. Then the adsorption dynamics of the compounds on inorganic materials must be characterized. We have found that during tantalum etching, a white powder is generated from the oxidation of the tantalum fluoride vapors. This suggests that filtration of airborne particles may need to be considered as well. Finally, it would be valuable to have an online detection system to ensure that the plasma jet is operating efficiently and in compliance with all environmental, health and safety regulations. By overcome these scientific and technological hurdles, we are confident that the atmospheric-pressure plasma jet may be implemented for a variety of D&D applications.

- h) Have other agencies or enterprises expressed interest in the project:*** Because of the exciting work done on this project, much interest has been shown from government agencies and commercial enterprises. The DOE-FETC Focus Area Lead, Dr. Paul Hart, has expressed keen interest in the work, and would like to move this project to the technology-demonstration stage as quickly as possible. The National Science Foundation has awarded a grant to UCLA to study the plasma-enhanced chemical vapor deposition of silicon dioxide and silicon nitride using the atmospheric-pressure plasma jet. The contact person at the NSF is Dr. Farley Fisher (ffisher@nsf.gov). The Department of Defense is interested in using atmospheric-pressure plasmas for the decontamination of chemical and biological weapons. The contact person at the DOD is Major Joe Kiple (joseph.kiple@apgea.army.gov). Several companies have expressed an interest in licensing the plasma jet technology. Licensing is being handled by Emil Waldron at UCLA (ewaldron@srnet.ucla.edu) and by David Salizar at LANL (davidj@lanl.gov).

Project Productivity

The project accomplished most of the proposed goals. We have gained a solid understanding of the basic physical principle of operating the atmospheric-pressure plasma jet. The observation of the continuum emission due to electron-neutral collision and subsequent determination of the electron density and energy was a first-class scientific achievement. We were also able to resolve the gas-phase chemical kinetics occurring in plasmas operated with oxygen and helium. When we began working on metal etching, the plasma was very unstable,

operation could not be sustained for long periods of time, and etch rates were low, less than 1.0 microns/minute. Through the EMSP grant, we made substantial improvements in the jet design, determined the effects of process conditions on the etching rate, and were able to boost the metal removal rates to 6.0 microns/minute. We also made substantial progress in understanding the surface reaction mechanism of heavy metal etching. This work was crucial to extending the plasma jet capability to the decontamination of transuranic wastes. The only part we were unable to achieve was the demonstration of uranium or plutonium etching with the plasma jet. This is mainly due to safety and security complications involved with nuclear materials, and to not having sufficient funds to pursue this aspect of the work.

Personnel Supported

Robert F. Hicks, UCLA Professor
Gary S. Selwyn, LANL Technical Staff, UCLA Adjunct Professor

Jaeyong Park, Post-doctoral Scholar
Andreas Schütze, Post-doctoral Scholar

James Y. Jeong, Graduate Student
Steven E. Babayan Graduate Student
Vincent J. Tu, Graduate Student

Publications

Publications in 1998

1. Jeong, J.Y., Babayan, S.E., Tu, V.J., Henins, I., Velarde, J., Selwyn, G.S. and Hicks, R.F., "Etching Materials with an Atmospheric-Pressure Plasma Jet," *Plasma Sources Sci. and Tech.* **7**, 282-285, 1998.
2. Babayan, S.E., Jeong, J.Y., Tu, V.J., Selwyn, G.S. and Hicks, R.F., "Deposition of Glass Films with an Atmospheric-Pressure Plasma Jet," *Plasma Sources Sci. and Tech.* **7**, 286-288, 1998.
3. Schütze, A., Jeong, J.Y., Babayan, S.E., Park, J., Selwyn, G.S. and Hicks, R.F., "The Atmospheric-Pressure Plasma Jet: A Review and Comparison to other Plasma Sources," *IEEE Trans. Plasma Sci.* **26**, 1685-1694, 1998.

Publications in 1999

4. Jeong, J.Y., Babayan, S.E., Schütze, A., Tu, V.J., Park, J., Henins, I., Selwyn, G.S. and Hicks, R.F., "Etching polyimide with a non-equilibrium atmospheric-pressure plasma jet," *J. Vac. Sci. Technol. A* **17**, 2581-2585, 1999.
5. Park, J., Henins, I., Herrmann, H.W., Selwyn, G.S., Jeong, J.Y., Hicks, R.F., Shim, D. and Chang, C.S., "An Atmospheric Pressure Plasma Source", accepted for *publication Appl. Phys. Lett.*, scheduled to appear in the Jan. 17, 2000 issue.

6. Park, J., Henins, I., Herrmann, H.W., Hicks, R.F. and Selwyn, G.S., "Discharge Phenomena of a Novel Atmospheric Pressure Plasma Source," submitted to *J. Appl. Phys*, June 1, 1999.
7. Park, J., Henins, I., Herrmann, H.W. and Selwyn, G.S., "Neutral Bremsstrahlung Measurement in Radio-Frequency (RF) Atmospheric-Pressure Discharge", submitted to *Phys. Rev. Lett.*, July 1, 1999.
8. Tu, V.J., Jeong, J.Y., Schütze, A., Babayan, S.E., Selwyn, G.S. and Hicks, R.F., "Tantalum Etching with a Non-Thermal Atmospheric-Pressure Plasma," submitted to *J. Vac. Sci. Technol. A*, July 28, 1999.
9. Jeong, J.Y., Park, J., Henins, I., Babayan, S.E., Tu, V.J., Selwyn, G.S. and Hicks, R.F., "Reaction Chemistry of an Oxygen-Helium, Atmospheric-Pressure Plasma," submitted to *J. Phys. Chem.*, August 2, 1999.

Interactions

This project has generated much enthusiasm in the scientific community and resulted in multiple presentations at various conferences. Below is a record of the presentations resulting from this project.

1. Hicks, R.F., Babayan, S.E., Jeong, J.Y., Henins, I. and Selwyn, G.S., "Atmospheric-Pressure Plasma Jet Processing of Materials," ISAPS Conference, Los Angeles, CA, September, 1997.
2. Jeong, J.Y., Babayan, S.E., Selwyn, G.S. and Hicks, R.F., "Atmospheric-Pressure Plasma Jet Etching of Materials," 44th International Symposium of the American Vacuum Society, San Jose, CA, October 20, 1997.
3. Selwyn, G.S., Henins, I., Jeong, J.Y., Babayan, S.E. and Hicks, R.F., "High Rate Cleaning of Surfaces using Atmospheric Pressure Generation of Reactive Metastable Species", American Vacuum Society Annual Meeting, San Jose, CA, October 22, 1997.
4. Selwyn, G.S., Henins, I., Velarde, J., Jeong, J.Y., Babayan, S.E. and Hicks, R.F., "Contamination Control for Future Device Processing: Good Vibrations to Plasma Jets," AIChE Annual Meeting, Los Angeles, CA, November 17, 1997.
5. Jeong, J.Y., Babayan, S.E., Henins, I., Velarde, J., Hicks, R.F. and Selwyn, G.S., "Atmospheric-Pressure Plasma Jet Etching of Materials," AIChE Annual Meeting, Los Angeles, CA, November 19, 1997.
6. Hicks, R.F., "Materials Processing with Atmospheric-Pressure Plasma Jets," Solid State Technology and Devices Seminar, Electrical Engineering and Computer Sciences Department, University of California, Berkeley, CA, February 27, 1998.
7. Selwyn, G.S. "Cleaning and Decontamination using the Atmospheric Pressure Plasma Jet", International Science and Technology Conference, Albuquerque, NM, May 5, 1998.

8. Schuetze, A., Park, J., Babayan, S.E., Jeong, J.Y., Tu, V.J., Selwyn, G.S. and Hicks, R.F., "The Atmospheric-Pressure Plasma Jet: Properties and Materials Applications," 45th International Symposium of the American Vacuum Society, Baltimore, MD, November 4, 1998.
9. Jeong, J.Y., Babayan, S.E., Schuetze, A., Park, J., Henins, I., Hicks R.F. and Selwyn, G.S., "Characterization of the Reactive Species in a Helium/Oxygen Atmospheric-Pressure Plasma Jet," 45th International Symposium of the American Vacuum Society, Baltimore, MD, November 5, 1998.
10. Hicks, R.F., Jeong, J.Y., Babayan, S.E., Schuetze, A., Park, J., Henins, I. and Selwyn, G.S., "Characterization of the Atmospheric Pressure Plasma Jet Effluent," AIChE Annual Meeting, Miami, FL, November 17, 1998.
11. Schuetze, A., Babayan, S.E., Jeong, J.Y., Tu, V.J. and Hicks, R.F., "Atmospheric-Pressure Plasma Cleaning of Si (100) Surfaces," AIChE Annual Meeting, Miami, FL, November 18, 1998.
12. Hicks, R.F., Babayan, S.E., Jeong, J.Y., Henins, I. and Selwyn, G.S., "Atmospheric-Pressure Plasma Jet Processing of Materials," The 25th International Conference on Plasma Science, Raleigh, NC, June 2, 1998.
13. Hicks, R.F., "Materials Processing with Atmospheric-Pressure Plasma Jets," Université D'Orléans, France, February 1, 1999.
14. Selwyn, G.S., Henins, I., Park, J., Snyder, H. and Herrmann, H., "The Atmospheric Pressure Plasma Jet", Watkins-Johnson, Scotts Valley, CA, March 18, 1999; IPEC-Precision, Bethel, CT, February 24, 1999.
15. Henins, I., Selwyn, G.S., Park, J., Snyder, H. and Herrmann, H., "The Atmospheric Pressure Plasma Jet" (2 talks, parts a & b), New Mexico Chapter Meeting of the American Vacuum Society, Albuquerque, NM, March 31, 1999.
16. Hicks, R.F., Jeong, J.Y., Babayan, S.E., Tu, V.J., Selwyn, G.S., Park, J. and Henins, I., "Gas-Phase Chemistry of Atmospheric Pressure Plasmas," AIChE Annual Meeting, Dallas, TX, November 2, 1999.

We have attended several EMSP workshops in an effort to better understand the environmental management problems that may be addressed with our technology. Moreover, this was a good forum for communicating our progress to DOE administrators. The EMSP workshops are listed below.

1. Schütze, A., Babayan, S.E., Jeong, J.Y., Tu, V.J., Hicks, R.F., Park, J., Henins, I. and Selwyn, G.S., "Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces," DOE EMSP Workshop, Idaho Falls, ID, April 1998.

2. Babayan, S.E., Jeong, J.Y., Tu, V.J., Schütze, A., Hicks, R.F., Park, J., Henins, I. and Selwyn, G.S., "Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces," DOE EMSP Workshop, Aiken, GA, July 1998.
3. Hicks, R.F., Babayan, S.E., Jeong, J.Y., Tu, V.J., Schütze, A., Park, J., Henins, I. and Selwyn, G.S., "Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces," DOE EMSP Workshop, Chicago, IL, July 1998.

In addition, Dr. Jaeyoung Park spent 2 months during the summer of 1998, in collaboration with faculties of Courant Institute of Mathematical Sciences in New York University. This collaboration resulted in our successful modeling of the discharge physics.

Transitions

The development of a source that operates at atmospheric pressure expands the range of applications of plasma technology within the U.S. Department of Energy. Clearly, the decommissioning and decontamination of radioactive wastes can benefit tremendously from this new device. With conventional low-pressure plasma sources, one would have to break up a building into small pieces and insert each piece into the vacuum chamber for treatment. This would be time consuming, worker intensive, and extremely expensive. With the atmospheric-pressure plasma, there would be no need to dismantle the building. The plasma source would be mounted on a robotic assembly that enters the structure and decontaminates the surfaces in place. Since the source design is adaptable to a variety of shapes and is easily scaled up, objects of any size, shape or location can be treated.

There is commercial interest in the plasma jet for several applications, including cleaning of semiconductor substrates and other materials, chemical vapor deposition of thin films, and sterilization of food and medical equipment. Licensing and commercialization of this technology is pending.

Patents:

One patent has issued to Dr. Gary S. Selwyn: "The Atmospheric-Pressure Plasma Jet," U.S. Patent No. 5,961,772. Five other patent applications are pending.

Future Work:

Future work needed to implement this device for D&D applications include (a) identification of the reactive species in CF_4/He and $\text{CF}_4/\text{O}_2/\text{He}$ plasma jets, (b) extension of the APPJ etching process to radioactive materials, (c) identification of volatile products and development of filtration techniques. Identification of the reactive species in the plasma jet is extremely important because we need this knowledge to increase metal etching efficiency, and to better understand how the volatile products are formed. It is also necessary to perform etching experiments with radioactive elements to determine the effectiveness of this tool for decontamination needs. Below is an explanation of the research to be performed on fluorine-containing atmospheric-pressure plasmas.

Source Physics

We will measure the electron temperature, T_e , and charged particle density, n_e , in fluorine-containing plasmas as a function of the applied power, total pressure and gas composition. Although probe theory is not well developed for a highly collisional plasmas [30], we will explore the use of novel measurement schemes such as a two-probe technique [31,32]. In addition, the plasma will be characterized by microwave and IR-laser interferometry. We also plan to analyze the optical emission from excited states of helium, argon and nitric oxide inside the plasma. Several researchers have showed that electron number densities may be extracted from measurements of the excited-state populations of these species [32-37].

Electric field measurements will be made using Stark broadening and Stark-mixing [38]. In this experiment, the helium emission line will be recorded, because it is the second lightest element and will have a relatively large Stark effect. The temperature of the neutrals and ions (T_n and T_i) will be recorded by high-resolution optical emission spectroscopy and laser-induced fluorescence with Doppler-broadening. We plan to map out these parameters as a function of the axial and radial positions inside the parallel-plate source, and compare the results to 1-D and 2-D numerical models of the plasma [12]. Measurements of T_e , T_i , T_n , and n_e will greatly enhance our understanding of the atmospheric-pressure plasma source and enable us to develop improved designs.

Gas-Phase Chemistry

So far we have characterized the reaction chemistry of plasma jets operated with oxygen and helium [13,39]. We now wish to extend this work to atmospheric-pressure plasmas containing fluorine, including CF_4 , NF_3 and SF_6 . The gas-phase reaction mechanism of carbon tetrafluoride is more complicated than that of oxygen, because CF_4 dissociates into many fragments. A variety of analytical techniques will be use to elucidate this mechanism. The concentrations of simple molecules, such as F_2 , CO , and CO_2 , will be measured by ultraviolet absorption spectroscopy. Optical emission spectroscopy will be used to determine the concentrations of electronically excited species, including long-lived metastable molecules. The concentrations of the radical fluorocarbon species, CF , CF_2 , and CF_3 , will be determined by infrared laser-absorption spectroscopy, using the experimental methods developed by Haverlag et al. [40]. Both actinometry and chemical titration will be employed to quantify the ground state fluorine atoms, which we believe are the active species in metal etching.

All the experimental data will be correlated against numerical models of the plasma and the afterglow. These models will incorporate a detailed reaction mechanism that includes He , CF_x ($x=1-4$), F_2 , and F atoms when carbon tetrafluoride and helium are fed to the plasma, and O_2 , O_2^* , CO , CO_2 , COF and COF_2 when oxygen is fed as well. Over the long term, we plan to develop a model of the plasma itself. In this case, Poisson's equation will be added to account for the ion and electron motions [30]. In addition, we will include all the ion-neutral and electron-neutral collisions in the mechanism, and the generation and/or consumption of ions and electrons at the electrode surfaces. By comparing the simulation results to careful measurements of the electron energy distributions in the plasma, we should learn a great deal about the plasma physics and chemistry.

Surface Chemistry

Surface chemistry plays a crucial role in plasma etching, yet it is probably the least understood part of the process. Our preliminary work suggests that the surface reaction of fluorine atoms with adsorbed tantalum fluoride species may be rate limiting. We will thoroughly study the surface chemistry by characterizing the elementary surface reactions with *in situ* scanning tunneling microscopy, x-ray photoemission spectroscopy, temperature-programmed desorption and molecular-beam mass spectrometry. To perform these experiments we will require a supersonic molecular beam in addition to our existing ultra-high vacuum analytical system. With the aid of this apparatus, we will extract the important surface kinetic parameters, such as the sticking probability, frequency factor and activation energy for the surface reaction, and the coverage of active tantalum fluorides. These kinetic parameters will be added to our numerical model of the plasma reactor and used to simulate the metal etching process. This work will lead to a comprehensive understanding of the surface chemistry of the plasma etching of metals.

Etching of Actinides

We have chosen to study the plasma etching of tantalum, because this element exhibits chemistry similar to plutonium and is a good surrogate material for the actinides [21,41]. However, we expect there to be differences between the surface chemistry of etching tantalum and actinide metals, and these differences should be explored. Therefore, in the future, we propose to investigate the atmospheric-pressure plasma etching of uranium oxide and metal films. Professor Jory Yarmoff, Physics Department, University of California, Riverside, has agreed to provide us with uranium oxide films (see letter at end of this proposal). These films are deposited on iron substrates, and they provide an excellent analogue to the contamination problems that are encountered in the field. In addition, we will look into acquiring uranium metal films (non-enriched with low radioactivity) from Los Alamos National Laboratory.

We also propose to collaborate with scientists at Los Alamos National Laboratory to demonstrate the use of the plasma jet for an actual decontamination problem. An excellent test case would be to remove plutonium from the surfaces of glove boxes. This work would be carried out in the specialized facilities available at the Los Alamos.

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Feedback

We have been pleased with the Department of Energy's administration of the project. It was helpful to receive full funding for the University portion of the work at the outset. This allowed us to bring in the students early and allocate resources efficiently to achieve the project goals. The reporting requirements were not burdensome, which allowed us to focus our attention on scientific achievement. The DOE program managers were courteous, knowledgeable and helpful. On the whole, we were very pleased to be part of EMSP, and we hope that we can continue our association with this program in the future.

Appendices

Thesis James Jeong, Ph.D.

Thesis Vincent Tu, M.S.