

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 demonstrate a practical, environmentally benign technology for the surface decontamination and decommissioning of radioactive waste. A low temperature, atmospheric pressure plasma has been developed with initial support from the Department of Energy, Environmental Management Sciences Program (Grant No. DE- FG07-96ER45621). This device selectively etches radioactive 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. The technology shows a great potential for accelerating the clean-up effort for the equipment and structures contaminated with radioactive materials within the DOE complex. The viability of this technology has been demonstrated by selectively and rapidly stripping uranium from stainless steel surfaces at low temperature. Studies on uranium oxide have shown that etch rates of 4.0 microns per minute can be achieved at temperature below 473 K. Over the past three years, we have made numerous improvements in the design of the atmospheric pressure plasma source. We are now able to scale up the plasma source to treat large surface areas.

We have made tremendous progress in identifying the scientific principles that govern the operation of the atmospheric pressure plasma and applying this technology to the environmental management of radioactive wastes. We have developed a novel plasma source, in which reagent gases are mixed with helium or argon and passed through two closely spaced electrodes. By applying radio frequency power to one of the electrodes, the gas becomes ionized with the dissociation of about 1% of the reagent molecules into atoms and radicals. The plasma is weakly ionized with a charged particle density of about 10^{11} cm^{-3} and an electron temperature from 1 to 3 eV. By contrast, the neutral temperature ranges from 300 to 450 K, depending on the process conditions. We found that when 2.0 vol.% oxygen, nitrogen, hydrogen, or carbon tetrafluoride

are added to the gas, a stream of O, N, H, or F atoms at $\sim 10^{15}$ cm⁻³ emerges from the source and impinges on the sample surface. This high density of reactive species promotes rapid processing rates. For D&D applications, this device may be fed with CF₄ and O₂, thereby generating F atoms which can strip uranium and plutonium from contaminated surfaces. Our understanding of the physics and chemistry of fluorine-containing atmospheric pressure plasmas has been advanced through this project. A detailed examination of the surface chemistry has revealed that the etching process may be limited by the reaction between fluorine atoms and adsorbed uranium oxyfluorides.

Our EMSP research program has been a tremendous success. A total of 15 journal publications, 4 patents, and 1 patent application have resulted from this project so far. We have presented 24 talks at scientific meetings. An outstanding research experience has been provided for 4 graduate students, Steven Babayan, Gregory Nowling, Maryam Moravej and Xiawan Yang, and 2 postdoctoral scholars, Jaeyoung Park and Guowen Ding. Moreover, the technology has been licensed to two startup companies, Apjet, Inc., and Surfx Technologies LLC, who are developing products for D&D and other commercial applications. Product sales have been made to DOE facilities.

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. Atmospheric-pressure plasmas show 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 result in technology transfer into industrial practice.

Research Objectives

The objectives of this program were to understand the scientific principles of operating the atmospheric-pressure plasma, 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 have several drawbacks: they are labor intensive, employ hazardous chemicals, produce large quantities of waste and present serious risks of exposure to workers [2]. In many cases, DOE personnel would rather package the entire object for long-term storage, than to attempt acid stripping of the actinide elements. 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 personnel [2]. In short, plasma technology is an environmentally safe and easy-to-use alternative to cleaning techniques now employed by DOE.

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 non-equilibrium, atmospheric-pressure plasma we developed is homogenous in time and space, and exhibits many characteristics of a conventional, low-pressure glow discharge [3,10-32]. The gas temperature ranges from room temperature to 450 K, depending on the processing condition. The electron density is $\sim 10^{11}$ cm^{-3} , and the electron temperature is 1 to 3 eV. Moreover, the discharge produces a high concentration reactive species, i.e., 10 to 100 ppm, for materials processing. Since this source does not have to be operated in a vacuum chamber, it can be applied to a much wider range of applications. Furthermore it can be scaled up to treat large surface areas.

The atmospheric-pressure plasma has generated substantial interest from other organizations. We have received funding from NSF, AMD, Motorola, and several University of California organizations, including the SMART program. Some of the support we have received is for the development of environmentally benign technologies. At the present time, most of these projects have been concluded. We are actively seeking further support for the application of the atmospheric pressure plasma to the decontamination of nuclear waste as well as chemical and biological hazards.

Methods and Results

Plasma Physics

The physics of the atmospheric pressure plasma was examined with the source provided by Surfx Technologies LLC, and shown in Fig. 1 [www.surfxtechnologies.com/]. It consisted of two perforated circular plates separated by a gap 1.6 mm across. The upper aluminum electrode was connected to a 1000-Watt RF power supply (13.56 MHz), while the lower electrode was grounded. The electrical properties of the discharge were studied using voltage, current and impedance probes attached directly to the source.

Presented in Fig. 2 is the dependence of the discharge voltage on the RF current for the helium plasma at pressures from 100 to 760 Torr [27]. The points on the curves indicate the breakdown voltages. The lines correspond to normal glow operation. Beyond the end of the lines, the plasma transforms into a filamentary arc. The plasma was turned off at this point, because in an arc the current is concentrated on a small area of the electrode and prolonged exposure can damage it. As expected, the breakdown voltage decreases from 180 V to 70 V as the pressure is reduced from 760 Torr to 100 Torr. The voltage and current also have been measured as a function of time during the RF cycle. For the normal glow, smooth sinusoidal curves are observed with the current waveform leading the voltage waveform by 86° . This behavior is characteristic of a capacitive discharge with bulk ionization of the gas. By contrast, in the arc mode, the current and voltage waveforms overlap each other, and they are no longer smooth curves.



Fig. 1. Plasma source (Atomflow 250TM) operating with helium and nitrogen at 10 W/cm^2 [33].

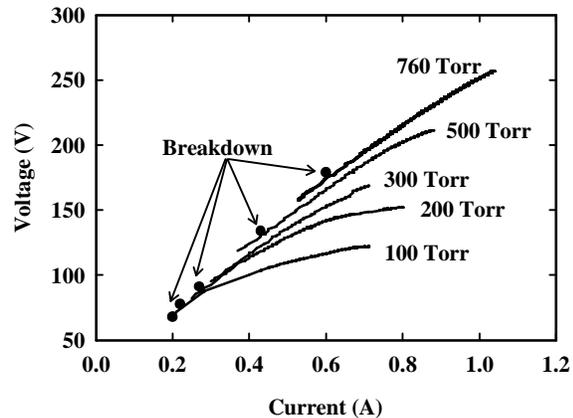


Fig. 2. Voltages as a function of current curves for a helium discharge.

To examine the cross-sectional spectra of the plasma, a plasma source with two parallel rectangular electrodes was used [17]. The sides of the duct parallel to the flow direction were sealed with quartz windows so that the gas could be probed by ultraviolet and visible spectroscopy. Light from the plasma was collected with a monochromator equipped with either a liquid-nitrogen cooled CCD or a photo-multiplier tube. A signal generator, lock-in amplifier and oscilloscope were available for transient, pulsed plasma studies with a time resolution of 2.0

μs . In Fig. 3 we present the dependence of the helium I emission intensity on the position between the powered and grounded electrodes. The intensity is low near the walls and in the center of the plasma. A maximum in the He I line is seen at 0.3 mm from each wall. The shape of this profile is invariant with respect to input power, gap spacing and gas composition. However, the maxima move closer to the walls with increasing power. The behavior seen in the figure is due to a space-charge sheath forming along the electrodes. Close to the walls, the gas is depleted of electrons so the emission is weak, whereas in the bulk discharge, the intensity is low due to the lower electric field strength there. At the inner edge of the sheath, i.e., 0.3 mm, the high electron density and large electric field combine to boost the plasma emission intensity to its highest value.

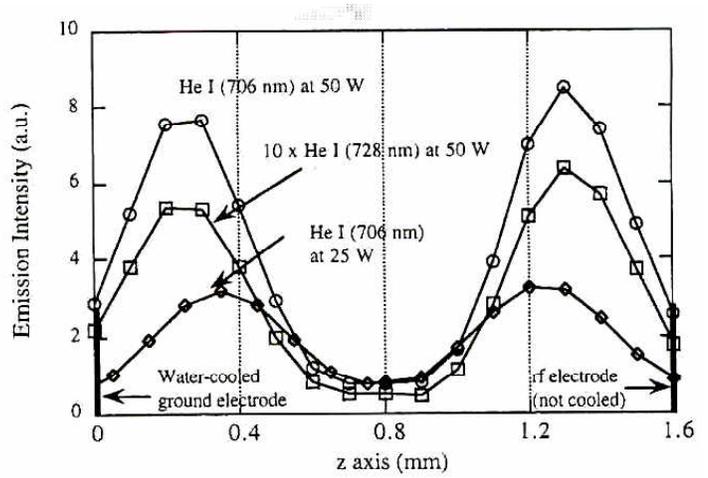


Fig. 3. Spatial profile of He I emission in a discharge operated at 600 Torr He and 20.8 W/cm^3 .

An estimate of the electron density, n_e , can be obtained from the relationship between the RF current density, J , and the bulk electric field strength, E [17]:

$$n_e = \frac{-J}{e\mathbf{m}E} \quad (1)$$

where e is a unit of electric charge, and \mathbf{m} is the electron mobility ($\text{cm}^2/\text{V}\cdot\text{s}$). The electric field of the plasma was calculated by finding the thickness and the voltage drop of the sheath, using a collisional sheath model, and then correcting for the sheaths [34]. Knowing the plasma density, the average electron temperature, T_e , can be calculated from a power balance, in which the input power, p_{in} , is primarily dissipated by electron collisions with neutrals [30]:

$$\mathbf{e} = n_e \frac{P}{K_B T_g} S_{CRM} I_1 + n_e \left[n_e \langle \mathbf{s}_{ei} \mathbf{u}_e \rangle + \frac{P}{K_B T_g} \langle \mathbf{s}_{ea} \mathbf{u}_e \rangle \right] \frac{2m_e}{M} \frac{3}{2} K_B (T_e - T_g) \quad (2)$$

Here, ϵ is the power density (W/m^3), P is the pressure (Pa), T_g is the gas temperature (eV), T_e is the electron temperature (eV), S_{CRM} is the ionization coefficient (which is a function of T_e), I_1 is the first ionization energy (eV), and $\langle \sigma_{ei} v_e \rangle$ and $\langle \sigma_{ea} v_e \rangle$ are the electron-ion and electron-atom collision rate coefficients (which are functions of n_e and T_e). From the measurement of the discharge voltage and current with the power probe, the plasma parameters were determined for the source shown in Fig. 1. At a constant current density of 138 mA/cm^2 , the plasma density decreased from 6.5×10^{11} to $1.0 \times 10^{11} \text{ cm}^{-3}$, while the electron temperature increased from 1.2 to 2.6 eV as the pressure was reduced from 760 to 30 Torr.

The electron density and temperature were also determined by analyzing the neutral bremsstrahlung emission from the atmospheric pressure helium plasma [16]. Neutral bremsstrahlung gives rise to the continuous background observed in the spectrum from 400 to 1000 nm. Using the expression for the emission cross-section developed by Dalgarno and Lane [36], and assuming a Maxwellian distribution of electron energies, a best fit to the continuum background was obtained with $n_e = 2.9 \times 10^{11} \text{ cm}^{-3}$ and $T_e = 1.9 \text{ eV}$. These data are in good agreement with the electron density and temperature calculated from equations (1) and (2) above.

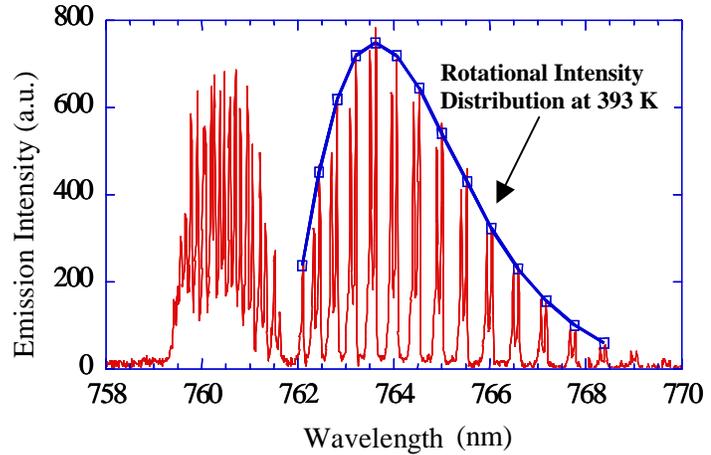


Fig. 4. Oxygen emission spectrum with calculated rotational intensity distribution at 596 Torr He, 4 Torr O₂, and 400 W.

The neutral temperature was determined to confirm that it falls within a regime acceptable for D&D applications. Shown in Fig. 4 is the emission spectrum for the atmospheric oxygen band at 762 nm. By fitting the Maxwell-Boltzmann rotational intensity distribution to the peak maxima, a neutral gas temperature of 393 K was obtained. This value agreed to within 20 K of the temperature measured with a thermocouple suspended in the gas.

Plasma Chemistry

With an electron density of $6.5 \times 10^{11} \text{ cm}^{-3}$ and an electron temperature of 1.2 eV, the atmospheric pressure noble gas discharge should produce high concentrations of reactive species. Previous investigations of the reaction chemistry in oxygen and nitrogen plasmas have revealed that the concentration of O and N atoms ranges from 10^{15} to 10^{16} cm^{-3} [14,20]. It was thought that similarly high levels of F atoms are generated in CF₄/He plasmas.

We measured the concentration of F atoms produced in a carbon tetrafluoride/helium discharge by titration with H₂ and by numerical modeling [23]. Fluorine atoms rapidly react with H₂ to produce HF, which may be detected by infrared absorption spectroscopy. The plasma source shown in Fig. 1 was used for these experiments, except that the quartz windows were replaced with barium fluoride. Hydrogen was fed to the system 3 mm downstream of the discharge through a linear array of 50 holes, 0.8 mm in diameter. The infrared spectrum of HF was collected at this position using a Biorad FTS-7 spectrometer and mercury-cadmium-telluride detector.

Shown in Fig. 5 on the next page is the infrared spectrum of HF obtained by adding $0.7 \times 10^{15} \text{ cm}^{-3}$ H₂ to the afterglow of the plasma. The source was operated at 739 Torr He, 12.6 Torr CF₄, and 300 W RF power. The rotational fine structure associated with the P and R branches of the vibrational spectrum is clearly observed. We have used one of the peaks in the R branch to monitor the amount of HF produced in the titration experiments. In the figure, the

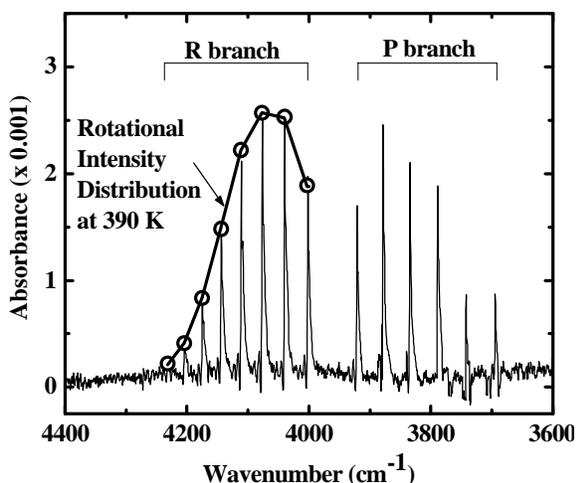


Fig. 5. Infrared spectrum of HF taken during the titration of F atoms with H₂ in the CF₄/He plasma afterglow.

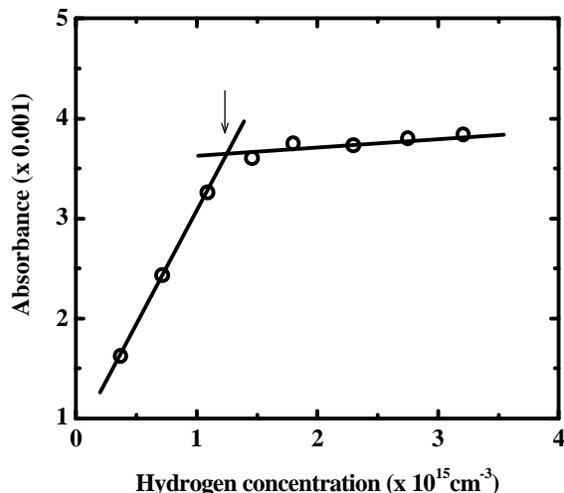


Fig. 6. The dependence of the intensity of the HF peak at 4039.7 cm⁻¹ on the H₂ concentration in the plasma afterglow.

curve connecting the peaks in the R branch is the rotational intensity distribution calculated from HITRAN data for a gas temperature of 390 K [37].

In Fig. 6, the height of the infrared peak at 4039.7 cm⁻¹ is plotted against the hydrogen concentration in the gas downstream of the plasma. The peak intensity increases linearly with the hydrogen concentration up to 1.2×10^{15} H₂ molecules per cm³, and thereafter remains constant. A plateau is observed at the point where the F atom concentration begins to limit the rate of production of hydrogen fluoride. Since the reaction stoichiometry is 1:1, the knee in the curve corresponds to a hydrogen concentration that equals the F atom concentration: $[F] = [H_2]$ (@ knee) = 1.2×10^{15} cm⁻³. Given the uncertainties inherent in this method, we estimate that this measurement is accurate to within $\pm 20\%$ of the actual value.

We have briefly studied the formation of CF_x radicals in the atmospheric pressure plasma. Presented in Fig. 7 are infrared spectra taken of the gas just downstream of the electrodes with the discharge turned on and off. The source was fed with 7.9 Torr CF₄ and powered at 300 W. When the discharge is turned on, one sees a band at 1114 cm⁻¹ due to the production of CF₂ radicals. It has been found that the intensity of this peak decreases in the presence of oxygen due to the conversion of CF₂ into CO and COF₂.

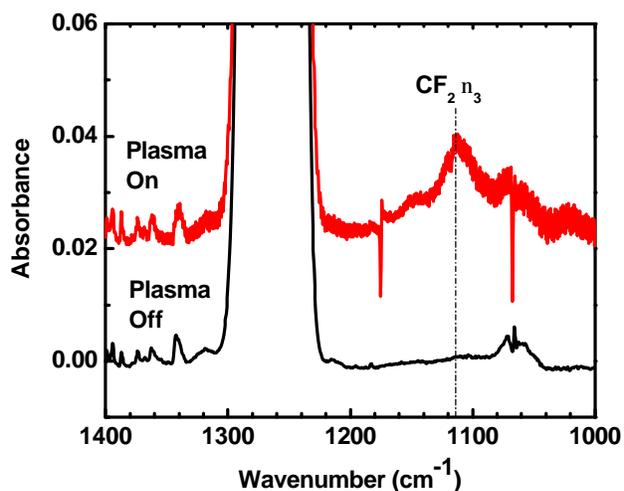


Fig. 7. Infrared spectra of the gas with the plasma turned on and off.

We have developed a numerical model to simulate the gas-phase reaction

kinetics occurring in the discharge and the afterglow of the CF₄/He plasma. This model provides a means of studying the fluorine atoms and other reactive species as they evolve in time or distance downstream of the reactor. The one-dimensional “plug-flow” model assumes there is no gas mixing in the axial flow direction and perfect mixing in the cross-stream direction. The reaction mechanism includes neutral species (He, CF₄, F, CF₃, CF₂, CF, C₂F₆, C₂F₅, C₂F₄, C₂F₃, and F₂), ions (F⁻, CF₃⁻, CF₃⁺, CF₂⁺, He⁺, He₂⁺), and electronically excited helium (He* and He₂^{*}) [38-46]. The numerical model comprises the simultaneous set of material balances for these nineteen species. For a given component, X, the material balance is:

$$\frac{d[X]}{dt} = \sum_i R_i, \quad (3)$$

where $[X]$ is the concentration (cm⁻³), and R_i is the rate of reaction i that produces or consumes X (cm⁻³s⁻¹).

Reactive species are generated in the plasma by electron impact with neutrals. For example, helium undergoes ionization via the following reaction:



The rate of this reaction is given by [38]:

$$R_2 = 2.58 \times 10^{-12} T_e^{0.68} \exp(-24.6/T_e) [He] n_e \quad (5)$$

This expression highlights the fact that one must know the electron temperature and density in the plasma in order to model the reaction kinetics. These parameters were estimated for the CF₄/He plasma using equations (1) and (2) above, and were found to be: $T_e = 2.5$ eV and $n_e = 6.1 \times 10^{11}$ cm⁻³.

Shown in Fig. 8 are the predicted densities of the ions and excited helium species in the discharge, assuming it was fed with 1.6 vol.% CF₄ in He at 760 Torr. The steady state densities of ions, He* and He₂^{*} are achieved within 1.0 mm of entering the plasma. Note that the density of He* is about 100 times higher than that of He₂^{*}. The most abundant ions are CF₃⁺, F⁻ and CF₃⁻, which are in the range of 10¹² to 10¹³ cm⁻³. The total charge summed over all these ions and electrons equals zero, confirming that the plasma is neutral. It is further noted that the F⁻ concentration is 3.0 × 10¹² cm⁻³, or about 5 times higher than the electron density. This indicates that the plasma is “electronegative,” which is consistent with studies of fluorine containing gas discharges [44].

Presented in Fig. 9 are the predicted profiles of the neutral species in the plasma and in the afterglow downstream of the electrodes. The carbon tetrafluoride is not shown in the figure. Its density is 3.1 × 10¹⁷ cm⁻³. The CF₄ is dissociated in the plasma into F, CF₂ and CF₃. The CF₂ and CF₃ achieve concentrations in the range of 10¹³ and 10¹⁴ cm⁻³ inside the discharge, but are rapidly converted to C₂F₆ in the afterglow. By contrast, the concentration of F atoms rises to 1.1 × 10¹⁵ cm⁻³ inside the plasma, and then remains relatively constant over 20 mm downstream. This is because the F atoms are consumed by a three-body collision, F + F + He = F₂ + He, which is a slow process at the plasma operating conditions [45]. The F atom density predicted

by the numerical simulation is in good agreement with the value measured by H₂ titration (see Fig. 6 above). This suggests that the numerical model is capturing the physics and chemistry of the process. However, further simulations must be performed to see if the model agrees with the experiments over a range of operating conditions.

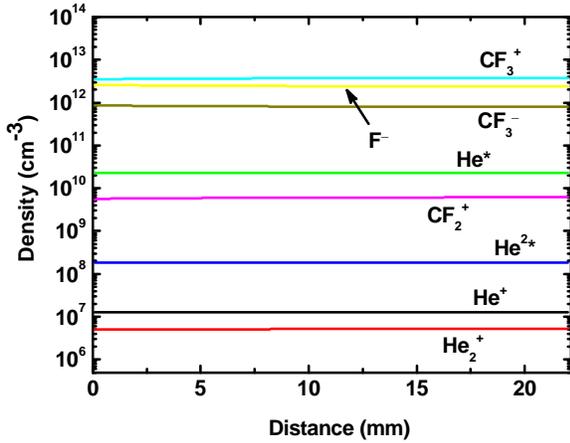


Fig. 8. Densities of ions and metastable helium in the CF₄/He plasma.

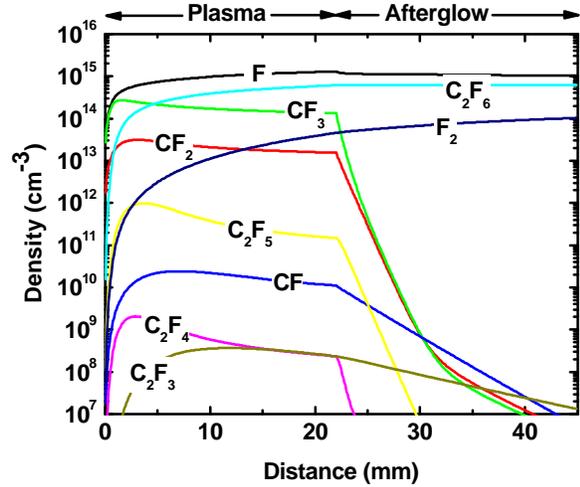
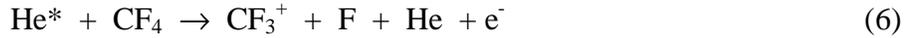


Fig. 9. Predicted profiles of the neutral species in the CF₄/He plasma and afterglow regions.

The active fluorine atoms are produced by several different processes in the plasma discharge. The CF₄ can be dissociated by collision with energetic helium atoms or electrons. The important reactions are:



According to the simulations, the reaction with metastable helium, Eq. (6), accounts for 70% of the fluorine atom production, whereas the electron impact reactions, Eqs. (7)-(9), account for the remainder.

To summarize the results present above, we have learned that our plasma source produces a high concentration of fluorine atoms, $\sim 10^{15} \text{ cm}^{-3}$, at atmospheric pressure and low temperatures, $\sim 390 \text{ K}$. The F atoms are generated primarily by impact with metastable helium atoms, which are in turn produced by collision with the energetic electrons in the discharge. The RF powered helium plasma exhibits an electron density and temperature in the range of $6.1 \times 10^{11} \text{ cm}^{-3}$ and 2.5 eV .

Uranium Oxide Etching

We have investigated the etching of uranium oxide with the atmospheric pressure plasma source [25]. The UO₂ samples were prepared by applying a uranyl nitrate solution to stainless

steel substrates. Then drying these samples in air at 343 K and baking them for 5 hours at 973 K. Each sample contained ~ 0.5 mg uranium. The plasma etching of UO_2 was performed with 15.0 Torr CF_4 , 6.6 Torr O_2 and 729.0 Torr He, at 300 W RF power and 473 K. Shown in Figs. 10 and 11 are scanning electron micrographs of samples before and after plasma etching for 2 min. It is found that the intact sample is a porous thin film about 20.0 microns thick. The image taken after etching reveals that the fluorine atoms penetrate into the layers, and strip away UF_6 from all the exposed surfaces. This process quickly reduces the film into small aggregates 100 to 500 nm in length.

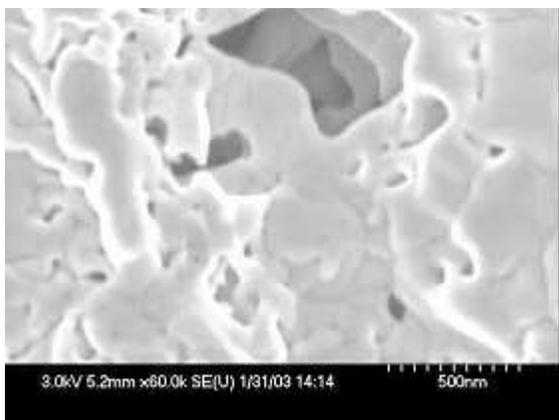


Fig. 10. Image of UO_2 film before etching.

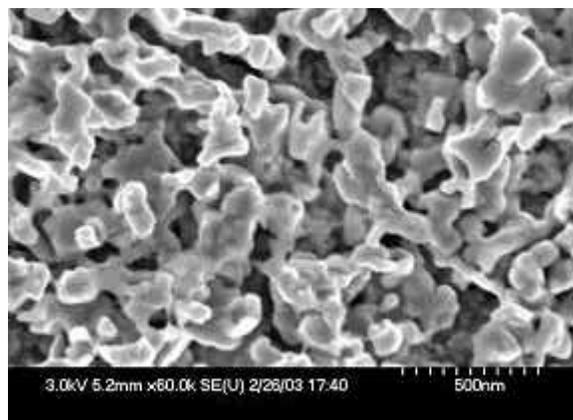


Fig. 11. Image of UO_2 film after a 2-min etch.

Shown in Fig. 12 are x-ray photoemission spectra of the U $4f_{5/2}$ and $4f_{7/2}$ states before and after etching uranium oxide samples with the $\text{CF}_4/\text{O}_2/\text{He}$ plasma. The U $4f_{7/2}$ of the fresh sample has a binding energy of 378.5 eV, which is indicative of the U^{+4} oxidation state (UO_2). After exposed to the plasma for 1 min., the $4f$ peaks shift 3.0 eV to higher binding energy due to uranium oxidation to U^{+6} . The intensity of photoemission peaks decrease rapidly with further treatment, such that after 5 min, essentially all of the uranium film has been removed. A plot of the integrated intensity of the U $4f_{7/2}$ peak with treatment time is shown in Fig. 13. Over the first

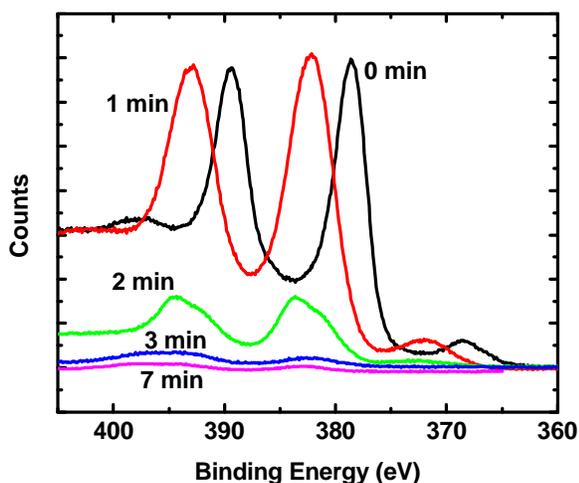


Fig. 12. XPS spectra of uranium oxide films before and after plasma etching.

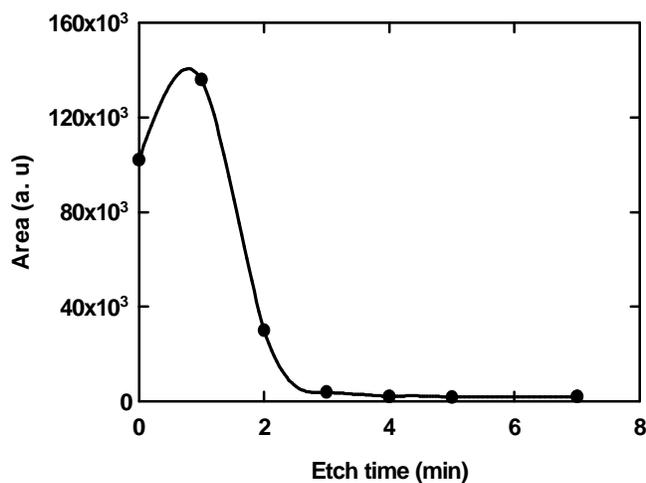


Fig. 13. Area of the U $4f_{7/2}$ peak as a function of plasma etching time.

minute, the intensity increases because the etching process initially increases the exposed surface area of the film. Then the intensity rapidly decays as the uranium oxide particles are stripped away.

Presented in Fig. 14 are deconvoluted U $4f_{7/2}$ photoemission spectra obtained after etching 2 min at 373 and 473 K. These spectra are composed of 3 overlapping bands due to the presence of different U^{+n} oxidation states. Initially, one peak at 380.8 eV is observed due to UO_2 . Upon exposure to the fluorine plasma, this peak disappears and is replaced by the 3 bands at 381.6, 383.3, and 386.0 eV. The lowest energy state is assigned to uranium oxyfluoride (UOF_2) with +4 valence, while the peaks at 383.3 and 386.0 eV are assigned to uranium oxyfluorides with +6 valence, i.e., UO_2F_2 and UOF_4 , respectively [47,48].

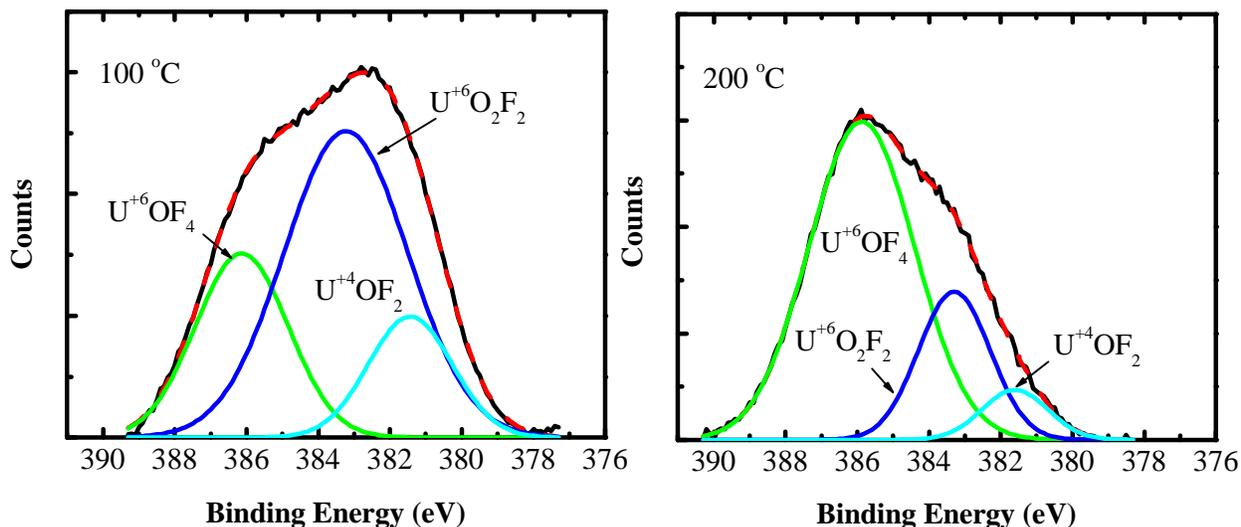


Fig. 14. Deconvolution of U $4f_{7/2}$ peaks after a 2-min etch at 100 and 200 °C.

The percentages of the uranium among the different chemical states have been calculated by taking the ratio of the area under a particular $4f_{7/2}$ band to that under all the $4f_{7/2}$ bands. It is found that UO_2F_2 is the dominant surface species following plasma etching at 373 K. On the other hand, UOF_4 constitutes 71% of the surface uranium at 473 K. The formation of UO_2F_2 has been observed after etching UO_2 in a low-pressure CF_4/O_2 plasma, and in UO_2 fluorination with F_2 [47,49]. The more heavily fluorinated species at 386.0 eV has not been observed previously. The etching rate at 473 K is 2 times faster than the etching rate at 373 K. Evidently, surface intermediates play an important role in the etching process.

To allow our results to be compared to other actinide etching studies, the surface reaction rate, R_s , may be estimated from the following equation:

$$R_s = \left(\frac{vAr}{M_{UO_2}} N_a \right) \frac{1}{S} \quad (\text{molecules/m}^2 \cdot \text{s}), \quad (10)$$

where r is the density of amorphous UO_2 (4.8 g/cm³) [50], N_a is Avogadro's number, M_{UO_2} is the molecular weight of UO_2 (270.03 g/mole), v is the etch rate ($\mu\text{m}/\text{min}$), A is the area of the sample, and S is the total surface area of the film. Based on the SEM image taken after 2 min of etching, the film may be assumed to contain 24 pores per μm^2 with an average pore diameter of

0.1 μm . If it is further assumed that the pores are cylindrical and uniform throughout, then a film surface area of $8.8 \text{ m}^2/\text{g}$ is obtained. For an etching rate of $4.0 \mu\text{m}/\text{min}$, a surface reaction rate of $1.9 \times 10^{19} \text{ UF}_6 \text{ molecules}/\text{m}^2 \cdot \text{s}$ is calculated from equation (10). This reaction rate compares favorably with other actinide etching studies. For example, a rate of $1.9 \times 10^{17} \text{ PuF}_6 \text{ molecules}/\text{m}^2 \cdot \text{s}$ was reported for the removal of PuO_2 films with a low pressure CF_4/O_2 plasma [2].

During etching, the surface of the uranium oxide film is quickly converted into uranium oxyfluoride, mainly UOF_4 . Evidently, these fluorinated species must build up on the surface before the incoming F atoms can react with it and produce the volatile UF_6 reaction product. This is consistent with previous studies of heavy metal etching. For example, Kim et al. [47] observed the formation of uranium oxyfluorides during the low-pressure plasma etching of UO_2 . In addition, we found that tantalum foil surfaces become covered with TaO_xF_y species upon exposure to the atmospheric pressure $\text{CF}_4/\text{O}_2/\text{He}$ plasma at 573 K [15].

Although we do not have enough evidence to make any definite conclusions, it appears that the kinetically slow step in the overall process may be the reaction of gas-phase or adsorbed F atoms with UOF_4 species to desorb UF_6 . Machiels and Olander [51] have proposed a similar mechanism for tantalum etching in an F_2 molecular beam, in which the rate-limiting step is the reaction between adsorbed F and a fluorinated surface layer. In this regard, it is interesting to estimate the collision rate of F atoms with the film surface relative to the rate of F atom conversion into UF_6 . From kinetic theory, the former rate is estimated to be $1.8 \times 10^{23} \text{ molecules}/\text{m}^2 \cdot \text{s}$ for an F atom density of $1 \times 10^{21} \text{ m}^{-3}$ above the film surface. On the other hand, equation (10) yields an F atom conversion rate into UF_6 of $1.1 \times 10^{20} \text{ molecules}/\text{m}^2 \cdot \text{s}$. These calculations suggest that in the present process, the overall reaction is not limited by the flux of F atoms to the surface.

The above discussion highlights what we have learned so far about the atmospheric-pressure plasma etching of radioactive elements. In fluorine-containing plasmas, uranium may be etched at rates up to 4.0 microns per minutes without any ion bombardment. Our study reveals that the atmospheric pressure plasma can produce high concentration of fluorine atoms, $\sim 10^{15}\text{-}10^{16} \text{ cm}^{-3}$, which are the main reactive species responsible for this reaction. The overall etch process is likely controlled by the reaction between fluorine atoms and adsorbed uranium oxyfluorides. These results demonstrated the viability of the atmospheric pressure plasma for decontamination and decommissioning of DOE facilities.

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. 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 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. We have established that this technology can rapidly and selectively strip uranium from steel surfaces at low temperature. Our research has demonstrated that the atmospheric pressure plasma is a viable and potentially superior alternative to current cleanup technologies.

- b) *How the new scientific knowledge will improve DOE compliance and cleanup approaches:*** The atmospheric-pressure plasma source produces a high flux of reactive fluorine species that etch radioactive metals at rates up to several microns per minutes. Uranium, plutonium and other actinide elements are converted into volatile fluorides, e.g., UF₆ and PuF₅, 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 atmospheric pressure plasma technology 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. Furthermore, the plasma source may be scaled up to treat large surface areas, or 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. 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 field-testing of D&D applications. In particular, we have demonstrated that the atmospheric pressure plasma can rapidly and selectively strip uranium from steel surface at low temperature. In addition, we have developed innovative plasma source designs for treating areas larger than 1 ft² and at much higher applied powers. Applying these results to plutonium etching would bring us to the point where we could test the plasma for decommissioning and decontamination purposes.
- d) *How the project has impacted individuals, laboratories and institutions:*** This EMSP project fostered a 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. The technology has been licensed to two startup companies, Apjet, Inc., and SurfX Technologies LLC, who are developing products for D&D and other commercial applications. In addition, the EMSP project provided funding for the education of 2 postdoctoral scholars (Jaeyoung Park and Guowen Ding) and 4 graduate students (Steve Babayan, Xiawan Yang, Gregory Nowling and Maryam Moravej). 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 for decontamination of TRU wastes. In particular, it is essential that we extend our “bench-top” results on uranium to 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 carbon tetrafluoride/helium plasmas, and have demonstrated the capability of the plasma technology for uranium etching. 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 plutonium and other actinide elements.
- 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. This collaboration has improved UCLA’s capabilities in gas phase spectroscopy and measurement of plasma physical properties.
- g) ***How the research has advanced our understanding in the area:*** This research has led to a fundamental understanding of the physics and chemistry of atmospheric-pressure plasmas and their interaction with materials. We have characterized the plasma physics of the atmospheric pressure plasma. At the same time, we have identified the gas-phase chemical reactions occurring in carbon tetrafluoride-containing plasmas, and investigated the surface kinetics occurring in plasma etching of uranium. In addition to significantly advancing plasma and materials science, this research project has led to new applications of plasmas in the ambient pressure regime. One of the most significant applications 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.
- h) ***Additional scientific and other hurdles to be overcome:*** We have a number of scientific and technological hurdles to overcome. The scientific hurdles include understanding the principles governing the operation of non-equilibrium argon and air plasmas at atmospheric pressure. Using argon or air would further reduce the operating costs. We also need to field test the atmospheric pressure plasma under realistic D&D conditions. This research is described in detail in the Future Work section below.

In addition, we must consider how to transform the atmospheric-pressure plasma technology into a serviceable tool for decontamination and decommissioning applications. The atmospheric-pressure plasma etches radioactive elements 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. Finally, it would be valuable to have an online detection system to ensure that the plasma 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 may be implemented for a variety of D&D applications.

- i) ***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 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. The contact person at the NSF is Dr. Farley Fisher (ffisher@nsf.gov). Several companies have expressed a strong interest in this technology. Apjet, Inc., and Surfex Technologies LLC, have licensed this technology from the University of California, and are developing a broad range of commercial products.

Project Productivity

The project accomplished most of the proposed goals. We have gained a solid understanding of the physical principles governing the operation of the atmospheric-pressure plasma. 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. In addition, we were able to resolve the gas-phase chemical kinetics occurring in plasmas operated with carbon tetrafluoride and helium. Through the EMSP grant, we made substantial improvements in the plasma source design, and were able to scale up the source to treat large surface areas. Moreover, we demonstrated that the fluorine-containing atmospheric pressure plasma can selectively etch uranium from steel surfaces at rates up to 4.0 microns per minute. We have made important progress in understanding the surface reaction mechanism of uranium etching. This work demonstrated the capability of the atmospheric pressure plasma to the decontamination of transuranic wastes. The only part we were unable to achieve was field-testing under realistic D&D conditions. This part of the work was supposed to be carried out at LANL, and was not done for reasons that are unknown to the author of this report (RFH).

Personnel Supported

Robert F. Hicks, UCLA Professor
Hans W. Herrmann, LANL Technical Staff

Jaeyong Park, Post-doctoral Scholar
Guowen Ding, Post-doctoral Scholar

Steven E. Babayan Graduate Student
Xiawan Yang, Graduate Student
Gregory R. Nowling, Graduate Student
Maryam Moravej, Graduate Student

Publications

Publications in 2000

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Publications in 2002

9. Nowling, G. R., Babayan, S. E., Jankovic, V., and Hicks, R. F., "Remote Plasma-Enhanced Chemical Vapour Deposition of Silicon Nitride at Atmospheric Pressure," *Plasma Sources Sci. Technol.* **11**, 97-103, 2002.

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Publications in 2003

11. Yang, X., Babayan, S. E., and Hicks, R. F., "Measurement of the Fluorine Atom Concentration in a Carbon Tetrafluoride and Helium Atmospheric-Pressure Plasma," *Plasma Sources Sci. Technol.*, **12**, 484-488, 2003.
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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. Babayan, S., Ding, G., Nowling, G., Yang, X., and Hicks, R. F., "Characterization of an Atmospheric-Pressure Nitrogen Plasma", American Vacuum Society, 47th International Symposium, Boston, MA, October 3, 2000.
2. Babayan, S., Ding, G., Nowling, G., and Hicks, R. F., "Determination of the Reactive Species in an Atmospheric-Pressure Nitrogen Plasma", American Institute of Chemical Engineers 2000 Annual Meeting, Los Angeles, CA. November 15, 2000.
3. Hicks, R. F., Babayan, S. E., Jeong, J. Y., Ding, G., and Selwyn, G. S., "Non-Equilibrium, Atmospheric Pressure Plasmas for Semiconductor Materials Processing," 199th Meeting of The Electrochemical Society, Washington D.C., March 29, 2001
4. Nowling, G., Babayan, S. E., Jankovic, V., and Hicks, R. F., "Silicon Nitride PECVD at

- Atmospheric Pressure,” American Vacuum Society 48th International Symposium, San Francisco, CA, October 29, 2001.
5. Nowling, G. R., Babayan, S. E., Jankovic, V., and Hicks, R. F., “Silicon Nitride PECVD at Ambient Pressure” American Institute of Chemical Engineers Annual Meeting, Reno, NV, November 7, 2001.
 6. Hicks, R. F., and Babayan, S. E., “High Pressure Photoresist Ashing Process,” Third International Conference on Microelectronic Interfaces,” Santa Clara, CA, February 14, 2002.
 7. Nowling, G. R., Babayan, S. E., Jankovic, V., and Hicks, R. F., “Deposition of Silicon Nitride at Atmospheric Pressure,” Spring Materials Research Society Meeting, San Francisco, CA, April 2, 2002.
 8. Babayan, S. E., Nowling, G. R., Jankovic, V., and Hicks, R. F., “Deposition of Silicon Nitride at Atmospheric Pressure,” International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 26, 2002.
 9. Hicks, R. F., “Non-Equilibrium Atmospheric Pressure Plasmas for Surface Treatment,” Gordon Research Conference on Plasma Processing Science, Tilton, NH, July 25, 2002.
 10. Hicks, R. F., “Low-Temperature, Atmospheric-Pressure Plasma Processing of Materials,” 49th International Symposium of the American Vacuum Society, Denver, CO, November 5, 2002.
 11. Moravej, M., Babayan, S. E., Nowling, G. R., Yang, X., and Hicks, R. F., “Plasma Enhanced Chemical Vapor Deposition of Hydrogenated Amorphous Silicon at Atmospheric Pressure,” American Vacuum Society 49th International Symposium, Denver, CO, November 5, 2002.
 12. Nowling, G. R., Babayan, S. E., and Hicks, R. F., “Gas-Phase Chemistry of Silicon Nitride PECVD Process at Ambient Pressure,” American Institute of Chemical Engineers Annual Meeting, Indianapolis, IN, November 8, 2002.
 13. Hicks, R. F. “Low-Temperature, Atmospheric Pressure Plasma Processing of Materials,” Seminar at Advanced Micro Devices, Sunnyvale, CA, December 12, 2002.
 14. Hicks, R. F., "Low-Temperature, Atmospheric Pressure Plasma Processing of Materials," International Microprocesses and Nanotechnology Conference, Tokyo Fashion Town, Tokyo, Japan, October 29, 2003.
 15. Moravej M, Babayan, S. E., Yang, X., Nowling, G. R., and Hicks, R. F., “Physics of High-Pressure Helium and Argon Plasmas,” American Vacuum Society 50th International Symposium, Baltimore, MD, November 3, 2003.
 16. Yang, X., Babayan, S. E., Nowling, G. R., Moravej, M., and Hicks, R. F., “Measurement of

the Fluorine Atom Concentration in a Carbon Tetrafluoride and Helium Atmospheric-Pressure Plasma,” American Vacuum Society 50th International Symposium, Baltimore, MD, November 5, 2003.

17. Hicks, R. F., "Atmospheric Pressure Plasma Sources for Low-Temperature Materials Processing," Plasma Etch Users Group, Northern California Chapter of the American Vacuum Society, Sunnyvale, CA, November 13, 2003.
18. Babayan, S. E., "Commercial Atmospheric Pressure Plasma Sources and Applications," Plasma Etch Users Group, Northern California Chapter of the American Vacuum Society, Sunnyvale, CA, November 13, 2003.
19. Yang, X., Moravej, M., Babayan, S. E., Nowling, G. R., and Hicks, R. F., "Etching of Uranium Oxide with a Non-Thermal, Atmospheric Pressure CF₄/O₂/He Plasma," American Institute of Chemical Engineers Annual Meeting, San Francisco, CA, November 18, 2003.
20. Nowling, G. R., Babayan, S. E., Yang, X., Moravej, M., and Hicks, R. F., "Silicon Nitride PECVD at Elevated Pressures," American Institute of Chemical Engineers Annual Meeting, San Francisco, CA, November 18, 2003.

We have attended several EMSP workshops and Symposiums 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 and Symposiums are listed below.

1. Babayan, S.B., Ding, G., Park, J., Henins, I., Hermann, H., Hicks, R.F., "Atmospheric Pressure Plasma Cleaning of Contaminated Surfaces," DOE EMSP Workshop, Atlanta, GA, April 26, 2000.
2. Yang, X., Nowling, G., Moravej, M., Babayan, S. E., Park, J., Herrmann, H., and Hicks, R. F., "Atmospheric Pressure Plasma Decontamination of Heavy Metals," EMSP Symposium at the 222nd ACS National Meeting, Chicago, IL, August 29, 2001.
3. Hicks, R. F., "Atmospheric Pressure Plasma Cleaning of Contaminated Surfaces," DOE EMSP Workshop, Oak Ridge, TN, November 27, 2001.
4. Yang, X., Babayan, S. E., Moravej, M., and Hicks, R. F., "Plasma Technologies for Detection and Removal of Transuranic Elements," EMSP Symposium at the 226th ACS National Meeting, New York, NY, September 11, 2003.

Transitions

With the demonstrated capability of etching transuranic waste, the atmospheric pressure plasma expands the range of applications of plasma technology within the U.S. Department of Energy. The decommissioning and decontamination of radioactive wastes can benefit

tremendously from this technology. 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 increasing commercial interest in the atmospheric pressure plasma for several applications, including surface treatment of plastics and other materials, deposition of thin films, and sterilization of food packages and medical equipment. This technology has been licensed to two startup companies, Apjet, Inc., and Surfx Technologies LLC, who are developing and marketing many exciting new products.

Patents

1. G. S. Selwyn, "Atmospheric-pressure plasma jet," U.S. Patent 5,961,772, October 5, 1999.
2. S. E. Babayan, G. S. Selwyn, and R. F. Hicks, "Deposition of coatings using an atmospheric-pressure plasma jet," U.S. Patent 6,194,036, February 27, 2001.
3. G. S. Selwyn, I. Henins, S. E. Babayan, and R. F. Hicks, "Large-area atmospheric pressure plasma jet," U.S. Patent 6,262,523, July 17, 2001.
4. H. W. Herrmann and G. S. Selwyn, "Atmospheric-pressure plasma decontamination/sterilization chamber," U.S. Patent 6,228,330, May 8, 2001.
5. S. E. Babayan and R. F. Hicks, "Low-temperature compatible, wide-pressure-range plasma flow device," U.S. Patent Application No. 20020129902, September 19, 2002.

Future Work

Future work needed to implement the atmospheric pressure plasma technology for D&D applications include (a) characterize the physics and chemistry of atmospheric pressure plasma containing carbon tetrafluoride, argon, and air, (b) determine the uranium oxide etching kinetics and its dependence on the density of fluorine atoms generated in the plasma, (c) carry out technology demonstration on TRU-contaminated waste at a DOE complex. With the knowledge gained from this research we will be able to optimize TRU etching rates, reduce operating costs, and extend the range of D&D applications.

Using argon to replace helium can reduce the operating costs in the atmospheric pressure plasma. We recently succeeded in generating an argon plasma. It exhibits an intense white glow that is much brighter than that observed with helium. This suggests that the argon plasma may have a higher electron density and/or temperature, which in turn, may be used to increase the flux of F atoms for TRU etching. However, before this can be attempted, we need to understand the physics and chemistry of the argon plasma. In particular, what is the range of conditions for

normal glow operation (flow rate, gap spacing, temperature, and RF power)? What are the electron temperature and density, and what is the rate of CF₄ dissociation into F and CF_x in this system? Experiments to generate low-temperature air plasmas have not been successful so far. However, we have several exciting avenues of research to explore that could someday make this technology a reality.

We would have liked to field test a prototype plasma system on TRU waste in collaboration with scientists at the Idaho National Environmental and Engineering Laboratory. Together with them, we could have investigated the decontamination of Pu-238, 239 and 240 coated materials.

Our technology shows great potential for providing the U.S. Department of Energy with a cost-effective solution to cleaning hundreds of contaminated buildings and structures throughout the nuclear weapons complex. Moreover, it can remove TRU contamination from equipment utilized by DOE personnel and thereby greatly reduce their health risks. It is our sincere hope that the Environmental Management Sciences Program will support this exciting research program once again in the future.

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Feedback

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