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ANALYSIS OF POTENTIAL COMPONENT CLEANING TECHNIQUES
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Abstract

Elevated temperature, elevated pressure water, supercritical carbon dioxide and helical resonator plasmas were investigated for potential use in surface cleaning. A surface analysis system consisting of X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy was used to evaluate surfaces exposed to water and supercritical carbon dioxide. Langmuir probe and silicon oxidation studies were used to evaluate the effect of oxygen plasmas on silicon surfaces. Silicon oxides were removed from silicon surfaces by water at temperatures above 260°C and pressures above 2000 psi; silicon oxidation and simultaneous dissolution of the oxide grown occurred under these conditions. A new approach for in-situ monitoring of subcritical and supercritical fluid density was devised.

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INTRODUCTION

Surface cleaning and surface preparation are critical processes for materials that contact plutonium. The use of organic solvent cleans typically generates significant contaminated waste and is often ineffective in removing radiolytically polymerized organic residues (encountered when oils are exposed to radio nuclides). As a result, vapor phase methods or the use of liquids that do not present environmental hazards are of much interest in current and future cleaning approaches. Promising methods of cleaning surfaces or altering surface properties that are consistent with the above limitations utilize supercritical or near-critical fluids and plasmas(1,2).

In this study, supercritical carbon dioxide (SCCD), elevated temperature, elevated pressure water, and oxygen plasmas have been investigated for their potential use in cleaning processes. Individual reactors were designed and built to study each of these processes, and preliminary characterization of surfaces exposed to the above fluids or plasmas was performed. Details of the equipment and the results obtained are described below.

EXPERIMENTAL DETAILS

Supercritical and Near-Critical Fluid Reactors

Three different types of reactors were designed and built for SCCD and high temperature, high pressure water experiments. The initial system used for measurements of fluid density in a static configuration was a stainless steel cell of volume 7.2 cm³. This cell could operate at temperatures up to 200°C and pressures to 10,000 psi and could hold a sample that was 1.3 cm on a side. A sapphire window allowed observation of the sample and permitted a laser beam to be incident on the sample in the cell.

Because of the need for surface analysis of cleaned samples, the reactor for SCCD flow (rather than static) studies had to be attached to a surface analysis (XPS and Auger Spectroscopy) unit so that in-situ transfer of samples into an ultra-high vacuum (UHV) chamber could be performed. The reactor design used to achieve this wide disparity in pressure incorporated a stainless steel VCR gasket into a "bayonette" style arrangement. This system has an upper and lower section which, when pressed together, seal off a small sample treatment (high pressure) chamber. The seal between the upper and lower sections is made with an imitated 3/4" VCR fitting and gasket. Figure 1 shows diagrams of the high pressure chamber at different points during an experiment. Figure 1a displays a sample (on a sample stub) being placed onto the stub holder. In Fig. 1b, the upper and lower sections are pressed together to form the high pressure seal; in this high pressure chamber, exposure of the sample to a supercritical fluid (SCF) occurs. After sample exposure, the SCF can be evacuated to a pressure of approximately 100 mtorr via a roughing pump (Fig. 1c). The high pressure chamber is then opened to the UHV chamber (Fig. 1d), and the remaining SCF removed by the UHV pump. The sample is then ready for transfer to the surface analysis system.

A six way cross with copper gasket flanges provides the UHV environment surrounding the high pressure chamber. The upper and lower flanges of this cross are bolted to the components which provide the linear motion required to open and close the cleaning chamber. These components are designed to provide over 50,000 pounds of force to establish the high pressure /high vacuum seal without stressing the vacuum fittings. A bellows assembly is used to maintain vacuum integrity around the moving parts. A simplified diagram of the chamber opening/closing apparatus is shown in Fig. 2.

One of the four remaining flanges on the six way cross is connected to a turbo pump, one to a nitrogen vent and roughing pump, one to a window/quick access door, and one to the surface analysis system. Pressure is measured with an ion gauge positioned between the turbo pump and the six way cross. An isolation valve allows the cross to be vented for gasket changing or repair (using nitrogen to avoid contamination) without shutting down the turbo pump. The window/quick access door permits viewing of the sample during transfer and provides pressure relief if the high pressure/high vacuum seal fails. Sample transfer is carried out through the flange connected to the surface analysis system using two transfer arms at right angles (Fig. 3). The two systems are separated by a gate valve that is open only during sample transfer.

In order to establish the supercritical conditions needed in the reactor chamber in a flow configuration, an ISCO 260D syringe pump capable of pressures up to 7500 psi and flows to 90 ml/min is used. As shown in Fig. 4, fluid from the pump flows through a temperature controlled heat exchanger into a 0.5 l mixing chamber (HiP GC-9). A temperature controller regulates the temperature of the mixing chamber. The fluid then moves through another heat exchanger into one of the cleaning chambers described above. A Brooks 5960 mass flow meter measures flow downstream from the cleaning chamber. A metering valve used in conjunction with the pump controls allows adjustment of the pressure and flowrate.

For elevated temperature, elevated pressure water (static) experiments, either a modified Nupro 50 check valve or a 3/4" Swagelock tee was used as a reactor. The system used to establish water conditions consisted of a high pressure manual syringe pump and a heat exchanger (Fig. 5). Pressure was measured with a transducer and controlled by adjusting the syringe pump displacement. Feedback temperature control maintained the proper temperature of the heat exchanger and sample chamber. The thermocouple used to control the sample chamber temperature was placed directly in the fluid to improve measurement accuracy. After placing the sample in the reactor, the chamber was purged with water vapor to remove air, and then sealed for the experiment.

Helical Resonator Plasma Reactor

A helical resonator plasma reactor system was designed and built (Fig. 6). The helical resonator source (quarter wave design) has a helical copper coil enclosed in a glass tube which, in turn, is surrounded by a grounded copper coaxial cylinder. rf power (3-30 MHz) can be coupled directly at a point on the helix. When an integral number of quarter waves of the rf field are exactly the same length as the copper coil, resonance is achieved and coupling of rf

energy to the low pressure gas within the quartz tube is very efficient. The plasma source can operate to pressures as low as 10^{-5} torr.

The helical resonator reactor chamber is made of aluminum, with flanges on two sides as well as the top and bottom. Roughing and turbo pumps connect to the bottom flange, while the one side flange connects via the quartz tube to the plasma source so that plasma can enter the sample chamber perpendicular to the substrate. The top flange houses the support rod for the substrate holder, external bias connection and heater connection for the substrate holder and a port for the Langmuir probe. Langmuir probe construction is shown in Fig. 7. A high vacuum gate valve is positioned at the turbo pump inlet and a butterfly valve at the roughing pump inlet. The turbo pump can be used to evacuate the chamber to 10^{-8} torr, while the mechanical pump supplies initial chamber evacuation and serves as the pump during processing. The butterfly valve permits pump throttling to establish pressure and pump speed. System base pressure reached $\sim 1.5 \times 10^{-6}$ torr.

Experiments utilized 75 mm diameter silicon wafers clamped onto an aluminum holder with an aluminum retaining ring. The holder and wafer were surrounded by a quartz enclosure with a 50 mm opening at the front so that a defined area of silicon was exposed to the plasma; this established current density during processing.

RESULTS AND DISCUSSION

Near-Critical Water Experiments

In these studies, a new method of stripping thermally-grown silicon dioxide layers, which utilizes the solubility of SiO_2 in water at elevated pressure and temperature is investigated. If optimized, this process may be attractive when compared to competing technologies such as liquid or vapor phase hydrofluoric acid (HF) treatments, due to the high costs associated with waste disposal and chemical handling in traditional methods. Deionized water is the only fluid used in this process and the only waste is water and silicon dioxide.

Considerable information exists on quartz solubility in water from geological studies (3) and from hydrothermal growth of silicon dioxide crystals (4). Thermally-grown silicon dioxide, formed by thermal oxidation of silicon at temperatures above 800°C , has the same stoichiometry as quartz, although the material is amorphous compared to crystalline quartz. Thus, similar water solubility effects are expected with the two materials.

Initial experiments to test the feasibility of thermal SiO_2 removal used a 50 nm oxide. After recording a silicon 2p XPS spectrum, the sample was exposed to water at 275°C and 3500 psi. After 4 minutes, the pressure was reduced to atmospheric pressure and another XPS spectrum recorded. The sample was placed back in the high pressure chamber, the temperature set to 280°C and a pressure of 3500 psi. After 30 min., the sample was removed from the chamber and another spectrum recorded. The three spectra are shown in Fig. 8. Before water treatment, only one peak appeared at 104 eV, consistent with a silicon dioxide

surface. After 4 min. of water exposure, a small elemental silicon peak was observed at 99 eV. In this electron energy range, XPS is sensitive to a depth of ~10 nm; the SiO₂ thickness was thus around this value. Also, the SiO₂ peak was shifted compared to the initial data, indicating reduced surface charging and thus a thinner oxide surface layer after water treatment. After 30 min., the SiO₂ peak was smaller and the silicon peak dominated; in addition, further peak shifting was observed, suggesting more oxide thinning.

Due to the high activity of elevated temperature elevated pressure water, attack of the stainless steel reactor parts is possible. None of the silicon or silicon dioxide samples investigated showed metal (iron or chromium) contamination, indicating that if metal dissolved and redeposited onto the sample surfaces, the concentration was below approximately 0.5 atomic percent.

Silicon dioxide dissolution rates were obtained by exposing 50 nm thermally grown oxides (B-doped, (100) wafers oxidized at 900°C in steam) to water at 2000 psi and temperatures between 260 and 305°C. Attempts to oxidize "bare" silicon at various pressures (above and below the critical point) and temperatures between 280 and 420°C indicated that after 15 min., 5 nm of SiO₂ formed on silicon at 420°C; we thus concluded that oxide growth under our conditions would not significantly affect our dissolution rate studies. Figure 9 shows SiO₂ removal data. From a linear fit of the data, the dissolution rates increased with increasing temperature.

Some of the data obtained when the remaining oxide film was less than 10 nm was not consistent with linear removal rates. In addition, for some samples, up to 10 nm of oxide remained when complete removal was expected. At least some of these results could be explained by silicon surface roughening. To evaluate this possibility, several samples that had been treated with elevated temperature and pressure water were examined with scanning electron microscopy (SEM). Silicon dioxide samples exposed to water at 305°C showed surface pitting, while samples exposed at 260 and 280°C did not. The morphology of the silicon surfaces was very different from that of the SiO₂ surfaces. At 260 and 280°C, crystalline structures, each approximately 100 to 1000 nm across, appeared on the surface; XPS indicated that these crystals were SiO₂. On the other hand, thermally-grown SiO₂ samples, etched only partially at temperatures of 260 and 280°C, showed reasonably smooth surfaces (rms roughness of 0.17 and 0.18, respectively, from atomic force microscope (AFM) measurements), with some features (~8/micron²) approximately 4 nm high and 60 nm across.

SEM and AFM results indicated that the silicon substrate, as well as the SiO₂, was attacked by the water. To confirm this, microbalance measurements of silicon samples were performed before and after water exposure. Samples exposed at 285°C and 3500 psi for 13 min. were etched significantly. Assuming uniform silicon removal, an etch rate of 154 nm/min. was calculated; this rate is ~25 times faster than that of SiO₂. At this etching rate, significant amounts of SiO₂ can accumulate in the fluid and subsequently precipitate when the chamber pressure is reduced. The SiO₂ crystals observed in the SEM and AFM images described above were most likely formed in this manner. Furthermore, the erratic ellipsometry data noted for samples with thin SiO₂ films remaining is also consistent with

these results. Silicon samples without thermally-grown SiO_2 remaining were attacked rapidly by the elevated temperature water, and displayed an increased precipitation of oxide when the experiment was terminated.

In order to evaluate the kinetics of SiO_2 dissolution, we began with an expression proposed previously for quartz dissolution in water (5)

$$\frac{r_{\text{Si(OH)}_4}}{\gamma_{\text{Si(OH)}_4}} \left(\frac{M}{A} \right) = k_+ (a_{\text{SiO}_2}) (a_{\text{H}_2\text{O}})^2 - k_- (a_{\text{Si(OH)}_4}) \quad [1]$$

where $r_{\text{Si(OH)}_4}$ is the rate of molality increase of the dissolved species Si(OH)_4 per unit surface area of quartz, M is the mass of water, A is the quartz surface area, $\gamma_{\text{Si(OH)}_4}$ is the activity coefficient of the dissolved species, a_{SiO_2} is the activity of the dissolved species, k_+ is the quartz dissolution rate constant, and k_- is the quartz redeposition rate constant. Standardization of the equation to one kilogram of water gives an expression for the molar rate of appearance of the dissolved species per unit surface area. Since the concentration of Si(OH)_4 is close to zero in these experiments, the activity of the Si(OH)_4 and the activity coefficient were assumed to be zero and unity, respectively. Activities of the quartz and water are assumed to be unity due to their high density (Poynting factor close to unity). With these assumptions, the equation becomes

$$\frac{r_{\text{Si(OH)}_4}}{A} = k_+ \quad [2]$$

thereby relating directly the molar rate of Si(OH)_4 appearance to the forward rate constant. For the flat wafer samples used, molar removal rate per unit area can be expressed as

$$\frac{r_{\text{SiO}_2}}{A} = \frac{\rho V}{A dt} = \frac{\rho A dx}{A dt} = \rho dx/dt \quad [3]$$

where ρ is the molar density of silicon dioxide, V is the volume of silicon dioxide removed, and dx is the thickness of silicon dioxide removed. Since the silicon dioxide removal rate is equivalent to the appearance of Si(OH)_4 , the last two equations can be combined to give an expression relating the forward rate constant to the oxide thickness removed per unit time.

$$k_+ = \rho dx/dt \quad [4]$$

Etch rate constants calculated using Eqn. [4] are listed in Table 1. The equations of Dove and Crerar (5) were used to predict rate constants for quartz at the temperatures used in the present study; these values are listed in Table 1 for comparison. The rates for thermally-grown SiO_2 from the present study are consistently higher than those predicted for quartz. This result is reasonable since thermally-grown SiO_2 is amorphous and thus less dense, with more sites for easy water attack when compared to quartz.

Table 1. Rate constants for the removal of thermally-grown SiO_2 and quartz in water.

	Thermally Grown Silicon Dioxide	Quartz (Ref. 5)
Temperature ($^{\circ}\text{C}$)	$\log k_+$	$\log k_+$
260	-5.75	-6.88
280	-5.47	-6.61
305	-5.16	-6.27

Fig. 10 shows an Arrhenius plot of the rate constants obtained for dissolution of thermally-grown SiO_2 . The slope yields an activation energy of 76.6 (+/-6.3) kJ/mol; activation energy values reported for quartz dissolution range from 65 to 95 kJ/mol (6-8). For the temperature range 200 to 300°C, Dove and Crerar (5) report a value of 71.3 (+/-8) kJ/mol. Our value of the activation energy is within the range of reported values for quartz. The agreement of the activation energies along with the similarity of chemical composition, suggests that the dominant mechanism for quartz and thermally-grown SiO_2 dissolution in elevated temperature and pressure water is the same.

Supercritical CO_2 (SCCD) Experiments

Preliminary experiments were performed to determine if an organic resist material (phenolformaldehyde resin) could be removed by SCCD exposure in our static cell. A 50 nm resist film on a silicon substrate was exposed to SCCD at conditions ranging from 35-70°C and pressures up to 4000 psi. These attempts at film removal were unsuccessful, resulting in no detectable film removal nor film swelling. However, when a 10% methanol/ CO_2 mixture at 1700 psi and 60°C was used for 10-15 sec., interference color changes were noted in the resist material. Clearly, film is being removed with this mixture.

Our initial efforts to monitor organic film thickness during SCCD studies invoked in-situ interferometry using a He-Ne laser beam. During these attempts, we noted that the laser beam, which reflected off the silicon surface through the window in the static cell, was shifted in position as critical conditions were approached and supercritical conditions established. The beam displacement was measured and the refractive index calculated; results of these calculations agreed closely with Lorentz-Lorenz predictions (9), as shown in Fig. 11. Furthermore, both displacement and refractive index were nearly linear functions of density (Fig. 12), as calculated from an Equation of State for CO_2 (10). These relationships might permit the development of a real-time, rapid method to monitor fluid density. Since refractive index is also a near linear function of composition (11), this technique may be applicable to mixtures.

Preliminary studies were performed to ascertain the utility of the beam displacement method for determination of density in SCCD mixtures. Methanol was chosen as the cosolvent since its solubility is high in the supercritical state. Mixtures were prepared in the 500 ml mixing chamber attached to the high pressure cleaning chamber. The appropriate amount of methanol for a specific mixture at 80°C and 3000 psig was injected into the mixing chamber. After equilibration, CO_2 was pumped slowly into the chamber until the pressure reached the desired level. The system was then allowed to equilibrate for several hours.

Refractive index versus density data for a 10% methanol in CO_2 mixture are shown in Fig. 13. Obviously, the mixture refractivity is not predicted well by a linear combination of methanol and CO_2 refractivities:

$$R_{LL}(\text{mixture}) = x_c[R_{LL}(\text{carbon dioxide})] + x_m[R_{LL}(\text{methanol})] \quad [5]$$

where x is weight percent and R_{LL} is refractivity. The observed refractivity is higher than predicted, indicating significant chemical interaction between methanol and CO_2 . The refractivity of the mixture did not change with density, suggesting that the chemical interactions in the mixture are essentially constant under the conditions studied. Additional studies are needed here, but first a method of obtaining exact mixture compositions at the elevated pressure and temperature conditions must be developed.

Initial experiments using SCCD to remove a "native" silicon dioxide layer (~ 0.8 - 1.2 nm oxide grown on clean silicon surfaces during air exposure) were performed. XPS was used to establish changes in surface composition due to SCCD exposure. A typical silicon spectrum displayed two peaks, one due to native silicon oxide and one due to the bulk silicon beneath. Since XPS samples a surface to a depth of 5-10 nm, the relative heights of these two peaks are an indication of the thickness of the oxide present on the silicon surface. At 2500 psi, 60°C and an SCCD exposure of 10 min., the native oxide thickness decreased; Fig. 14 shows the changes in XPS spectra before and after SCCD exposure. The bulk silicon peak occurred at 100.5 eV, while the silicon oxide peak occurred at 104 eV. Clearly, Fig. 14 indicates that the silicon oxide peak is smaller after a carbon dioxide treatment.

Further studies were performed with SCCD exposure of a 50 nm thermally-grown SiO_2 film formed at 900°C . Ellipsometric measurements indicated that no oxide was removed at 95°C and 3500 psi. The primary difference between the native oxide layer and the thermally-grown film is the water content (H_2O and OH bonds) and film density. Additional SCCD studies were performed on a 5 nm oxide film grown in our helical resonator plasma reactor at 30°C . This film is both less dense and has OH bonds in it. At 2500 psi and 60°C , little removal was noted. At 80°C , 3000 psi and 10 min. exposure, however, the oxide thickness decreased as indicated in Fig. 15. In addition to a reduction in the silicon oxide peak intensity, peak positions shifted. This shifting was due to a reduction in surface charging as a result of a decrease in dielectric thickness.

Subsequent studies with SCCD removal of native oxide layers on silicon indicated that reproducibility was a concern; sometimes SCCD could remove the layer easily and at other times removal was not observed. These results strongly suggest that the differences noted between samples related to the silicon surface cleaning procedure (prior to silicon substrate exposure to air to form the native oxide layer) and the water (and/or OH) content of the oxide layer. Subsequent studies will utilize a standard cleaning procedure (RCA clean) and mixtures of CO_2 with water and perhaps methanol.

As described in the previous section, water at elevated temperature and pressure can rapidly attack silicon surfaces. Experiments were thus performed to determine if CO_2 can oxidize or react with silicon surfaces. After sputter cleaning of the silicon surface so that only a silicon peak was observed by XPS, the sample was transferred (under vacuum) into the reactor chamber and exposed to CO_2 at 90°C and either 150 or 3000 psi pressure to obtain an indication of the effect of density on oxidation. After exposure at 150 psi for 15 min., little oxide was observed; upon exposure for another 15 min., no additional oxide formed. The total oxide thickness was less than that corresponding to a native oxide layer. Analogous

results were observed at 3000 psi. Obviously, silicon surfaces do not oxidize readily upon CO₂ exposure at 90°C.

Since SCCD can remove at least a portion of the passivating oxide on silicon, we performed similar experiments to determine if analogous results are observed on stainless steel (SS) surfaces. With silicon substrates, the conditions favoring oxide removal were high flow rate, and relatively high temperature and pressure. Thus, the conditions chosen for SS studies were temperatures between 70 and 90°C, pressures from 2500 to 3000 psi and flow rates up to 30 ml/min. Unfortunately, XPS is much less sensitive to Fe and Cr than to Si, and the passivating oxide layer on 316 SS is ~7 nm compared to <1.5 nm for silicon. The combination of these factors made detection of oxide thickness changes impossible. Although Fe to Cr ratios are difficult to calculate from XPS results, an approximate value can be obtained. This approach permits preferential etching of Fe or Cr to be detected. Surface sensitivity was enhanced by invoking angle-resolved XPS. Thus far, no conclusive evidence of preferential etching has been detected. Sputter cleaning of samples offers another route to increased sensitivity. Removal of surface carbon and oxygen increases the intensity of Fe and Cr peaks, and thereby improves the ability to obtain quantitative results. Unfortunately, sputter cleaning also removes the passivating oxide from SS, leaving behind a high energy surface. Also, reaction of the surface with CO₂ can change peak shapes and confuse data analysis. Therefore, a study of the oxidation behavior of SS in CO₂ is needed.

A 316 SS sample was sputter cleaned with argon until the Fe and Cr 2p XPS peaks indicated that only metal (no oxide) and a small amount of carbon, remained. The sample was then placed in the high pressure cell without air exposure and treated with SCCD at 3000 psi and 90°C for 10 min. Subsequent XPS analysis indicated that the surface oxygen had increased significantly; additional carbon was also present. The Fe 2p peak revealed that the sample had oxidized to a depth of ~7 nm, the thickness of the native or passivating oxide that forms upon air exposure. Analysis of the Cr 2p peak confirmed this result. The SS surface had either removed O from CO₂, or CO₂ was chemisorbed (perhaps dissociatively) onto the surface. Since Fe is a Fischer-Tropsch catalyst, this latter possibility is a likely scenario.

An additional indication of the high reactivity of SCCD with methanol additions arose from two observations during our studies. An aluminum bracket, used to hold the sample in our refractive index measurements describe above, was severely pitted and etched after a total exposure time of 5-7 days, to pure CO₂ and mixtures of CO₂ with 1-10% methanol at conditions ranging up to 4000 psi and 80°C. The conditions under which the etching took place were thus unknown. A few experiments were performed to determine the severity of conditions needed to obtain such results. A one micron layer of evaporated aluminum (on a silicon substrate) was exposed to a 1% methanol/CO₂ mixture at conditions up to 3500 psi and 80°C; no observable aluminum attack occurred. Finally, one of the silicon samples utilized in our studies with methanol/CO₂ mixtures had a small amount of nickel on the surface as indicated by XPS analysis. The nickel peak disappeared after mixture exposure. Since cleaning of metal substrates is an important application of SCCD technology, it is critical that the possibility of metal etching, and the conditions that lead to this effect are defined in subsequent studies.

Helical Resonator Plasma Studies

Helical resonator (HR) plasma sources are reported to be high density, low cost units capable of high etch rates (12,13). Unlike more expensive approaches to high density plasmas such as electron cyclotron resonance (ECR) sources that operate at gigahertz frequencies, HR does not require a magnetic field, uses megahertz frequencies and can operate at pressures between 10^{-5} to 10 torr. As will be seen below, we have not found all of these features to be amenable to stable operating points for the HR reactor, at least under the conditions investigated.

Since we must be able to assess plasma stability and operating characteristics, especially for a relatively new source, we began our studies by designing a system that allowed routine monitoring of the plasma density using a Langmuir probe. Furthermore, we felt that one way of determining the routine stability and control afforded with the HR unit was to investigate the feasibility of silicon oxidation, a process well-known and reasonably well-understood; these studies will establish a benchmark for cleaning investigations.

Initial plasma characterization studies using oxygen discharges at ~13 MHz indicated that the electron density could be increased into the low 10^{10} cm⁻³ range by changing the position of the rf tap point on the HR copper coil (Fig. 6). This change apparently lowered the capacitive coupling of power, which substantially reduced the substrate heating problems originally encountered. The change thus permitted higher rf power levels (up to 300 W) to be used, and higher electron densities to be obtained. Figure 16 shows the electron density and electron temperature as a function of rf power. Due to the higher value for electron density, 300 W was chosen as the power level for subsequent studies. Above 300 W, plasma stability degraded; the cause for this instability is currently unknown, but more will be reported concerning instabilities later in this report. The effect of gas pressure on electron density and electron temperature is shown in Fig. 17. Consistent with electron energy arguments, an increase in pressure resulted in a decrease in electron density and temperature. Despite a small decrease in electron density at 30 mtorr, this was the pressure chosen for subsequent studies. The choice was based on the magnitude of the floating potential (18 V at 10 mtorr compared to ~8 V at 30 mtorr), since the higher floating potential would require an increased bias to perform anodization experiments. Decreasing the residence time by increasing the oxygen flow rate from 25 to 40 sccm did not increase the ion density. Thus, the process conditions chosen for initial oxidation and anodization (positive external bias applied to the substrate holder) experiments were: 300 W rf power, 10 sccm oxygen flow rate, and 30 mtorr oxygen pressure.

Plasma oxidation under substrate floating conditions for one hour at a substrate temperature of 300°C resulted in an oxide thickness of ~13 nm as measured by ellipsometry. Under these conditions, the final thickness did not change with an increase of temperature to 400°C; apparently, the oxidation is being driven by field-assisted oxygen ion transport across the growing oxide layer. In an attempt to increase the rate to obtain thicker oxides in less time, biases of +5 and +20 V were applied to perform constant voltage anodization. The normalized electron densities did not change as the substrate holder was biased from +5 to

+20 V, indicating that the plasma was not perturbed by biases of this magnitude. Unfortunately, due to the low current densities obtained ($<0.1 \text{ mA/cm}^2$), anodization (oxidation) rates were still low. At +5 V, plasma anodization did not yield a substantial increase in oxide thickness relative to the substrate floating case, probably because the applied bias was slightly less than the floating potential under these conditions. At +20 V, similar results were obtained; this suggests that the surface potential drops to that of the floating potential as the oxide thickness increases (i.e., the electric field was reduced as the oxide thickness decreased during growth). As a result, preliminary constant current anodizations were performed at a current density of 0.05 mA/cm^2 ; 10.6 nm of oxide grew in 15 min. Unless current densities $>0.6 \text{ mA/cm}^2$ were used, no increase in oxide thickness was observed. Oxides grown under these conditions displayed electrical properties similar to those obtained from thermal oxidation of silicon at temperatures above 900°C .

Despite the efforts to enhance the electron density, the above conditions gave densities too low to be considered a "high density" source as has been claimed for helical resonators. By comparison, an inductively coupled plasma source or a parallel plate diode plasma source can give electron densities between 10^9 and 10^{10} cm^{-3} . The low densities may have resulted from either operation of the HR source at an "off-resonance" condition, or loss of "active species" (e.g., radicals, electrons, ions) during transport of the plasma species from the source to the substrate surface. The primary resonance condition was established by optimizing the rf frequency and the tap position; for our system, these were 13.1 MHz and 2.8 turns of the coil. In an attempt to minimize the loss of electrons during transport to the sample surface, an electromagnet was installed between the helical resonator source and the sample chamber. These modifications yielded both a higher plasma density (due to more efficient coupling of the rf energy) and reduced wall collisions (due to the magnetic field) during electron transport from the plasma region to the silicon surface. Langmuir probe measurements indicated that the electron densities were in the mid 10^{10} cm^{-3} range, with electron temperatures between 4 and 6 eV. Both trends will enhance the rates of oxidation and cleaning processes since higher electron currents and negative floating potentials (due to electron confinement) improve silicon anodization and organic layer oxidation rates. As expected, the electron temperature and electron density both decreased with pressure over the range 1 - 50 mtorr.

Preliminary anodization studies in oxygen resulted in higher rates than observed prior to system modification. For instance, at 10 mtorr, 350°C , and 1.5 mA/cm^2 , the rate was 6.7 nm/min., compared to 4.4 nm/min., under the previous conditions at 350°C . Unfortunately, the electromagnet, supplied to us by AT&T, did not generate a uniform magnetic field, since anodization rates across the wafer varied by as much as 12%. This effect is minor compared to another complication which arose due to the application of the magnetic field.

Oxides grown under the same pressure, temperature, rf power, magnetic field, and current density displayed a variation in thickness (at the same position on the wafer) of 50%! Interestingly, the thickness jumped between these values at random; each value of thickness, for a specific anodization time, was reproducible to less than 6%. It appears that the reactor is exhibiting multiple steady states (MSS).

Langmuir probe characterization showed a change in the floating potential and thus the current density through the wafer holder from run to run due to the magnetic field. Nevertheless, two distinct states characterized by two distinct values for electron temperature and electron density have not been identified. Since the current density during an anodization run is controlled by the current/voltage source, it is possible that the neutral species density in the plasma contributed substantially to the oxidation rate; optical emission studies may allow further investigation of this possibility. Preliminary efforts to move outside the MSS zone were invoked by varying the power from 300 to 250 W, the applied magnetic field from 125 to 100 G, and current density from 5 to 7.5 mA/cm², one parameter at a time. The behavior continued to mimic what appeared to be MSS (It should be noted that without an applied magnetic field, excellent reproducibility and no apparent MSS were observed).

A plot of oxide thickness versus time at 10 mtorr, 350°C, 300 W, 125 G and 5 mA/cm² is shown in Fig. 18a. This "lower" state resulted in a relatively low oxide thickness. The higher oxide thickness required higher voltage to draw the same current; thus, the "state" existing during anodization can be ascertained by monitoring the voltage drop. Fig. 18b shows the oxidation rate at the same conditions as above, but in the "higher" state, with a higher oxide thickness and higher voltage drop than that in Fig. 18a. The voltage drop ($V_{\text{appl}} - V_{\text{surface}}$) across the oxide versus the oxidation time is shown in Figs. 19a ("lower" state) and 19b ("higher" state).

Due to the large number of complications involved in using magnetic fields in helical resonator plasma sources, we decided to eliminate this aspect of the system, and accept a factor of two lower plasma density. Under such conditions, the plasma, as monitored by Langmuir probe measurements, appeared stable for the first time since the magnetic field was applied. Constant current anodizations of silicon were performed at 300 W, 30 mtorr oxygen, 350°C and 3.8 mA/cm². Oxide thickness reproducibility within 3% was obtained under these conditions; Fig. 20 shows typical data. These data are now being fit to various oxidation rate models, including those of Deal-Grove and Wolters/Zegers-van Duynhoven, in order to determine kinetic rate coefficients (14,15).

SUMMARY AND CONCLUSIONS

Preliminary studies of the use of elevated pressure, elevated temperature water, supercritical carbon dioxide (SCCD) and oxygen plasmas were performed to assess the suitability of such approaches to surface cleaning. Reactors were designed and built in a manner that permitted diagnostic techniques to be incorporated into or attached directly to these reactors so that control and assessment of the cleaning processes could be performed easily. Both approaches offer considerable potential for vapor phase surface cleaning.

Elevated pressure, elevated temperature water displayed a high reactivity with silicon dioxide films grown thermally on silicon substrates. Oxide removal rates were characterized by kinetic rate coefficients determined from a simple model for oxide dissolution. The chemical activity of these water atmospheres indicated that cleaning of a variety of contaminants, including

metals and organics, is possible at reasonably low temperatures; however, such results also suggested that care be exercised in the choice of reactor materials.

Indication was obtained that removal of "native" oxide layers from silicon and stainless steel was possible using SCCD. The studies indicated that the controlling factors in the removal of these "native" oxides involve the amount of water (or OH bonding) in the oxide layers as well as the layer density. Such observations were consistent with the ability of water to dissolve silicon dioxide films, and suggested that cleaning processes using SCCD may require the addition of water to be effective. Several experiments utilizing methanol additions to SCCD indicated that this may also be an effective cleaning additive.

The abrupt change in density and thus refractive index of carbon dioxide as it approaches and exceeds the critical point offered the possibility of direct, real-time measurements of density for near-critical and supercritical fluids. The refraction and resulting displacement of a He-Ne laser beam directed through the fluid was correlated with density of near-critical and supercritical carbon dioxide. Attempts to determine the density of methanol/carbon dioxide mixtures were less successful, although trends were consistent with expected values.

A helical resonator (HR) plasma source was used to establish medium density oxygen plasmas for surface cleaning. Characterization of the plasma was accomplished by the use of Langmuir probes and silicon oxidation studies. As measured by these diagnostics, the HR source proved difficult to control due to the need to invoke a magnetic field in order to achieve medium density plasmas. The magnetic field apparently led to the establishment of multiple steady states within the reactor; oxidation and anodization studies on silicon displayed two distinct but reproducible results on oxidation rates and plasma characteristics, which occurred at random. Such observations dictated that the magnetic field not be used. Plasma densities thus decreased, but reproducibility and control of plasma characteristics and oxidation/anodization rates were excellent. Compared to oxidation without a plasma, substantial increases in rate were observed with these medium density plasmas. The rates showed little effect on temperature, since the oxidation rate was driven by transport of oxygen ions through the growing oxide film.

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FIG. 1. HIGH PRESSURE/HIGH VACUUM REACTOR AT VARIOUS STAGES OF AN EXPERIMENTAL RUN.

FIG. 2. APPARATUS USED TO OPEN AND CLOSE THE HIGH PRESSURE CHAMBER.

FIG. 3. ARRANGEMENT OF CLEANING AND SURFACE ANALYSIS CHAMBERS.

FIG. 4. SCHEMATIC OF HIGH PRESSURE CLEANING SYSTEM.

FIG. 5. SCHEMATIC OF HIGH PRESSURE WATER SYSTEM.

FIG. 6. SCHEMATIC OF HELICAL RESONATOR PLASMA SYSTEM.

FIG. 7. SCHEMATIC OF LANGMUIR PROBE USED FOR PLASMA CHARACTERIZATION STUDIES.

FIG. 8. XPS SPECTRA OF SI 2P PEAK AS A FUNCTION OF WATER EXPOSURE:
(A) NO EXPOSURE; (B) 4 MIN. AT 3500 PSI AND 275°C;
(C) 30 MIN. AT 3500 PSI AND 280°C.

FIG. 9. SILICON DIOXIDE REMOVAL DATA IN WATER AS A FUNCTION OF TIME AND TEMPERATURE AT 2000 PSI. (A) 260°C (2.7 NM/MIN.); (B) 280°C (5.4 NM/MIN.); (C) 305°C (11.2 NM/MIN.)

FIG. 10. ARRHENIUS PLOT OF ETCH RATE COEFFICIENTS AT 2000 PSI AND 260, 280 AND 305°C.

FIG. 11. REFRACTIVE INDEX VERSUS DENSITY FOR CO₂.

FIG. 12. HE-NE LASER BEAM DISPLACEMENTS VERSUS CO₂ DENSITY.

+ Data — RLL combination

FIG. 13. REFRACTIVE INDEX VERSUS DENSITY FOR 10% METHANOL/CO₂ MIXTURES COMPARED TO A LINEAR COMBINATION OF REFRACTIVE INDICES.

FIG. 14. REMOVAL OF "NATIVE" SILICON OXIDE BY EXPOSURE TO CO₂ AT 60°C AND 2500 PSI.

FIG. 15. REMOVAL OF 5 NM PLASMA-GROWN SILICON OXIDE BY EXPOSURE TO CO₂ AT 80°C AND 3000 PSI.

FIG. 16. ELECTRON DENSITY (TOP) AND ELECTRON TEMPERATURE (BOTTOM) VERSUS APPLIED RF POWER IN A 30 MTORR O₂ PLASMA.

FIG. 17. ELECTRON DENSITY (TOP) AND ELECTRON TEMPERATURE (BOTTOM) VERSUS PRESSURE IN A 300 W O₂ PLASMA.

FIG. 18. OXIDE THICKNESS VERSUS TIME AT 10 MTORR O_2 , $350^\circ C$, 300 W, 125 G AND $5 \text{ MA}/\text{CM}^2$ FOR THE "LOWER" STATE (TOP) AND THE "HIGHER" STATE (BOTTOM).

FIG. 19. DIFFERENCE IN APPLIED AND SURFACE VOLTAGE VERSUS OXIDATION TIME AT 10 MTORR O_2 , $350^\circ C$, 300 W, 125 G AND $5 \text{ MA}/\text{CM}^2$ FOR THE "LOWER" STATE (TOP) AND THE "HIGHER" STATE (BOTTOM).

FIG. 20. SILICON OXIDE THICKNESS VERSUS OXIDATION TIME AT 300 W, 350 °C, 30 MTORR AND 3.8 MA/CM².