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A MICROWAVE PLASMA CLEANING APPARATUS

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Abstract

In a microwave electron cyclotron resonance plasma source, reactive plasmas of oxygen and its mixtures of argon have been used for evaluating plasma cleaning technologies. Small aluminum samples (0.95 × 1.9 cm) were coated with thin films (≤ 20 μm in thickness) of Shell Vitrea oil and cleaned with reactive plasmas. The discharge parameters, such as gas pressure, magnetic field, substrate biasing, and microwave power, were varied to change cleaning conditions. A mass spectroscopy (or residual gas analyzer) was used to monitor the status of plasma cleaning. Mass loss of the samples after plasma cleaning was measured to estimate cleaning rates. Measured cleaning rates of low-pressure (0.5-mtorr) argon/oxygen plasmas were as high as 2.7 μm/min. X-ray photoelectron spectroscopy was used to determine cleanliness of the sample surfaces. In this paper, significant results of the plasma cleaning are reported and discussed.

I. INTRODUCTION

Plasma surface cleaning has been widely used to clean surfaces in fusion energy research, in high-energy accelerators, and in materials processing (Refs. 1-4). This cleaning method utilizes radical species generated in reactive gas discharges to remove surface contaminants. The energetic species in these discharges consist of photons, electrons, ions, and reactive neutral species. Physically, these energetic particles attack surfaces to cause sputtering, thermal evaporation, or photodecomposition. Chemically, these energetic particles dissipate their energy to raise surface temperatures and greatly enhance chemical reactions. These impinging particles are generally very hot; for example, 1 eV of energy equivalent to a temperature of ~ 11,600 K. Thus, the hot plasma particles have higher rates of surface cleaning than those of thermal reactive gas particles.

It is well known that reactive oxygen plasmas are very effective for removing organic contaminants from surfaces. Recently, we developed a microwave electron cyclotron resonance (ECR) plasma source to generate reactive species of oxygen for plasma etching on silicon wafers (5). The plasma density and its distribution could be varied by the source parameters including source magnetic fields, sample bias potentials, and gas pressures. Typical low-pressure (≤ 1-mtorr) discharges can produce uniform plasmas having electron densities of ~1×10^{11} cm^{-3} and electron temperatures of 2 to 5 eV. Using this source, we have prepared a microwave plasma cleaning apparatus for removing organic contaminants (6). By controlling gas pressure, applied power, and other discharge parameters of this apparatus, we have evaluated plasma cleaning technologies for performing damage-free cleaning on oil film contaminated surfaces of finished workpieces. Such plasma cleaning technologies are being developed for replacing conventional solvent cleaning. In this paper, we describe the plasma cleaning apparatus, and preliminary results of plasma cleaning on small samples coated with a thin oil film. The significant results using reactive plasmas of oxygen and argon/oxygen mixture are then further discussed.

II. PLASMA CLEANING APPARATUS

Figure 1 shows main components of the microwave plasma cleaning apparatus being used for evaluating advanced cleaning technologies. These components are the microwave plasma source, a vacuum chamber, and a turbomolecular pump. The vacuum chamber is mounted under a supporting frame. The microwave plasma source is mounted on the top of the vacuum chamber. The turbomolecular pump is installed beside the vacuum chamber and has a pumping speed of ~ 400 L/s for air. Installed in the vacuum chamber is an rf feedthrough on which a sample holder is fastened. The sample holder is at the down stream end of the plasma source. The source pressure is measured by a capacitance manometer (MKS Baratron Type 170M-6C) on the top flange of the source, and the pressure in the vacuum chamber is measured by an ionization gauge on the side port. Achievable base pressures are often below 1×10^{-6} torr. A throughput control valve on the turbomolecular pump regulates the pumping speed. The working gas is fed continuously into the plasma source, and the gas flow rate is measured by a flowmeter. Both the pumping speed and the flow rate are used to adjust the source pressure.

Other supporting equipment (not shown in Fig. 1) are electrical supplies, electronics equipment, and a water-cooling system. The outputs of these supplies are adjustable. The 1500-W microwave (2.45-GHz) supply is used for creating plasmas. The 200-W radio frequency (rf, 13.56-MHz) supply is used to provide a negative bias potential to the sample holder. Sometimes, the 400-V dc supply is used for providing a negative bias potential. Two low-voltage supplies (respectively rated at 500 and 40 A) are used to provide exciting currents to a source coil (or magnet) and an enhancing magnet for controlling plasma properties and cleaning conditions.

Both the bias potential of the sample holder and the enhancing magnetic field can provide a flexibility in controlling plasma density distributions (**5, 6**). The plasma density adjacent to the sample holder tends to be higher for the case with the negative bias potential and lower for the positive bias holder. However, when the source coil and the enhancing magnet have the opposite polarity, the magnetic cusp fields so formed can improve confinement of plasma particles. Thus, the plasma density and uniformity do not vary significantly with the bias potential of the sample holder. With the flexibility of varying plasma density and ion energy, this plasma cleaning apparatus is suitable for evaluating plasma cleaning technologies.

III. PLASMA CLEANING

III.1 Sample Preparation

Plasma cleaning technologies have been evaluated by using reactive plasmas of pure oxygen and/or mixtures with argon to remove oil films on small test samples (0.95×1.91 cm) made of aluminum 6061. Each test sample was prepared by cleaning the top surfaces with alcohol spray, drying with an air jet, and then coating with a thin film of Shell Vitrea oil. Some bare samples were polished to achieve a mirror surface (~ 0.5-μm flatness) and then ultrasonically cleaned. The mass of the oil film on each test sample was measured by weighing the sample before and after oil coating. With a density of 865 mg/cm^3, the typical thickness of a 1-mg oil film is ~ 6 μm. The test sample with oil film was then placed on the center of the sample holder for plasma cleaning.

III.2 Operating Conditions

The plasma cleanings were conducted by using pulsed microwave plasmas while the working gas was fed continuously. The pulsed microwave plasmas were usually created by applying both a pulsed exciting current to the source coil and a pulsed microwave power to the plasma source simultaneously. The nominal pulse width was set to be 1 s at a duty factor of 10%. The pulsed rf power was adjusted to provide a desired negative bias potential to the sample. During plasma cleaning, the current density of the plasma was measured by using a Langmuir probe. Other operating parameters—such as gas pressure, gas flow rate,

microwave power, magnet current, sample-bias potential, and operating time (or accumulated plasma exposure time)—were also recorded. Signal amplitude changes of carbon monoxide (CO) of a mass spectrometer, a UTI Model 100C residual gas analyzer (RGA), were recorded for each sample being plasma cleaned. After plasma cleaning, the mass loss of each sample was measured. Subsequently, test sample surfaces were studied for cleanliness by using X-ray photoelectron spectroscopy (XPS) analysis.

III.3 Preliminary Results

We have conducted a plasma cleaning study on 56 small samples (6). Preliminary results reveal that the microwave plasma cleaning works well for samples coated with oil films with thickness approaching 20 μm. The reactive plasmas of oxygen or oxygen/argon were created in low-pressure (ranging from 0.3- to 5-mtorr) microwave discharges. During plasma cleaning, the samples were biased negatively either by using the rf or the dc supply. Table 1 lists some cleaning parameters for 11 plasma-cleaned samples, part of the 56 samples. The column "oil mass" is the mass of oil film coated on sample surfaces, and the column "mass loss" is the mass removed by the plasma cleaning. The estimated film removed during the operating (plasma-on) time is used to calculate the average cleaning rate. Significant results of these 11 samples are summarized below.

1. The first six samples with a negative dc bias potential ranging from 0 to 100 V were cleaned by oxygen plasmas at a source pressure of ~ 0.5 mtorr. The surfaces of sample 92-51 with –100-V biasing were cleaned but damaged with etched spots.

2. The last five samples were cleaned by oxygen plasmas at a source pressure of 5 mtorr. Samples 92-73 and -74 (with negative dc bias) were not completely cleaned. Instead, the residue of oil films became plastic materials. However, oil films of the last three samples with negative rf bias were cleaned up. No visual residue on the sample surfaces was observed.

These features imply that energy and flux of plasma ions can play a dominant role in the plasma cleaning. The reactive oxygen plasmas created in low-pressure (0.5-mtorr) discharges were found to be very effective in cleaning samples coated thin oil films, as described in item 1 above. With a negatively biasing (dc or rf) potential to the sample, plasma ions can be accelerated to high energies. Such energetic ion bombardment on sample surfaces enhances chemical reactions between hydrocarbon molecules and plasma particles, leading to decomposition and vaporization of the oil film in the form of a volatile gas effluent. Plasma cleaning rate increases with the current density and the energy of impinging ions, which increases proportional with the negative bias potential. Thus, the average cleaning rate increases with the rf bias potential as shown in Fig. 2.

However, the different effects of dc and rf biasing as mentioned in item 2 above may be influenced by insulated particles produced in plasmas. Oxygen plasmas at 5 mtorr may produce some insulated particles and deposit them on the sample surfaces. In this case, owing to the dielectric property of these particles, the applied dc voltage cannot establish an electric field in the plasma sheath to accelerate ions. This will lower kinetic energy of ions and slow down plasma cleaning rates. Consequently, the oxygen plasmas cannot clean up oil films on Samples 92-73 and -74 that were dc biased. But, the insulated particles cannot prevent the applied rf voltage from establishing an electric field in the plasma sheath to accelerate plasma ions. Thus, the plasma ions impinge on the rf biased samples at an energy equivalent to the bias potential. Consequently, in Table 1, the last three samples with rf biasing were cleaned up at higher rates. Following the above discussions, we conclude that energetic ions in oxygen plasmas are the dominant reactive particles for cleaning surfaces with oil film contaminants.

III.4 RGA Signal

With oxygen plasma cleaning, the dominant species of the gaseous effluent measured by the mass spectrometer (or RGA) are H_2, O, OH, H_2O, CO, O_2, and CO_2. These volatile gas molecules are produced by chemical reactions of bombarding oxygen plasma particles and hydrocarbon molecules in the oil film on sample surfaces. One of the dominant effluent gas signals, carbon monoxide (CO), changes greatly during

each pulsed discharge. Figure 3 shows the amplitude changes of mass 28 peak of CO for a sample that has been cleaned under a sequence of pulsed discharges. At the beginning of the sequence, the amplitude of the mass 28 increased rapidly to a maximum, then decreased slowly. At the end of the sequence, the amplitude of the mass 28 decreased slightly during the pulsed discharge. For this type of plasma cleaning, the waveform of mass 28 (or CO) signal closely correlates to the cleanliness of the sample surfaces. Thus, the waveform of CO signal was used for recording the history of plasma cleaning and for indicating the end point of the cleaning (6).

III.5 XPS Analysis

To verify surface cleanliness of plasma cleaned samples, X-ray photoelectron spectroscopy (XPS) has been used. The XPS survey analyzes the surface composition of the top 40-Å surface layer. With a sample size of 9.5 × 19.1 mm, the 0.8-mm spot survey on a representative surface area to perform quantitative analysis of surface composition. The ratio of carbon-to-aluminum concentration measured by the XPS analysis is denoted by C/Al. In Table 1, the sample is considered clean if its value of C/Al ratio is below the average value of 1.15 that is measured for bare control samples. (Refer to the row "Control mean" in Table 2 .) Similarly, the oxide layer is thinned down by plasmas, if the value of O/Al ratio is below 3.34 of the bare control samples. In Table 1 the surfaces of unsuccessfully cleaned samples 92-73 and -74 have C/Al ratios to be 10's to 100's times higher than 1.15.

Table 2 shows the surface composition measured by the XPS analysis of three bare samples and their plasma-cleaned samples. The alloy composition of the bare samples is 98% Al, 0.8 to 1.2% Mg, 0.4 to 0.8% Si, 0.2% Cr, and 0.3% Cu. This table also lists the composition of analyzed bare samples as Control in the rows 92-50-CON, -72-CON, and -100-CON and their mean in the row "Control mean." The average composition of these control samples is 17.2% Al, 57.5% O, 19.8% C, 0% Mg, 0.7% Ca, 0.9% Si, 0% Cu, 0% Ag, 3.2% P, and 0% Cr. The average surface composition of plasma cleaned samples 92-50, -72, and -100 (or "Sample mean) listed is 22.1% Al, 48.6% O, 25.7% C, 1.9% Mg, 0.1% Ca, 0.4% Si, 0.6% Cu, 0.1% Ag, 0% P, and 0% Cr. Comparing the values in the rows "Sample mean," "Control mean," and "Bulk alloy," we highlight the following significant points.

1. The surface of these control samples was covered with a thin oxide layer with impurities of carbon and others. In fact, the XPS survey did not detect the elements Mg, Cu, and Cr of the bulk alloy.

2. The surfaces of plasma cleaned samples received fewer impurities than those of the control bare samples. For example, compared to its own control bare sample, the plasma cleaned samples 92 50, -72, and -100 had higher Al atomic concentration, lower O/Al ratio, and lower C/Al ratio (except Sample 92-100).

3. The great decrease of impurities Ca, Si, and P on plasma cleaned samples indicated that the impurities on the bare-sample surfaces were removed by oxygen plasmas. The presence of magnesium on the plasma cleaned samples indicated that the surface layer was partially removed.

VI. CONCLUSIONS

Preliminary results reveal that reactive plasma cleaning using a microwave ECR source works well for test samples coated with Shell Vitrea oil films with thicknesses approaching 20 μm. In low-pressure (ranging from 0.3- to 5-mtorr) discharges, reactive plasmas have been created and powered by microwave energies. The fifty-six small, flat aluminum samples have been plasma cleaned, and their surface cleanliness has been confirmed by the XPS. Significant results are summarized below (6).

1. The dominant cleaning particles in oxygen and argon/oxygen plasmas are energetic ions.

2. Argon/oxygen plasmas have cleaning rates 2 to 3 times higher than those of oxygen plasmas.

3. The cleaning rates of oxygen/30%-argon plasmas can be as high as 2.7 μm/min.

4. For thick oil films (~ 20 μm), only samples with rf biasing can be effectively cleaned in high-pressure (~ 5-mtorr oxygen) plasmas, but samples with dc biasing cannot.

5. Samples with –200-V rf biasing can be cleaned without etch damage, but samples with –75-V dc biasing tend to have etch damage on sample surfaces.

6. The XPS analysis for measuring relative concentration of aluminum, carbon, and oxygen on sample surfaces confirmed that the surfaces of plasma cleaned samples can be cleaner than the surfaces of control bare samples.

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Table 1. Oxygen plasma cleaning on aluminum samples coated with thin oil films

Sample	Oil mass mo (mg)	Mass loss m' (mg)	Bias potential Vsh (V)	Surface feature	Remarks	C/Al 1.15	O/Al 3.34
#92-50	0.8	0.8	-50	Clean	DC	0.75	2.34
#92-51	1.0	1.2	-100	Clean / Eteched	DC	0.85	2.62
#92-57	0.9	0.9	0	Clean / Gold	DC	0.71	2.47
#92-96	0.9	0.7	-50	Clean	DC	0.74	2.76
#92-70	1.1	1.1	-75	Clean	DC	0.99	2.35
#92-72	0.9	0.8	-25	Clean with spots	DC	1.10	2.18
#92-73	1.0	0.6	-50	Etched, not clean	DC	340.33	21.33
#92-74	1.0	0.4	-25	Plastic drops	DC	109.72	8.44
#92-82	1.1	0.9	-25	Clean	RF	0.99	1.81
#92-84	1.1	1.0	-50	Clean, etched trees	RF	1.26	2.11
#92-100	1.3	1.3	-40	Clean	RF	1.91	2.04

Table 2. Surface composition of test samples in percentage											
					Elements						
Sample	Al	O	C	Mg	Ca	Si	Cu	Ag	P	Cr	N
92-50-CON	18.05	58.27	18.98	0.00	0.40	0.79	0.00	0.00	3.50	0.00	0.00
92-50	23.55	55.18	17.56	3.53	0.00	0.00	0.00	0.00	0.00	0.00	0.18
92-72-CON	16.23	55.35	21.61	0.00	1.17	0.68	0.00	0.00	3.11	0.00	1.84
92-72	22.72	49.57	24.97	0.91	0.29	0.67	0.00	0.00	0.00	0.00	0.87
92-100-CON	17.39	58.92	18.70	0.00	0.53	1.08	0.00	0.00	3.06	0.00	0.31
92-100	20.06	40.98	34.71	1.27	0.00	0.37	1.75	0.30	0.00	0.00	0.55
Sample mean	22.11	48.58	25.75	1.90	0.10	0.35	0.58	0.10	0.00	0.00	0.53
Control mean	17.22	57.51	19.76	0.00	0.70	0.85	0.00	0.00	3.22	0.00	0.72
Bulk alloy	97.90	0.00	0.00	1.00	0.00	0.60	0.28	0.00	0.00	0.25	0.00

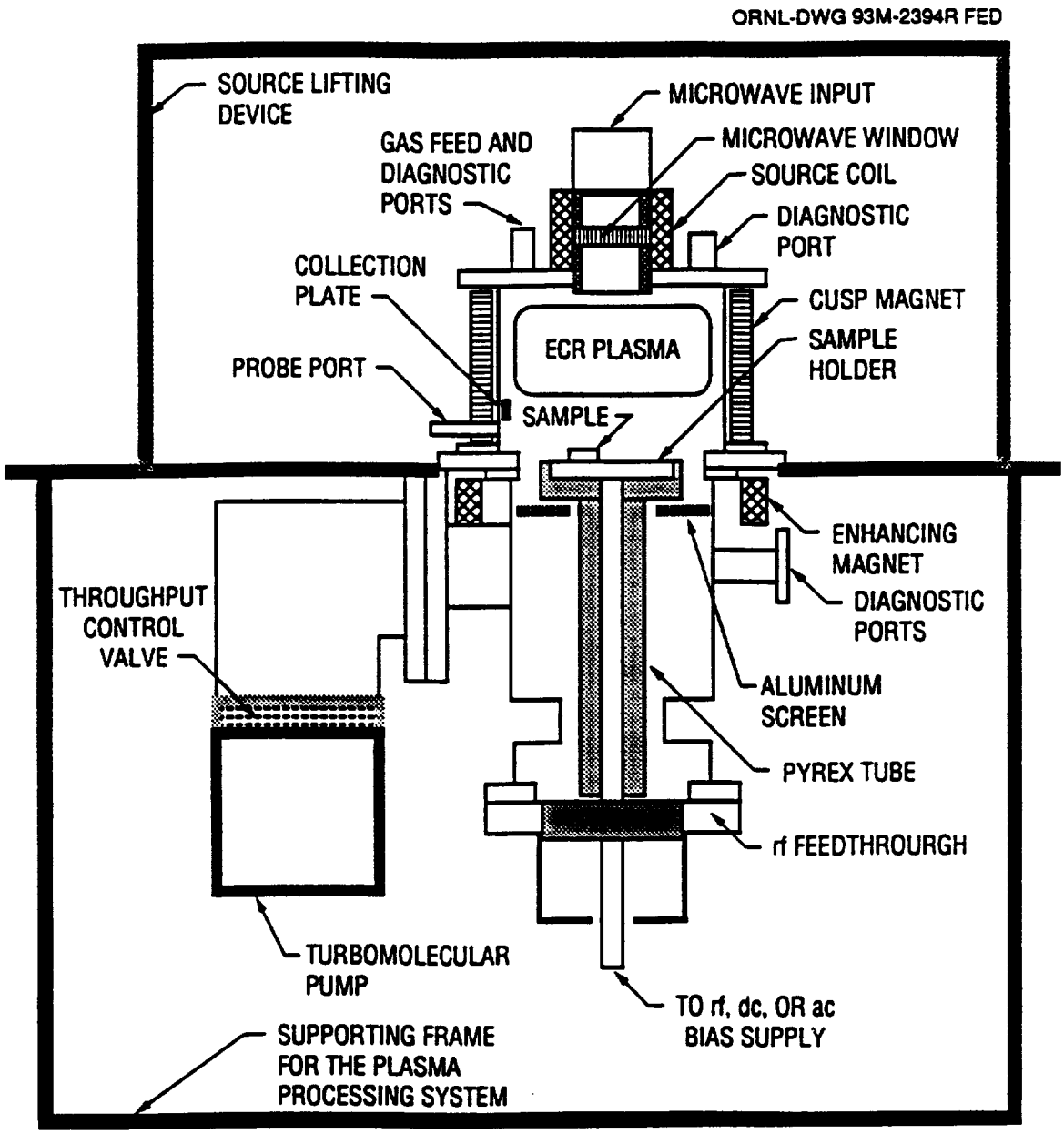

Fig. 1. A plasma cleaning apparatus including a plasma source, sample holder, vacuum chamber, and vacuum system.

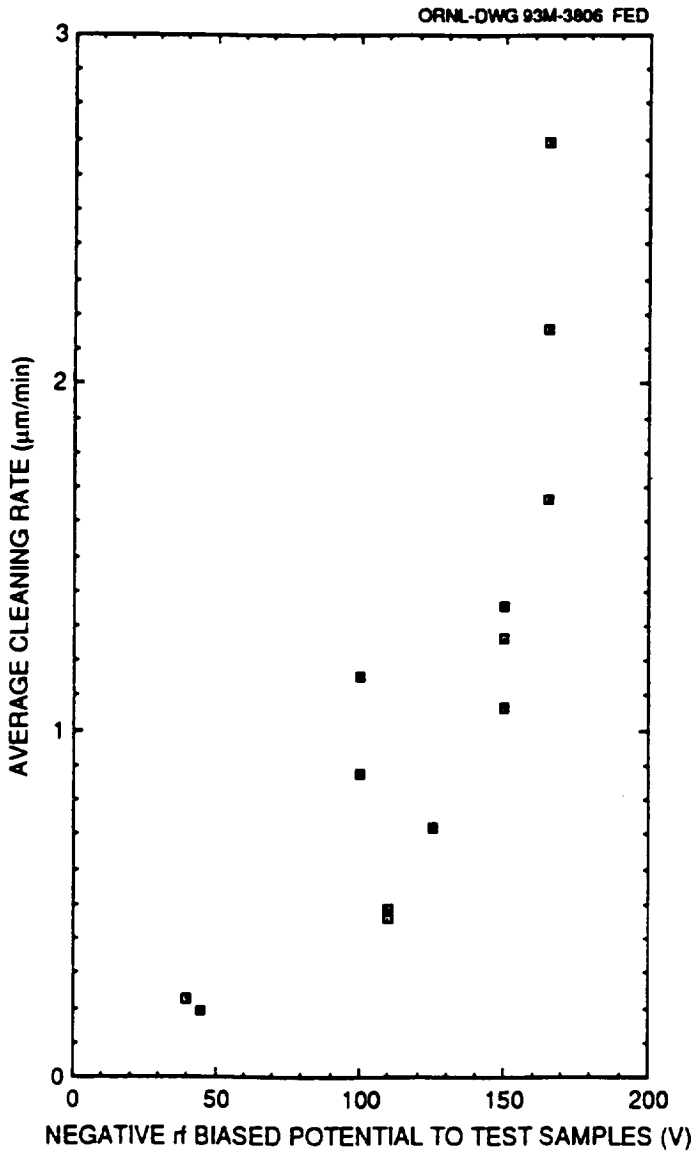

Fig. 2. The change of average cleaning rate as a function of rf bias potential to the sample holder.

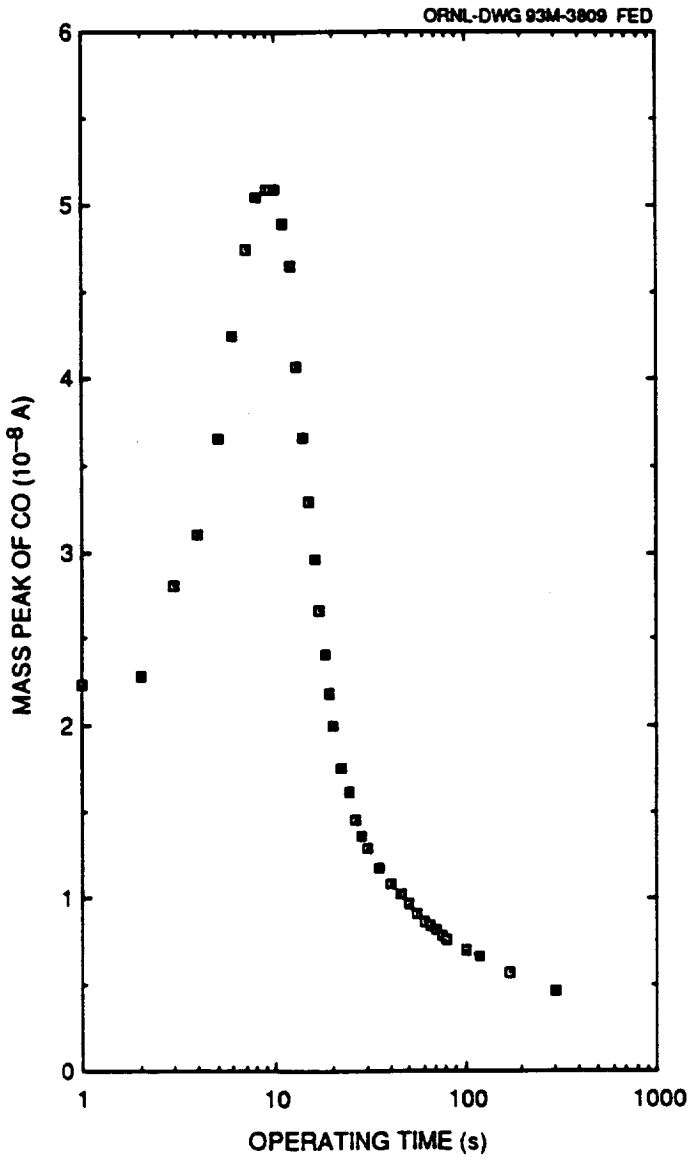

Fig. 3. Signal changes of mass peak of CO (28 amu) during oxygen plasma cleaning with a test sample.

NON-CFC CLEANING SOLVENTS, PROCESSES AND PARAMETERS 1