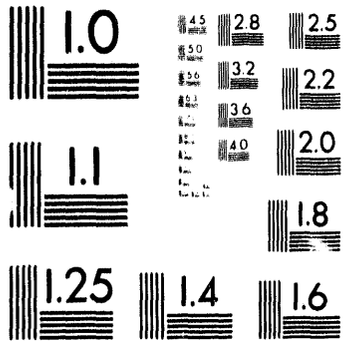

1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0

1 of 1

Conf-9311110--1

Y/DV-1298

Y-12

OAK RIDGE
Y-12
PLANT

Plasma Surface Cleaning Using Microwave Plasmas

C. C. Tsai, H. H. Haselton, W. D. Nelson,
D. E. Schechter, ORNL; L. M. Thompson,
V. B. Campbell, A. L. Glover, J. M. Googin,
Y-12 Plant

Plasma Technology
Fusion Energy Division

Preprint for submission to:

Fortieth Annual Vacuum Society Science Symposium and Topical Conference, Research Triangle Park, North Carolina, November 15-19, 1993

Prepared by the Oak Ridge Y-12 Plant
Oak Ridge, Tennessee 37831
managed by
Martin Marietta Energy Systems, Inc.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-840R21400

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Abstract # : 695
Program # : PS-WeP10
Put on JVST manuscript

Plasma surface cleaning using microwave plasmas

C. C. Tsai, H. H. Haselton, W. D. Nelson, and D. E. Schechter
Oak Ridge National Laboratory, P.O. Box 2009
Oak Ridge, Tennessee 37831-8071

L. M. Thompson, V. B. Campbell, A. L. Glover, and J. M. Googin
Y-12 Plant* P.O. Box 2009
Oak Ridge, Tennessee 37831-8175

In a microwave electron cyclotron resonance (ECR) plasma source, reactive plasmas of oxygen and its mixture with argon are used for plasma-cleaning experiments. Aluminum test samples (0.95 × 1.9 cm) were coated with thin films (≤20 μm in thickness) of Shell Vitrea oil and cleaned by using such reactive plasmas. The plasma cleaning was done in various discharge conditions with fixed microwave power, rf power, biased potential, gas pressures (0.5 and 5 mtorr), and operating time up to 35 min. The status of plasma cleaning has been monitored by using mass spectroscopy. Mass loss of the samples after plasma cleaning was measured to estimate cleaning rates. Measured clean 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 and confirm the effectiveness of plasma cleaning in achieving atomic levels of surface cleanliness. In this paper, significant results are reported and discussed.

I. INTRODUCTION

Plasma surface cleaning has been widely used to achieve clean surfaces in fusion energy research, in high-energy accelerators, and in materials processing.[1–3] This cleaning method utilizes radical species generated in reactive gas discharges to remove surface contaminants. The energetic radical species in these discharges consist of photons, electrons, ions, and reactive neutral species. Physically, these energetic particles impact on surfaces to cause sputtering, thermal evaporation, or photodecomposition. Chemically, the surface heating caused by these energetic

* Managed by Martin Marietta Energy Systems, Inc., for the U. S. Department of Energy under contract DE-AC05-840R21400.

particles greatly enhances 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 energetic plasma particles have higher rates of surface decontamination than those of thermal reactive gas particles.

It is well known that reactive oxygen plasmas are very effective for removing organic contaminants from surfaces. The dominant reactive species in oxygen plasmas—hot electrons, energetic ions, atomic radicals, ozone, and ultraviolet (UV) photons—actively clean organic contaminants by physical sputtering, thermal evaporation, chemical reaction, or photodecomposition. Surface-cleaning techniques using such reactive plasma particles with suitable energy and flux can be developed to perform gentle, damage-free cleaning. The techniques should be developed to provide uniform surface cleaning over workpieces with complex shapes, eliminate physical distortion, and minimize production of secondary wastes. Such environment-friendly cleaning techniques are ideal for replacing conventional solvent cleaning techniques.

A plasma source for developing such plasma-cleaning techniques should be capable of producing useful reactive plasmas with suitable density and energy distributions. Given their capability for producing reactive plasmas for industrial applications, microwave electron cyclotron resonance (ECR) plasma sources[4] have been chosen. To this end, an experimental test stand has been prepared and equipped with an existing ECR plasma source.[5] In the following sections, we describe experimental arrangement and cleaning experiments on aluminum test samples using reactive plasmas of oxygen, argon, or their mixtures. Significant results and surface cleanliness of test samples are then reported and discussed.

II. EXPERIMENTAL ARRANGEMENT

Using the existing ECR microwave plasma source,[5] an experimental test stand (Fig. 1) has been prepared with a motorized source lifting device, a vacuum chamber, and an associated vacuum pump. Other supporting equipment (not shown) are control consoles, electrical supplies, electronics equipment, and a water-cooling system. The prime supplies are a microwave (2.45 GHz) supply for creating plasmas and a radio frequency (rf) (13.56 MHz) supply (or a 400-V dc supply) for providing a biased potential to test samples. Two low-voltage supplies

(respectively rated at 500 and 40 A) are used to excite the source coil (or magnet) and the enhancing magnet.

The ECR plasma source is set on the top flange of the vacuum chamber that is mounted on the frame of the test stand. All of them are grounded. On the top of the test stand, the motorized lifting device is used to raise the source chamber for changing test samples. Bolted on the bottom flange of the vacuum chamber is the rf feedthrough on which the sample holder is fastened. The vacuum chamber is evacuated by a turbomolecular pump at speeds of ~400 L/s for air. The gas pressure in the plasma source is measured by a capacitance manometer (MKS Baratron Type 170M-6C), and that in the vacuum chamber is measured by an ionization gauge. Achievable base pressures are often below 1×10^{-6} torr. A butterfly throttle valve on the turbomolecular pump controls the pumping speed. The working gas is fed continuously into the top flange of the plasma chamber through a needle valve that regulates the gas flow rate measured by a flowmeter. Both the needle valve and the throttle valve are used to adjust the gas pressure in the plasma chamber.

III. PLASMA PROPERTIES

The ECR plasma source (Fig. 1) consists of a microwave launcher, a source coil (or magnet), a multicusp plasma chamber, and a sample holder. The source coil surrounding the microwave launcher can be excited to provide an 875-G field for establishing an ECR zone in which electrons gain energy from the applied 2.45-GHz microwave electric field. On the outside walls of the multicusp plasma chamber (30 cm in diameter and 20 cm in height), 20 columns of samarium cobalt permanent magnets are equally spaced with alternating polarity for forming a multiple-line cusp configuration. This magnetic configuration confines both the energetic ECR electrons and the cold plasma electrons and thus enhances the ionization and the efficiency of ECR discharges. This plasma source has been operated to produce plasmas with axially peaked or hollow profiles in a probe plane adjacent to the sample holder at the downstream end of the discharge chamber, as that reported elsewhere.[5,6] Typical argon plasmas in low-pressure ($\leq$1 mtorr) discharges have electron densities of ~1×10^{11} cm^{-3}, electron temperatures of 2 to 5 eV, and a production efficiency near 200 W/A (200 eV/ion).

With a new sample holder and enhancing magnet, the plasma source in Fig. 1 has additional flexibility in controlling plasma distributions. We have reported our recent study[7] on plasma density distributions as functions of the biased potentials of the sample holder and the exciting currents of the enhancing magnet. Similar to the gas pressure effects,[5,6] this plasma source can create useful plasmas in low-pressure discharges with peak or hollow density profiles suitable for plasma-cleaning experiments.[7] For diode discharges with the grounded sample holder, the enhancing magnet with the opposite polarity will form a cusp field, improve electron confinement, enhance ionization, increase plasma density, and improve plasma uniformity. For reflex discharges with the floated sample holder, the enhancing magnet with the same polarity of the source coil will increase the magnetic field, improve the confinement of energetic electrons, intensify the discharges near the chamber axis, and achieve higher ion currents as measured.

IV. PLASMA CLEANING

A. Experiments

Plasma-cleaning experiments have been conducted with reactive plasmas of oxygen and its mixture with argon to remove oil films on small test samples (0.95 × 1.91 cm) made of aluminum 6061. The samples are prepared by cleaning the top surfaces with alcohol spray, using an air jet to dry, and then coating the top surfaces with a thin film of Shell Vitrea oil. Some samples are prepared to achieve mirror surface (~0.5 μm in flatness) by polishing and ultrasonic cleaning before oil coating. The mass of the oil film on each test sample is determined by weighing the sample before and after the coating with oil film. With an oil density of 865 mg/cm^3, the typical thickness of 1-mg oil films uniformly coated over the sample surfaces is ~6 μm. The prepared test sample is then placed on the center of the sample holder. After plasma cleaning, the mass loss of each sample is measured, and surface texture changes are examined visually. Subsequently, test sample surfaces are studied using the X-ray photoelectron spectroscopy (XPS) analysis.

When the vacuum chamber is evacuated down to ~2×10^{-6} torr, a mass spectroscopy or residual gas analyzer (RGA) can be turned on to confirm that it is free of vacuum leakage. The cooling water for the test stand is turned on first. The desired gas pressure in the plasma chamber

is adjusted by regulating gas flow rate and pumping speed. The RGA is used to measure gas purity and record various mass peaks on a chart record. If needed, the enhancing magnet can be powered with a constant exciting current. Subsequently, the source coil, rf, and microwave power supplies are armed for pulsed operations. Following the above initial preparation, the microwave ECR discharges are initiated and sustained by applying both a pulsed current to the source coil and a pulsed power to the microwave launcher simultaneously. The source coil current is variable up to 500 A, while the microwave power is variable up to 1500 W. The typical pulse-on time is 1 to 5 s at a duty factor of 10 to 50%, respectively. The pulsed rf power can be changed to bias the sample holder with various negative potentials up to –200 V. During the plasma cleaning experiments, the current density of the plasma is monitored with the electrical probe. Other operating parameters—such as gas pressure, gas flow rate, microwave forward and reflected powers, magnet currents, biasing potential of the sample holder, and operating time (or accumulated plasma exposure time)—are also recorded.

Table 1 lists relevant parameters and cleanliness of 11 plasma-cleaned samples, part of ~60 samples. Oil mass is the oil coated on the sample surface. Mass loss is the mass removed by plasma cleaning and is used to estimate thickness of film removed by plasma cleaning. The film removed and operating (plasma-on) time can estimate the average cleaning rate. Surface feature is used to highlight the apparent changes of sample surfaces. It reveals that samples tend to have etched and sputtered surface damage when negative dc biased potentials exceed 50 V. However, test samples with rf biasing tend to be free of etched damage even though negatively biased potentials exceed 150 V.

B. Results and discussion

With oxygen plasma cleaning, the dominant species of gaseous effluent arriving at the residual gas analyzer (RGA) are H_2, O, OH, H_2O, CO, O_2, and CO_2. These volatile gas molecules are produced by intense chemical reactions among bombarding oxygen plasma particles and hydrocarbon molecules in the oil film on sample surfaces. One of the dominant products is carbon monoxide, CO that changes greatly during the pulsed discharge. Figure 2 records the amplitude changes of mass 28 peak of CO during a sequence of pulsed plasma cleaning. At the

beginning of the plasma cleaning, the amplitude of the mass 28 increases rapidly to a maximum, then decreases slowly. For this type of plasma cleaning, the waveform of mass 28 (or CO) peak closely correlates to the cleanliness of the sample surfaces. It is ideal to use CO waveforms for recording the history of plasma cleaning and for indicating the end point of the cleaning.[7]

The XPS survey analyzed the surface composition of the top 40-Å surface layers. With a sample size of 9.5 × 19.1 mm, the 0.8-mm spot survey revealed only the typical surface composition. The ratio of carbon to aluminum measured by the XPS analysis is denoted by C/Al. In Table 1, with its value of C/Al below the average value of 1.46 from bare control samples, the test sample is clean. Similarly, the oxide layer has been thinned down by plasmas, if the value of O/Al is below 3.34 of the bare control samples. Significant results of the 11 samples listed in Table 1 are summarized below.

1. All samples were cleaned with a thinner oxide layer except samples 92-73 and -74.
2. The first six samples were cleaned by oxygen plasmas at a source pressure of ~0.5 mtorr with a negative dc biasing potential ranging from 0 to 100 V. The sample surface was damaged with etch marks under high biased potential; for example, sample 92-51 was biased negatively at 100 V.
3. The last five samples were cleaned by oxygen plasmas at a source pressure of 5 mtorr. Samples 92-73 and -74 (with dc biasing) indicated that the oxygen plasma was ineffective in cleaning oil contaminants. However, the plasmas were very effective for cleaning the last three samples with rf biasing. This feature associated with the sample biasing implies that plasma ions are dominant particles in the plasma surface cleaning. We speculated that the insulated oil film on the sample surfaces may reduce ion energies gained under dc biasing.

The alloy composition of bare test samples is Al 98%, Mg 0.8 to 1.2%, Si 0.4 to 0.8%, Cr 0.2 %, and Cu 0.3 %, as listed in Table 2. 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 Al 17.2%, O 57.5%, C 19.8%, Mg 0%, Ca 0.7%, Si 0.9%, Cu 0%, Ag 0%, P 3.2%, and Cr 0%. The average surface composition of plasma-cleaned samples 92-50, -72, and -100 (or Sample Mean) listed is Al

22.1%, O 48.6%, C 25.7%, Mg 1.9%, Ca 0.1%, Si 0.4%, Cu 0.6%, Ag 0.1%, P 0%, and Cr 0%. Comparing the values in the rows Sample Mean, Control Mean, and Bulk Alloy, we can highlight the following significant points.

1. The surface of these control samples was covered with a thin oxide layer with impurities of carbon and materials of polishing powders. In fact, the XPS survey did not detect the elements Mg, Cu, and Cr of the bulk alloy, but Ca, Si, and P of the polishing powders.
2. Cleaner than those of the control bare samples, the surfaces of the plasma-cleaned samples, compared with samples 92-50 and -72, have higher Al atomic concentration, lower O concentration, and lower C/Al.
3. The great decrease of Ca, Si, and P on post-plasma-cleaned samples indicates that the polished powder contaminates on surfaces were cleaned up by oxygen plasmas. The presence of magnesium on these plasma-cleaned samples indicates that the surface layer has been partially removed.

The reactive plasma discharges of oxygen or oxygen/argon are effective in cleaning thin oil films. With a negatively biased sample holder, plasma ions are accelerated to high energies. Such energetic ion bombardment on sample surfaces enhances chemical reactions between hydrocarbon molecules and plasma particles, leads to decomposition and vaporization of the oil film, and produces a volatile gas effluent. Thus, plasma-cleaning rate is a sensitive function of plasma density and ion energy, which can be affected by the biased potential to the test samples. Figure 3 shows that the average cleaning rate on these test samples increases with the biased potential. The maximum cleaning rate of 2.7 μm/min occurs at a rf biased potential of about −165 V. This implies that energetic ions play the prime role in cleaning up oil films. This feature is similar to those observed in etching polymers in pure oxygen plasmas.[8] Furthermore, we noticed that plasmas of an oxygen/argon gas mixture can influence cleaning rates on the sample surfaces. In such plasmas, the energetic argon ions actively and effectively break carbon-oxygen bonds in organic layers formed on the sample surfaces and shorten the plasma-cleaning time by two to three times.

VI. CONCLUSIONS

Preliminary results reveal that reactive plasma cleaning works well for test samples coated with Shell Vitrea oil films with thicknesses approaching 20 μm. The experimental facility has been operated to demonstrate its capability of creating reactive plasmas of oxygen or oxygen/argon and performing surface cleaning. In low-pressure (ranging from 0.3 to 5 mtorr) discharges, reactive plasmas have been created and powered by microwave and rf energies. Various plasma distributions, either axially peak or hollow profiles, can be controlled by both the enhancing magnet and the biased sample holder. Small flat aluminum samples coated with thin films (<20 μm) of Shell Vitrea oil have been plasma cleaned, and their surface cleanliness has been analyzed by the XPS. The significant results are summarized below.

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, which cannot clean a dc biased sample.
5. Samples with rf biasing can be cleaned without etch damage at biased potentials up to 200 V, 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 post-plasma-clean samples can be cleaner than the control bare samples.

VII. ACKNOWLEDGMENTS

The authors would like to thank their colleagues who helped with this project, particularly L. A. Berry, P. M. Ryan, and W. L. Stirling for their valuable discussion; B. E. Argo and G. C. Barber for their technical support on keeping electrical and electronic equipment functional at the facility, and J. E. Simpkins for his advice on the use of a residual gas analyzer.

VIII. REFERENCES

1. H. F. Dylla, "Glow discharge techniques for conditioning high-vacuum systems," J. Vac. Sci. Technol. A **6** (3), 1276–1287 (1988).
2. J. W. Coburn, "Surface processing with partially ionized plasmas," IEEE Trans. on Plasma Science **19** (6), 1048–1062 (1991).
3. W. Shmayda and A. Antoniazzi, "Tritium decontamination—plasma driven decontamination technique," Canadian Fusion Fuels Technology Project Journal **8** (3), ISSN 0847–9437, May 1992.
4. J. Asmussen, "Electron cyclotron resonance microwave discharges for etching and thin film deposition," in *Handbook of Plasma Processing Technology*, edited by S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood (Noyes Publication, 1990), Chap. 11.
5. C. C. Tsai et al., "Potential applications of an electron cyclotron resonance multicusp plasma source," J. Vac. Sci. Technol. A **8** (3), 2900–2903 (1990).
6. C. C. Tsai, "Potential applications of a new microwave electron cyclotron resonance multicusp plasma source," Nucl. Instr. and Methods in Physics Research B **56/57**, 1166–1170 (1991).
7. C. C. Tsai, H. H. Haselton, W. D. Nelson, D. E. Schechter, L. M. Thompson, V. B. Cambell, A. L. Glover, and J. M. Googin, "Plasma surface cleaning in a microwave plasma source," to be issued as ORNL/TM-12495.
8. G. N. Taylor and T. M. Wolf, "Oxygen plasma removal of thin polymer films," J. Polymer Eng. Sci. **20**, 1087 (1980).

FIGURE CAPTIONS

Fig. 1. A test stand including a plasma source, sample holder, vacuum chamber, and vacuum system, which is set up for plasma cleaning.

Fig. 2. Signal changes of mass peak of CO (28 amu) during oxygen plasma cleaning with a test sample.

Fig. 3. The change of average cleaning rate as a function of rf-biased potential to the sample holder.

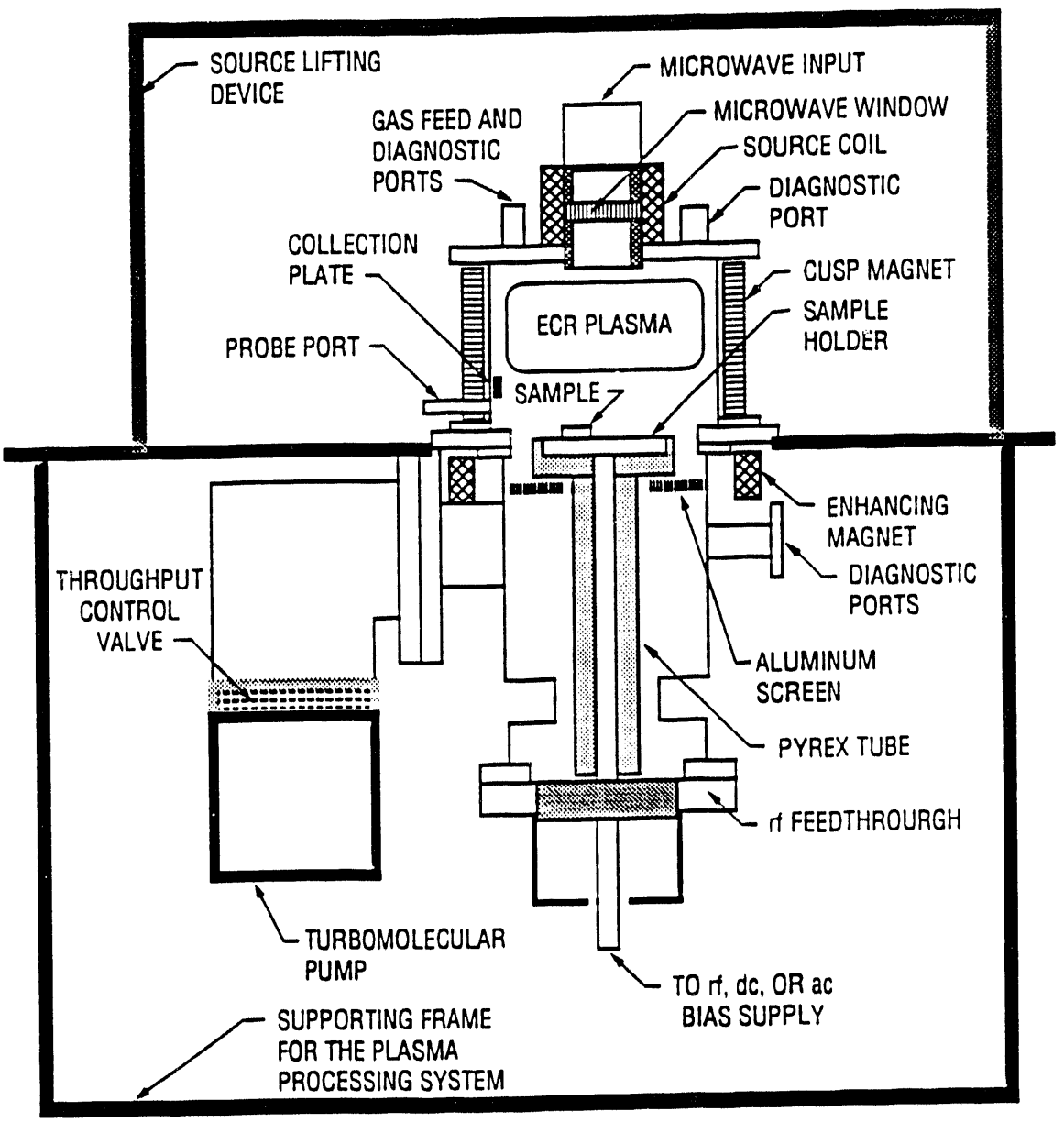
Table 1. Oxygen plasma cleaning on aluminum samples coated with thin oil films.

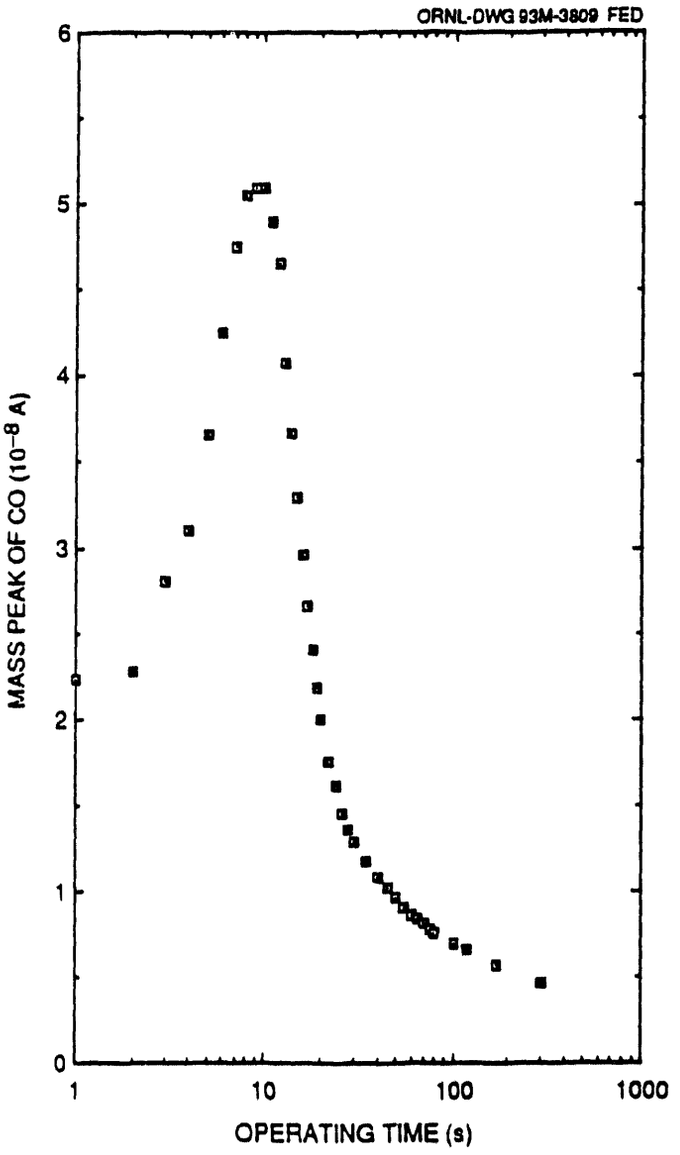
Sample ID	Oil mass mo (mg)	Mass loss m' (mg)	Biased potential Vsh (V)	Operating time t (min.)	Source pressure psc (mtorr)	Current density J (mA/cm^2)	Microwave power Pμw (W)	C/Al 1.46	O/Al 3.34	Bare surfaces	Surface feature	Remarks
92-50	0.8	0.8	-50	20	0.50	8	550	0.94	2.34	Polished	Clean	dc
92-51	1.0	1.2	-100	20	0.50	8	550	1.08	2.62	Polished	Clean & Etched	dc
92-57	0.9	0.9	0	20	0.53	8	550	0.89	2.47	Polished	Clean & Gold	dc
92-96	0.9	0.7	-50	20	0.50	10	550	0.93	2.76	Unpolished	Clean	dc
92-70	1.1	1.1	-75	20	0.53	10	560	1.25	2.35	Polished	Clean	dc
92-72	0.9	0.8	-25	20	0.52	9	560	1.39	2.18	Polished	Clean with spots	dc
92-73	1.0	0.6	-50	20	5.00	1.5	385	438.60	21.33	Polished	Etched, not clean	dc
92-74	1.0	0.4	-25	31	5.10	1	360	138.60	8.44	Polished	Plastic drops	dc
92-82	1.1	0.9	-25	20	5.00	2.2	540	1.25	1.81	Polished	Clean, smooth	rf
92-84	1.1	1.0	-50	20	5.00	2.8	540	1.60	2.11	Polished	Clean, etched trees	rf
92-100	1.3	1.3	-40	20	5.00	2.5	550	2.19	2.04	Polished	Smooth, clean	rf

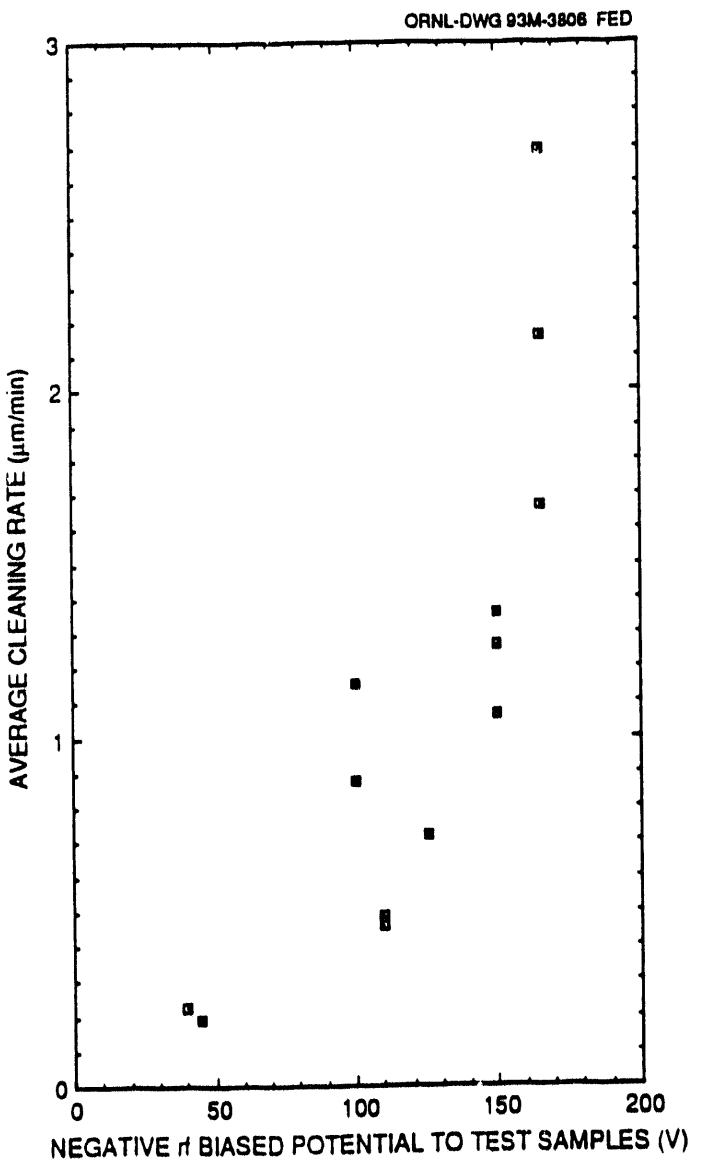
Table 2. Surface composition in percentage of test samples.

Sample \ Element	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

ORNL-DWG 93M-2394R FED




ORNL-DWG 93M-3809 FED
MASS PEAK OF CO (10^{-8} A)
0
1
2
3
4
5
6
1
10
100
1000
OPERATING TIME (s)


ORNL-DWG 93M-3806 FED
AVERAGE CLEANING RATE (µm/min)
0
1
2
3
0
50
100
150
200
NEGATIVE rf BIASED POTENTIAL TO TEST SAMPLES (V)

DATE FILMED

1 / 5 / 94

END