

Plasma Processing of Specimens for Electron Microscopy and Microanalysis

**Nestor J. Zaluzec
Argonne National Laboratory**

Introduction

One of the most vexing problems which plagues microanalysts today remains specimen contamination particularly that which occurs during the course of an experiment. This effect typically manifests itself as a gradual build up of material on the surface of the sample and concentrating itself in the immediate vicinity of the electron probe. This deposit not only obscures the area of the specimen, but also adversely affects the entire range of microanalytical characterization experiments which are being conducted. There are two basic sources of the contaminate, the instrument environment and/or any material which is transported into the instrument environment by the sample itself. A number of studies have documented this effect and suggested methodology to minimize it's accumulation[1]. All of these procedures have up to now been mainly passive mitigation, that is, they slow down or delay the onset, and rarely directly attack the source of the contamination. In this chapter we outline a procedure which, in modern instruments, attacks the problem at its source.

In the past, the principle source of contamination in electron column instruments could be attributed directly to the relatively poor vacuum, however, in the modern instruments of the last decade, this is no longer the case. Careful redesign of the microanalytical equipment has minimized and in some cases even eliminated the vacuum system as the primary source of this phenomenon. Unfortunately, the development of

high brightness electron sources (LaB6 and Field Emission), now accessible to the average laboratory environment, has elevated the problem of specimen borne contamination to a major issue which affects the successful use and operation of these instruments.

In this chapter we will focus upon the application of a relatively application of an old technique, namely plasma enhanced reactions, to mitigate and in most cases eliminate the source of specimen borne contamination problem [2]. In addition, when contaminants are affixed to the interior of an instrument an extension of this same procedure can also be used to clean the instrument itself [2].

Background:

Contamination, the bane of the electron microscopist/microanalyst, frequently takes the form of a deposited mass of material on the surface of the specimen. Examples of this are shown in Figure 1a for a Transmission Electron (TEM) and in Figure 1b for a Scanning Electron Microscope (SEM). In the former we see a dark electron opaque region concentrated about the periphery of the focussed electron probe, while in the latter a lighter region in the shape of the electron raster, or if the probe is static a gradually developing cone. In all cases, spectroscopic analysis shows this deposited material to be principally composed of carbon. In the past the most common culprit for this substance was attributed to the various oils and greases employed in the pumping systems of the microscopes. As described by Hren [1], these organic hydrocarbons have the propensity to accumulate in the immediate vicinity of the electron probe and under the action of that same probe polymerize to form stable deposits on the surface of the specimen. Once the partial pressure of hydrocarbons backstreamed from the various vacuum system components have been minimized, then the next most important source becomes transport into the microscope environment by the specimen. For the sake of brevity we will for the remainder of this text only refer to hydrocarbons transported by the specimen, however, the reader should keep in mind all the points made herein apply equally well to any stage mechanism used to hold the specimen. This is

especially true when the specimen is mounted in this device on the typical laboratory benchtop and is then transferred directly into the microanalytical system.

Regardless of the specimen being studied, it is safe to say that it will at some time during its existence have had its surface exposed to organic hydrocarbons. This could be either through handling, cleaning with solvents, or transportation through the ambient environment. While it is possible to slow the process of surface diffusion of any hydrocarbons to the vicinity of the electron beam, this only delays the onset of contamination. Ultimately the deposits will form albeit delayed by some fixed time constant. Logically, the appropriate procedure to eliminate a contamination effect would be to attack the problem at its source, namely removal of the various molecular species from the surface of the specimen before it enters the environment of the instrument. This is not a new concept, organic and inorganic material removal and has been the subject of numerous methodologies for decades, and in fact forms the basis of many specimen preparation methods in EM for both the life and physical sciences. However, the difference in this situation is that those latter techniques (dissolution, embedding/cutting, chemical/electrochemical polishing, mechanical polishing) are designed by their nature to remove large quantities of material [see chapters X, Y, Z of this book]. In the scenario we are considering the analyst has already spent a great deal of time (and effort) to establish the conditions for the removal of various layers of material from their specimen. The key is to now remove the last few layers of any substance, particularly organic hydrocarbons which may have been left on the surface without disturbing the ultrastructure of the substrate which is obviously the area of interest.

There are a number of techniques which can be employed to remove surface layers from substrates and include washing, heating, sputtering, and finally plasma induced volatilization. Washing of course will once again expose a surface to a foreign substance and for some materials this suffices to remove debris, except when the surface layer is insoluble or tightly bound to the substrate. Heating in vacuum and/or inert atmospheres has been also used successfully for many years, but has an obvious limitation for a range of specimens. Energetic particle sputtering (electron, ions, and/or neutrals)

has been employed successfully for decades but can have deleterious effects frequently changing substrates surface structure and sometimes even its composition. Plasma induced volatilization, on the other hand, can be selectively tailored to react with molecular species on the surface of a specimen and effect removal of organic compounds by conversion of bound hydrocarbon to a gaseous phase. Once converted into a gas, it can be passively carried away from the sample. It is, potentially, one of the least aggressive methods available today to perform the final cleaning of the surface of a specimen prior to electron microscopy. The balance of this chapter will focus on the plasma process and present examples of the efficacy of the procedure.

Plasma Basics

A plasma is an ionized conductive gaseous form of matter in which ions, electrons and neutrals coexist simultaneously [3]. Plasma's can be produced through the action of either high temperatures, or strong electromagnetic fields. In this chapter we only consider plasmas produced by the latter. In this situation, the field can be produced by dc, rf, or microwave generators and the net effect of the EMF is to cause electrons to be removed from a reduced pressure gas near any electrodes. These stripped electrons are then accelerated by the same imposed field through the remaining gas and lose energy by collision with gas molecules forming a variety of active species including additional electrons, free radicals, ions and neutral atoms. Any substance inserted into this plasma will be subjected to bombardment by these species and the kinetic or potential energy which these products contain.

There are two types of plasmas: low energy (1-20 eV) sometimes termed glow discharge, low temperature (or cold plasmas) and high temperature plasma's where the mean temperature of the gas can range from hundreds to millions of degrees. We will only concern ourselves with the former type of plasma, in which the effective temperature of the larger ionized gas molecules is only a few tens of degrees. These are sometimes referred to as non-equilibrium plasmas as the mean temperature of the larger ions and neutrals is far less than that

of the free electrons. The free electrons in these plasma's can, however, have relatively high energies (10-20 eV) and at these energies the electrons are of sufficient energy to ionize neutral gas molecules causing the visible glow commonly observed in these systems.

Experimental Equipment:

DC plasma generators can be built from simple high voltage power supplies, electrodes and a suitable gas container. In a typical arrangement two electrodes are placed in a reactor connected to a variable high voltage supply and gas source. The exact gas pressure, voltage, and inter-electrode spacing varies depending upon the gas chosen. Commonly, pressures of less than 1 torr and a DC potential of 10-100 V/cm are required to create the plasma. These devices are generally not found in the commercial market but can be readily built in the laboratory. Microwave level plasma generators can also be constructed but these devices generally operate at much high power and pressures. Most microwave based devices are designed for larger scale industrial applications. Microwave induced plasmas are more difficult to initiate and are difficult to sustain at low pressures, they also tend to produce higher temperature plasmas and are more often used in pyrolytic decomposition, rather than gentle cleaning of EM samples as is our purpose herein.

The most common commercial plasma processing systems now employed for surface cleaning in the microanalysis community employ simple rf generators operating at 13.6 MHz. Unlike the DC systems, at these higher frequencies, direct contact of the gas with an electrode is not required since the energy can be introduced into the carrier gas by inductive or capacitive coupling. Two different geometries (figure 2) are most often found. In the first geometry (2a) two electrodes are placed along side (or within the reactor) and ionizes the gas via inductive coupling. In the second configuration (2b) a coil or electrode is wound around the periphery of a reactor inducing an energy transfer by capacitive coupling. Both geometries work equally well in producing a suitable gas plasma. In the range of 1-200 MHz there is little frequency dependence of plasma reaction, and the frequency chosen is usually dictated

by handling, shielding and interference effects with external scientific equipment. For the purposes of contamination removal, plasma generators with fixed frequency and adjustable power are the most appropriate. Adjustable power levels allow the user to tune the nature of the plasma processing reaction from a mild volatilization level, through a sputtering/etching range, to the higher power microincineration regime. The typical gas pressure in the plasma chamber for rf applications is usually in the range of 50-300 mTorr and the power in the range of 1-10 W.

A typical experimental arrangement for a complete plasma processing system using an rf based system is shown in figure 3. It consists of a reactor chamber, adjustable gas supply, adjustable rf source, airlock, and pumping system. The nature of the pump is irrelevant to the whole plasma processing procedure so long as proper vacuum system operating procedures and a continuous gas flow across the specimen is maintained. Only when a pumping system is operated incorrectly and allowed to reach the molecular flow regime, causing backstreaming of oils from the pump does the nature of the pump (oil free vs conventional) become important. As this is contrary to good laboratory practice (pumps should be maintained in the viscous flow regime) we shall ignore the backstreaming condition as irrelevant to the remainder of this discussion.

Plasma Processing: Volatilization of Hydrocarbons

The entire process of organic hydrocarbon removal using plasma processing can be reduced to a simple concept. Removal of surface bound hydrocarbons will occur when sufficient energy is introduced to change the hydrocarbon/substrate bonds in such a way that it is more energetically favorable for the organic compound to detach itself from the sample surface. Once detached, a simple inert gas flow can be used to sweep the resulting molecular species away from the surface of the sample.

The energy need for this bond breakage can be transferred from the plasma to the specimen through any of three mechanisms: optical radiation, neutral particle fluxes or charged particle bombardment. This energy is absorbed by the

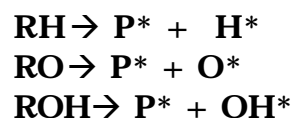
hydrocarbon and subsequently dissipated by a variety of secondary processes and it is these processes which give rise to the desired surface cleaning. The details of these processes are well beyond the scope of this text and the interested reader is referred to the literature [4]. Briefly we can summarize how each of these three mechanisms transfers its energy as follows.

The optical radiation in a plasma contains both infrared (IR) and ultraviolet (UV) components. UV radiation is generally strongly absorbed by polymers and results in the formation of free radicals which tend to be active sites and can readily react with gas components of the plasma. The IR radiation transferred from a the low temperature plasma's has a negligible effect.

Neutral particles in the plasma bombard the sample continuously and impart energy in the form of kinetic, vibrational, dissociations and excitational modes. The kinetic and vibrational modes tend to mildly "heat" the specimen, while the dissociative and excitational modes (particularly in hydrocarbons) create free radicals.

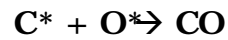
Lastly the charged particle flux carries kinetic, vibrational, and electronic energy which can impart heat, and if of sufficiently high energy may also cause sputtering. In the process they also can create free radicals.

Apart from the obvious sputtering process, which is akin to a mechanical removal of the surface contaminant, the formation of free radicals is the most important step in the removal of hydrocarbons. These free radicals can involve a number of species including O, OH, H and C bonds. The exact process which occurs depends upon the specific hydrocarbon which is present, we can however outline the process which occurs as one of the following:



here RH, RO, ROH, are symbolic representations the various hydrocarbons having a low energy bond to H, OH, or O while P* the product free radical which results once the H, OH, or O bond

has been broken by the energy transferred by the plasma. Once a free radical is formed the released components (H, O, OH) can combine with any of the remaining component of the "system" and ultimately, after a number of steps, reducing the hydrocarbon to CO, CO₂ and/or H₂O, all of which are readily removed from the system by the continuous gas flow via a process which may be any of the following:



Clearly there are numerous intermediate steps in the breakup of the hydrocarbon, however, eventually all the C,H,O bound up in the original hydrocarbon is converted to a gaseous phase and thereby released/removed from the specimen surface. Because the hydrocarbon can in effect also be the source of it's own oxidant, inert gases (Ar, N₂, H₂...) can be used for the plasma as well as reactive gases (O, CF₄...) . The advantage of employing a reactive gas such as O₂ is in the speed of the conversion of the hydrocarbon to a gasous phase since the C + O → CO reaction can be a rate limiting step. While in some cases this may prove to be advantageous, in others it can be detrimental, particularly when the substrate or the principle component of the sample is mainly carbon. In these situations, a milder less aggressive and more controlled process is afforded by employing only inert gases such as Argon. The use of even more aggressive gases such as CF₄ , NH₃, and SiH₄/N₂O is well documented in the semiconductor industry[5] and is applicable in select cases, however, overall the most commonly used gases are pure Argon, pure Oxygen, or mixtures thereof.

Experimental Details

The majority of the results described below have been conducted using an inductively coupled plasma cleaning system described in the literature [6,7], however, similiar results have been also obtained using a capacitively coupled system. A list of manufacturers of commerical plasma cleaning systems can be found at the following URL

(<http://www.amc.anl.gov/Docs/ANL/TechTrans/PlasmaCleaning.html>) as well as appendix 1 of this document.

In order to assess the magnitude of contamination mitigation by plasma processing it is essential to document a measurement protocol to determine the efficacy of the cleaning process. The procedure for this was developed by Zaluzec [6] in 1996. This method relies on the fact that the deposition of material on the surface of a specimen increases the local mass thickness. By employing a TEM based microanalysis technique namely: Electron Energy Loss Spectroscopy (EELS) the instantaneous rate of change of the specimen thickness can be measured. This is done by measuring via EELS, the carbon inelastic scattering peak (at $E = 23$ eV) relative to the elastic scattering peak at ($E = 0$ eV), which is proportional to the amount of material being deposited on a specimen. In figure 4, we show the change in an EELS spectrum as a function of time, recorded in a TEM while contamination is building up. At the left we see a TEM image of the 304 SS specimen area with dark "contamination" marks which have built up under the action of a focused electron probe for 15, 30, 60, 120 seconds respectively, while at the right selected EELS data showing the change in the spectra with increasing contamination. From the integrated spectral data one can quantitatively measure the intensity of the inelastic to elastic scattering and from that derive a measure of the nominal thickness of material which was deposited, and is shown also in the figure. After 120 seconds we see that a thickness of over 500 nm of carbonaceous material is deposited completely obscuring the sample.

By continuously measuring spectra as a function of time and then plotting the instantaneous value of mass thickness ($t / \ln(I[\text{inelastic}]/I[\text{elastic}])$) we can quantitatively measure the amount of contamination building up on the specimen [6]. Next by subjecting the specimen to various plasma processing conditions and repeating the measurements on neighboring areas of the specimen the effect of plasma processing on the contamination rate can be precisely determined. For the purposes of the remaining discussion we will measure the amount of contamination by simply plotting the normalized mass thickness ($t / [t_{\text{at time} > 0} / t_{\text{at time} = 0}]$) of the specimen with time. If no contamination develops, then the value of normalized mass thickness should remain constant at a value of

unity, while if the specimen contaminates the value)of (t/ will increase. A classic example of this is shown in figure 5, again for an electropolished 304 SS TEM specimen. Here the topmost curve illustrates the contamination buildup for a virgin (untreated) specimen. In this figure we see that after only 300 second the mass thickness under the beam has increased over 900%. If we take this specimen and process it in a pure Argon plasma for 5 minutes, in a commercial plasma cleaner [7], and return to the neighboring area repeating the measurements we see that the contamination is reduced (in this example) nearly 20 fold.

Continued processing by increasing the plasma exposure time in 5 minute increments, we observe a continuous decrease in the contamination rate (slope of the t vs t plot) as shown in Figure 6. In this figure we have suppressed the initial untreated data (shown in figure 5) for clarity, and from this data we see that additional processing incrementally decreases the contamination rate, and thus by inference increase the removal of the hydrocarbon from the surface. Increasing the processing time beyond 15 minutes will continue to mitigate contamination. Significant to note, in this example, is that the reduction in contamination rate was achieved using pure Argon as the carrier gas of the plasma. This clearly demonstrates that cleaning (i.e. the removal of hydrocarbons) can be achieved without the use of any reactive gases. Since we know that the contaminant initially contained carbon (via the EELS measurements alluded to earlier), and subsequent measurements show the absence of carbon, we hypothesize that that the carbon is being removed by conversion from its solid hydrocarbon phase (as illustrated by the dark marks in of figure 4) to a gaseous phase (most likely CO or CO₂) using Oxygen evolving from the creation of free radicals. Although Argon as a carrier gas for plasma cleaning is effective, it has been occasionally found to be advantageous to change the carrier gas, particularly when the sample exhibits severe contamination. This is further illustrated in figure 6, where a brief final treatment of 5 minutes in a pure Oxygen plasma has been used to clean the sample. Experimentally, it has been found that a two step process (first Argon, then Oxygen) is in many cases sufficient to

mitigate the most extreme specimen borne contamination conditions.

In figure 7, we can see an example of how the plasma cleaning treatment affects the formation of visible contamination deposits. Shown here is an area of the 304 SS specimen in a TEM, where contamination formed readily by a focussed probe in the area indicated as "untreated". Next the specimen and stage was removed from the instrument, cleaned with Argon for 5 minutes and the experiment repeated under identical conditions of probe current, size and time. The obviously visible reduction in contaminant, as illustrated by the reduced thickness deposits on the left hand side (indicated by the arrow labeled 5 Min Ar) correlates with the results of figure 6. A second plasma processing treatment, this time of an additional 5 minutes in an Oxygen plasma completely eliminates any deposit, as can be seen in the figure. We hasten to point out, that EELS measurements show a small measurable contaminant being left on the surface, however, this is not detectable by simple imaging experiments. It is also important to note that the conditions used here, (200 mTorr gas, 10 W and 5 minutes of cleaning) were not sufficient to remove the polymerized contaminant previously deposited on the surface of the specimen. These deposits are strongly bound to the surface and can only be removed by operating the plasma processing system in a microincineration mode [8]. Microincineration of material is particularly aggressive and should only be resorted to in extreme cases. Since the contamination deposits formed during the untreated observation are now polymerized and in effect strongly bound to the surface, their removal is not critical, nor do they contribute to further contamination of the sample. This is succinctly illustrated in figure 7, by the fact that a focussed probe located less than 100 nm away does not form any visible deposits even with the mass of hydrocarbon nearby.

The obvious question at this point becomes why not use oxygen either in its pure form or as a mixture with an inert gas at all times?

Firstly, the use of Oxygen is not always necessary. In figure 8, we illustrate the results of plasma cleaning of chemically polished silicon. Here, we compare the virgin sample, which

contaminates readily ($\tau/3$ after 300 sec) with the results of a 5 minute Argon plasma treatment, followed by a 5 minute Oxygen processing. In contrast to the results from the electropolished steel (figure 6), we see that there is a negligible difference between the Argon, followed by Oxygen. This can be attributed to the fact that initially the amount of contaminant was smaller ($\sim 1/3$ that of the steel) as well as the fact that the substrate material and initial polishing solutions were different to the metal foil. It is also a well known fact that the sticking coefficient of hydrocarbons to semiconductors is less than that of metals, which further increases the ease of cleaning.

Secondly, there are situations where carbon is an important part of the sample being studied. For example, it is a common practice in the physical sciences to prepare samples of brittle materials for examination in TEM by crushing and then suspending these particles in a solvent solution and then placing a drop of the suspension on a holey carbon film. When the solvent evaporates small pieces of the particles cling to the edges of holey carbon film which provide, in effect, a fine mesh grid to support submicron to nanometer size material (figure 8). The use of an reactive gas plasma in this situation should be avoided since the plasma will aggressively attack the support film. Here the milder Argon plasma treatment is the more logical procedure.

Finally, in figure 9, we compare the use of a 50/50 Argon/Oxygen carrier gas mixture used for 10 minutes, compared to a 5 minutes each of Argon and Oxygen on chemically polished Silicon. Here, as in figure 6, we have suppressed the untreated data and only compare the resulting showing contamination buildup after plasma processing. While both carrier gases very effectively clean the the sample, the two step process of Ar followed by O₂ was better at removing the hydrocarbon and for a longer time period than the Ar/O₂ gas mixture.

As we alluded to earlier, removal of contamination deposits on the surface of the specimen once formed is also achievable. These deposits are strongly bound to the surface of the substrate and require the plasma system to be operated as a microincineration system [8-11]. Copious amounts of reactive

Oxygen are required for this process either in pure state or mixed with Argon, and since the hydrocarbon is tightly bound, higher energy (power) levels are generally needed. As these conditions are more aggressive care must be taken so as not to affect the substrate (and also the specimen stage).

Plasma Conditions and the Effects on the Specimen/Stage

Varying the rf power level of the generator will clearly add more energy to the system, and there are positive and negative effects. As power levels are increased the energy imparted to all plasmas species increases. As the power levels increase both the specimen and stage can begin to heat as is illustrated in Figure 10. Here the power levels of the plasma system were increased from the nominal cleaning levels of ~ 10 W upwards to 40 W. Using a thermocouple the specimen and stage the temperature rise was monitored and we see that a 15 degree increase is easily achieved. This will of course increase the rate at which the sample is cleaned but at the cost of a temperature rise, mainly due to electron bombardment heating. Higher power levels also mean that higher energy plasma's are created and conditions corresponding to ion beam sputtering can be more readily achieved [9]. Again this process will clean the sample more effectively, but can also subject the specimen support to sputtering effects if the power is sufficiently high. If a instrument stage from the electron microscope is also inserted into the plasma, then this is a situation which should be avoided. At very high power ~ 50-100 W rf systems employing Oxygen become pyrolytic microincinerators and complete ashing of specimens is possible [8].

Since there are a number of different commercial plasma cleaning systems, it is difficult to generalize the optimal conditions for cleaning. However a few remarks are in order.

- 1.) The power level used should be set at a minimum possible, just enough to initiate a glow discharge. This is done insure that only a mildly energetic plasma is created. Higher power plasmas will not only clean the specimen but may also sputter the stage and/or reactor components (such as electrodes or wall material).

2.) Use the manufacturer's recommended settings as a starting point, but develop a set of conditions which work best for the type of samples you most often use. Gas pressures in the vicinity of 50-300 mTorr, and power levels ~ 10 Watts are reasonable starting conditions.

3.) Insure that you never create conditions which may cause backstreaming from the vacuum pumping system to enter the plasma reaction chamber. Always operate above the molecular flow regime of the pumping system used to create the gas flow.

4.) Vary the plasma processing time based upon the nature of the carrier gas. Inert gases work but require longer (~ 5-15 minutes) processing times than reactive gases (2-5 minutes). The more contaminated the sample the longer processing time will be required regardless of the carrier gas employed.

5.) A carrier gas of pure Argon is the least aggressive means of removing hydrocarbons and works reasonably well in all cases studied by this author . This includes the following

- electropolished metals,
- chemically polished semiconductors,
- ion-milled samples,
- evaporated metallic films
- crushed powders suspended on holey carbon films
- holey carbon films

6.) Carrier gases containing reactive gases such as Oxygen are more effective in removing tightly bound hydrocarbons, however care should be taken in it's use so as not to effect substrate materials. This could include not only sample support films (such as holey carbon), but also the specimen stage itself.

7.) If pure Argon plasma alone is insufficient to expeditiously remove the hydrocarbon source then a two step process of

Argon followed by Oxygen appears to work better than an Argon/Oxygen mixture.

Concluding Remarks.

In current generation of microanalytical instruments, the primary source of contamination has become that which is borne into the instrument by the sample and its supporting hardware. A technique has been developed which allows simultaneous cleaning of a sample and a specimen stage which minimizes and, in most cases eliminates, contamination of specimens analyzed via SEM, TEM, STEM and/or AEM. The technology involves subjecting the specimen and the specimen stage to a plasma (either DC or RF excited) which efficiently removes a wide range of contaminants from critical surfaces. The procedure may be carried out prior to inserting the specimen and specimen stage into the instrument by introducing the entire sample or sample assembly into a plasma reaction chamber. Once in the plasma, there are three basic mechanisms which are available to release bound hydrocarbon from the surface of a specimen. .

- Conversion of hydrocarbons on the surface of the specimen into chemically active species by reaction with plasma components.
- Thermal activation of the surface by bombardment of the surface by the electrons of the plasma.
- Sputtering of the surface by accelerated heavy ions in the plasma, this is similar to the process of ion milling covered elsewhere in this text book.

By selection of the initial gas species (or mixture thereof) and its plasma energy one can tailor the nature and extent of these surface interactions. Both reactive and noble (inert) gases can be used to form the plasma. When reactive gases, such as Oxygen, are used in the plasma then a chemically enhanced plasma is produced this generally accelerates the process of hydrocarbon removal, however, inert gases such as Argon also work extremely well and in some cases are the preferred choice .

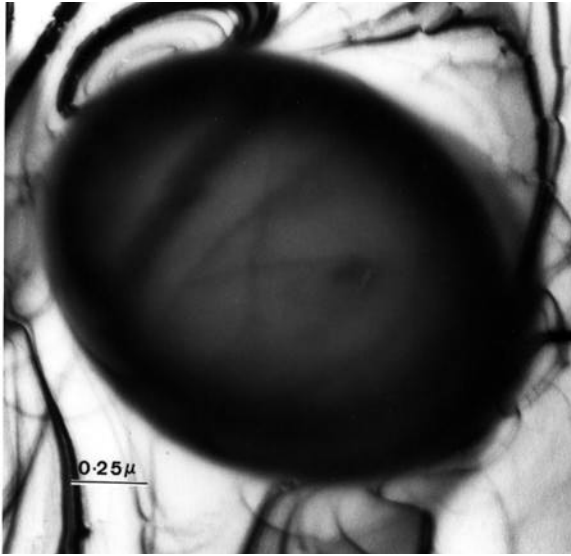


Figure 1a Contamination deposit formed by a large (~ 1 micron) focussed probe in a TEM

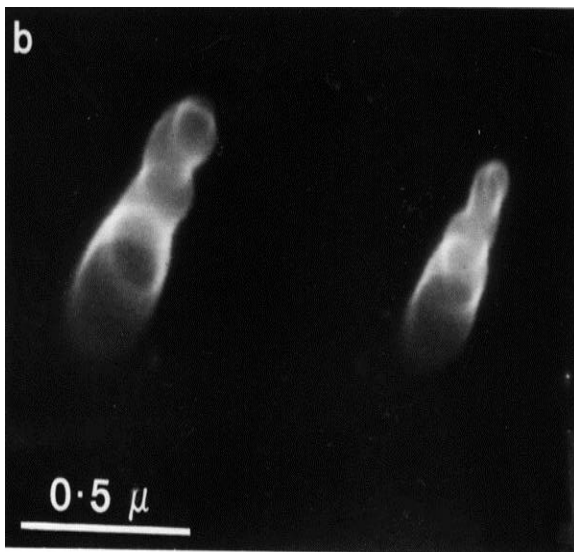


Figure 1b. Contamination deposit formed by 0.1 micron probe in an SEM.

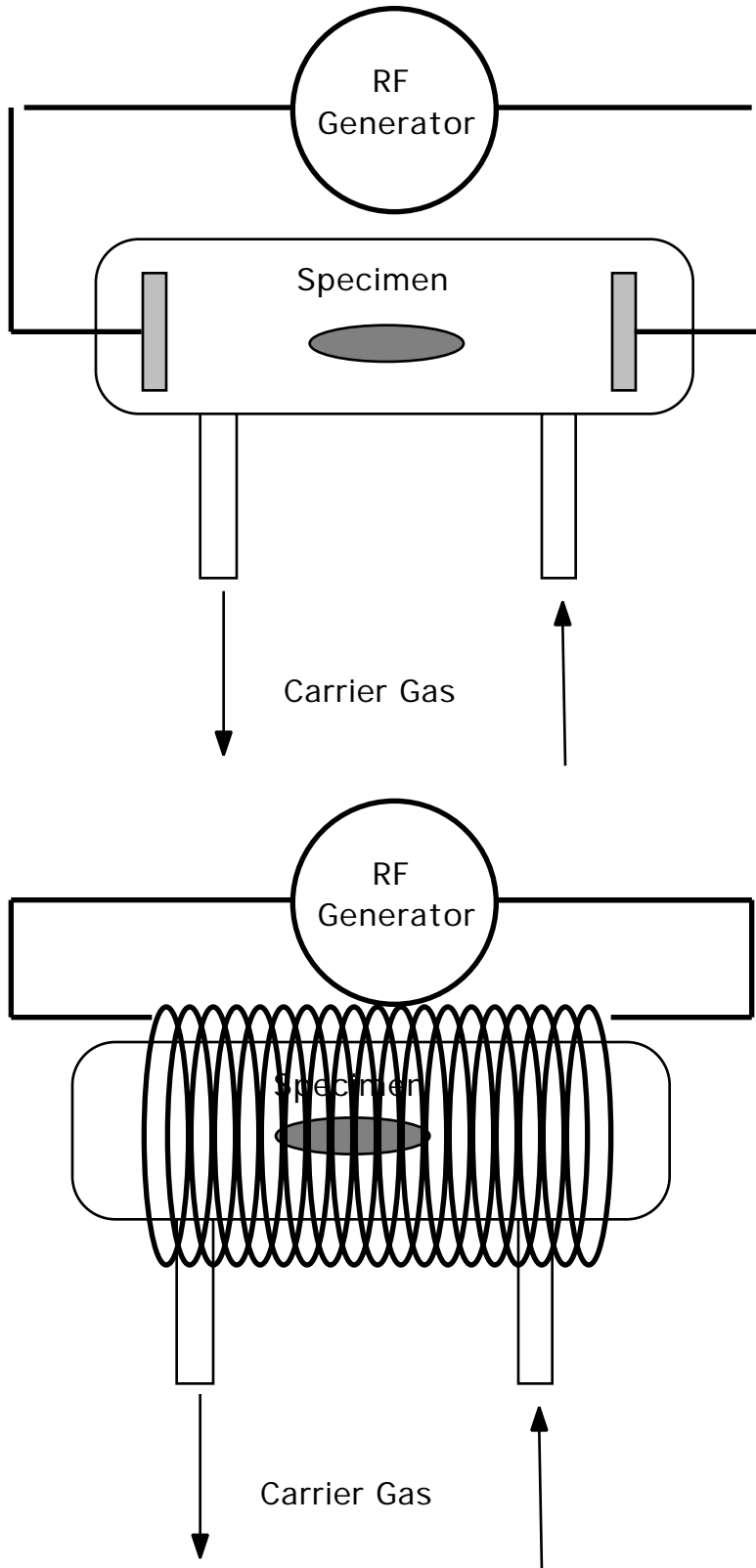


Figure 2. Typical geometries for inductive (2a) and capacitive coupled (2b) Radio Frequency (rf) plasma systems.

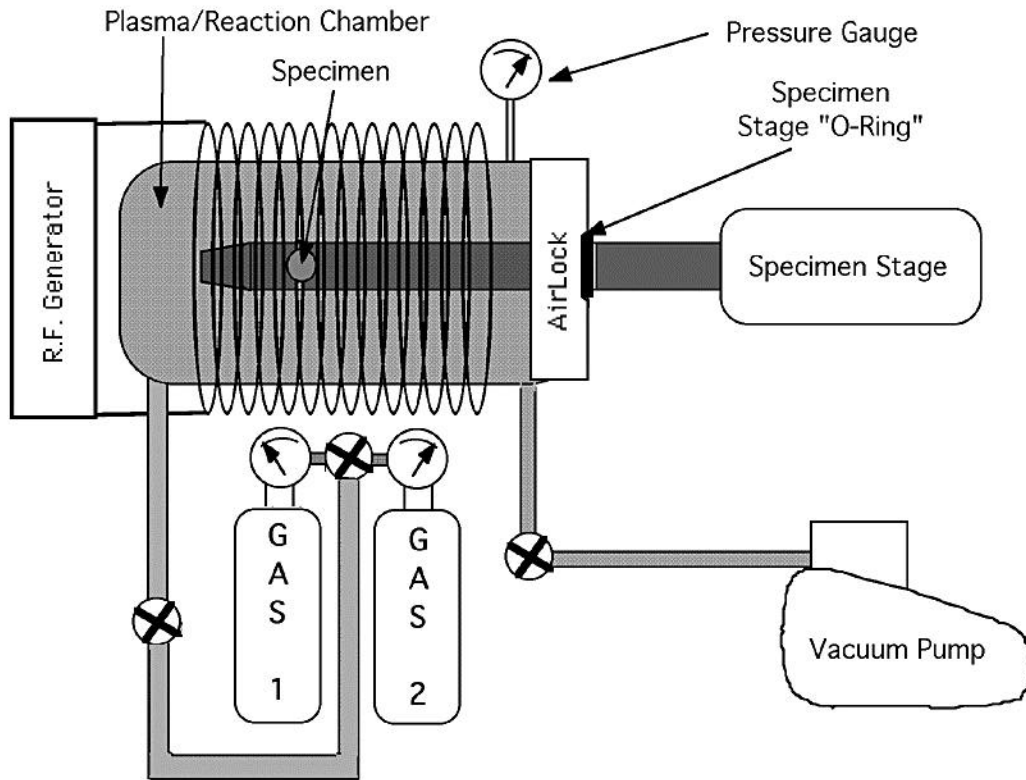


Figure 3. Typical configuration of a complete plasma processing system. Specimen is held in a stage which can be directly inserted into the electron microscope. For the case of a TEM, the specimen stage o-ring forms the seal on an airlock to the plasma/reaction chamber. In the case of an SEM the sample alone or the entire stage might be inserted into the chamber. The rf generator is shown as capacitively coupled but could equally well be inductively coupled. A pressure gauge is used to a measure the internal carrier gas pressure which is adjusted by a needle valve on the gas inlet. Mixing valves allow the choice of multiple gas sources. A simple mechanical roughing pump suffices to evacuate the chamber.

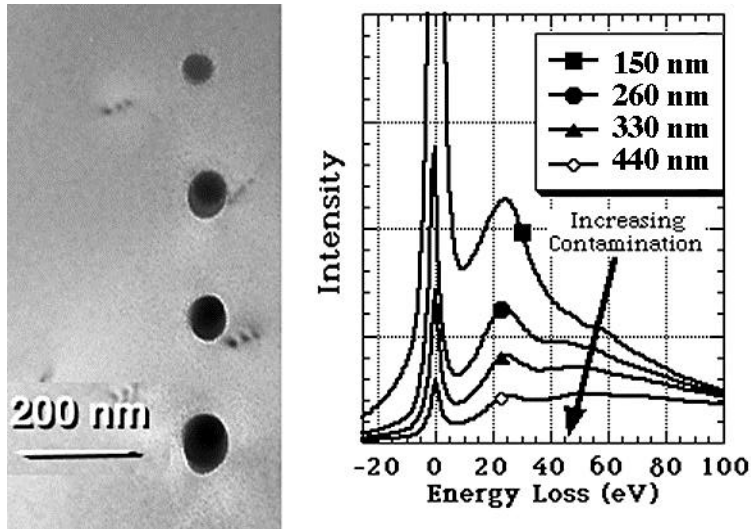


Figure 4. Left, contamination spots formed in a TEM during focussed probe analysis in 304 SS for 15, 30, 60 and 120 sec. . Right, experimental Electron Energy Loss Spectra as a function of contamination. The ratio of the peak at zero energy loss to that at 23 eV is inversely proportional to the mass thickness of hydrocarbon on the specimen. The nominal thicknesses of the hydrocarbon deposits formed are indicated on the graphs.

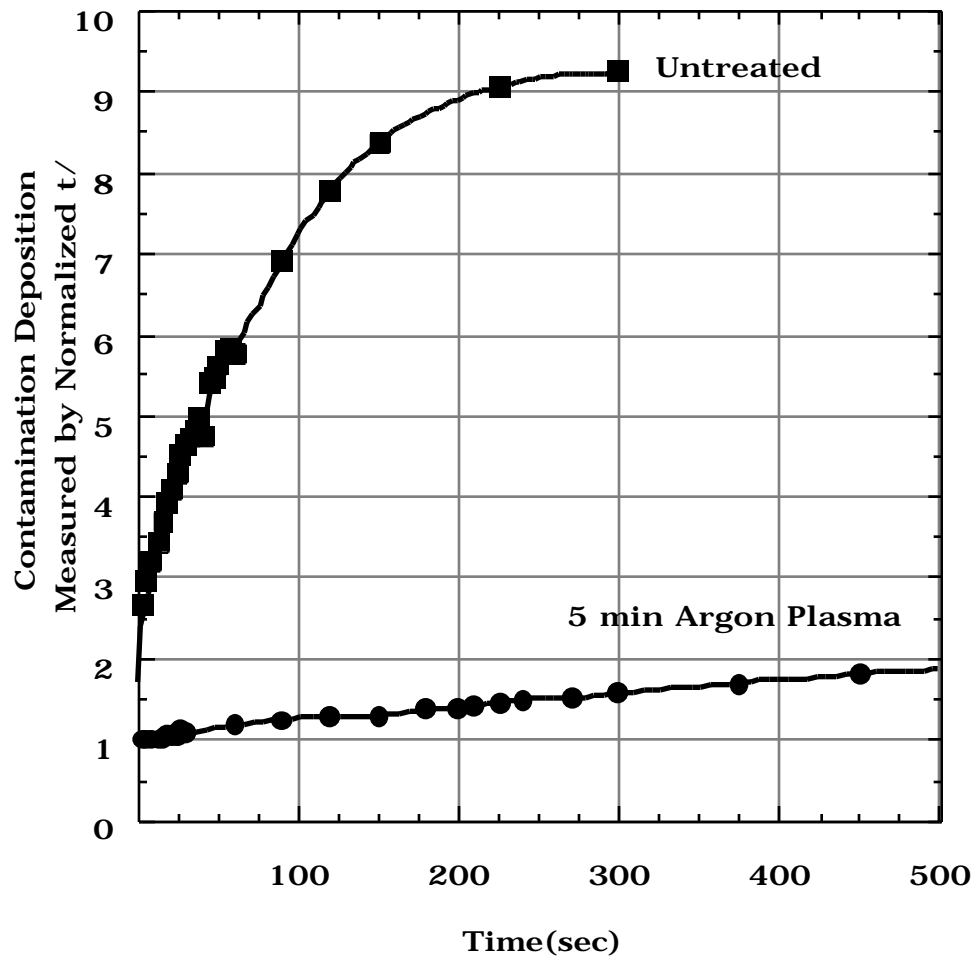


Figure 5. Experimental measurement of the mass deposition (contamination build up) on the a specimen of untreated electropolished 304 SS specimen, and a neighboring area under identical conditions after 5 minutes of plasma cleaning. Note the nearly 20 fold decrease in contamination. The contamination rate is determined by the instanteou slope of the curve. A slope of zero (constant value) would indicate zero contamination.

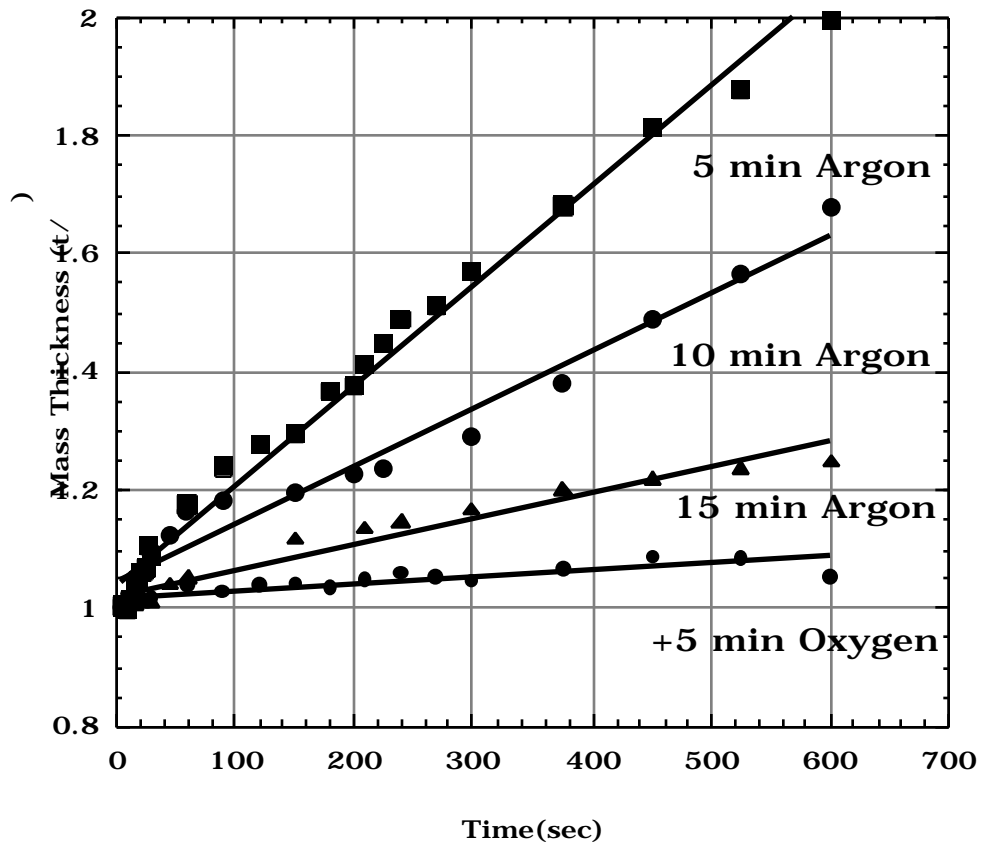


Figure 6. Continued reduction in contamination build up is achieved by successively longer treatments in Argon plasma. Same conditions as figure 5, however, the original untreated data is not shown for clarity. Note the final processing step consists of 5 minutes in a pure Oxygen plasma.

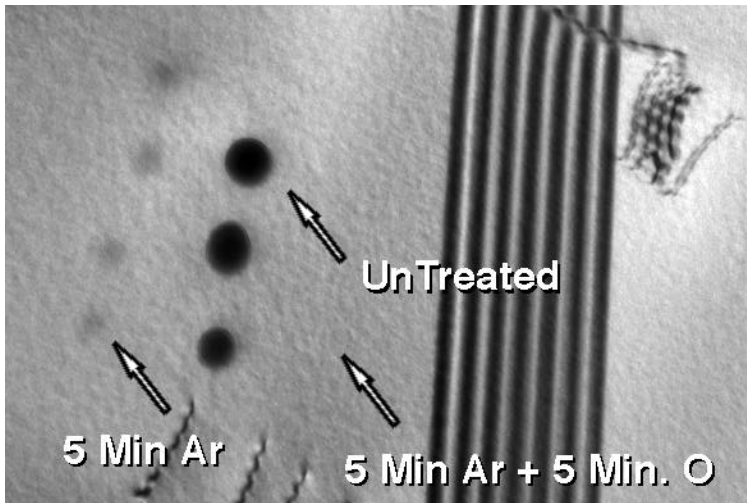


Figure 7. Micrograph showing the contamination before (untreated), after 5 minutes of Argon plasma processing, and after 5 minutes of Argon plasma processing followed by an additional 5 minutes of Oxygen plasma processing. The dark spot where the probe was located is no longer visible in the image after the second 5 minutes of Oxygen plasma processing. Arrows serve to indicate the position of the probe under each condition. Note that the cleaning process effectively removes the polymerized hydrocarbon previously deposited on the surface. This can be removed by microincineration (see text).

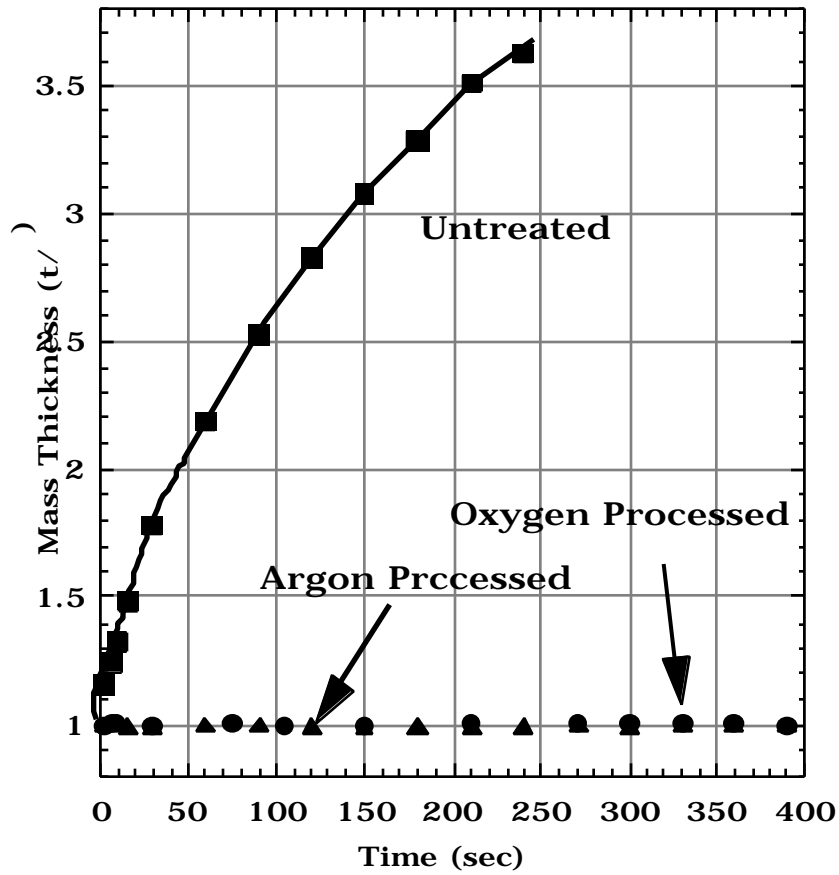


Figure 8. Comparison of Argon and Oxygen plasma cleaning on chemically polished silicon. Note there is negligible difference in the cleaning with Argon and Oxygen for this sample.

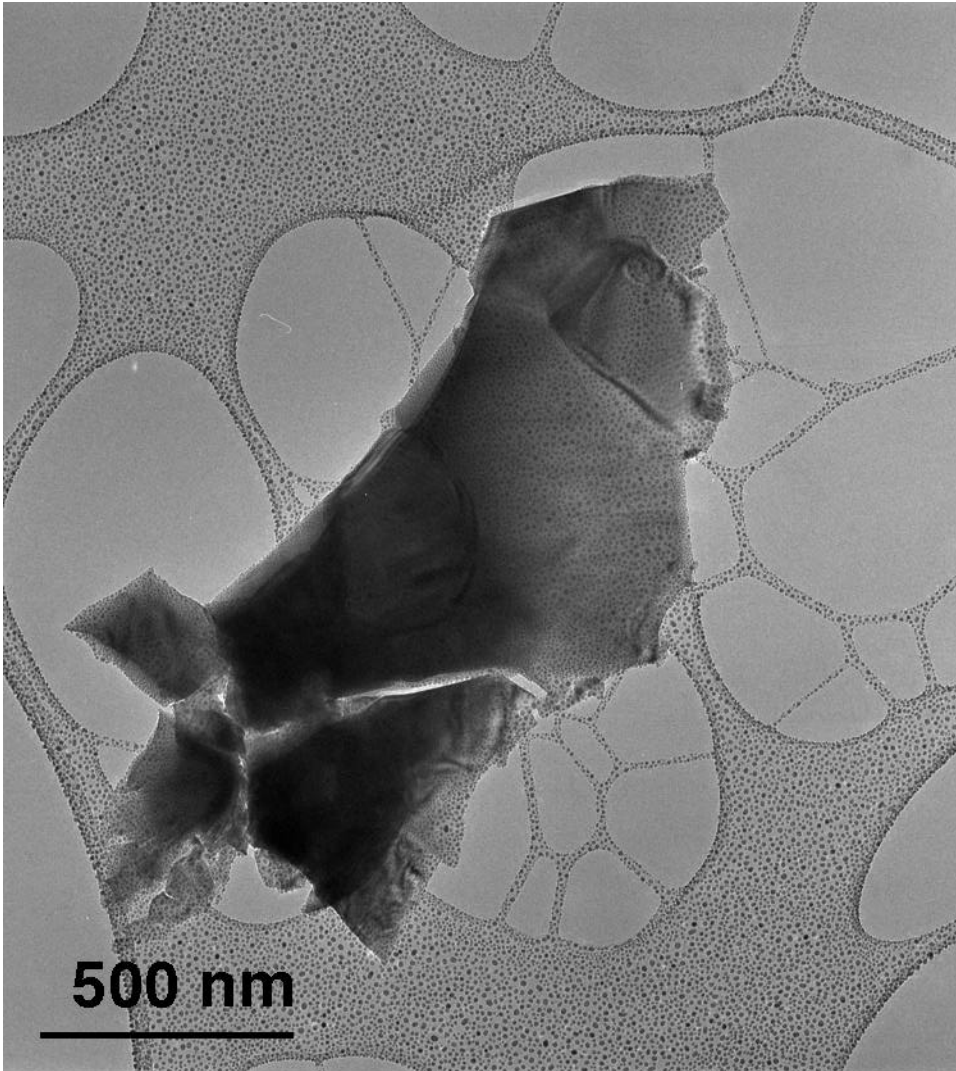


Figure 9. TEM sample of crushed mineral suspended by a holey carbon film. The use of reactive gases will cause attack of the support film and the sample may be lost.

Normalized Contamination Rate on Silicon

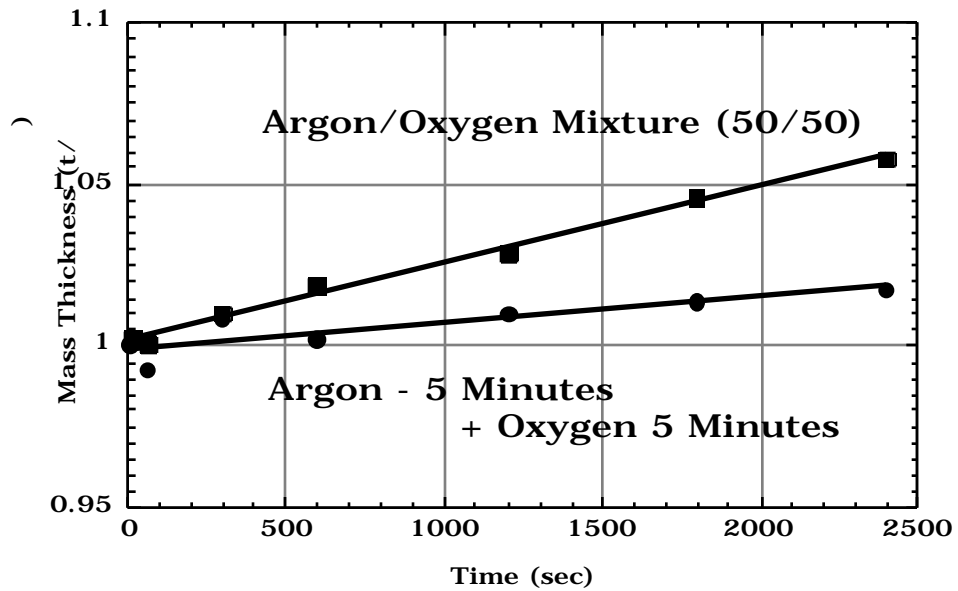


Figure 8. Comparison of successive 5 minute cleaning treatments of chemically polished Silicon using pure Argon followed by pure Oxygen, compared to a 10 minute Argon/Oxygen mixture.

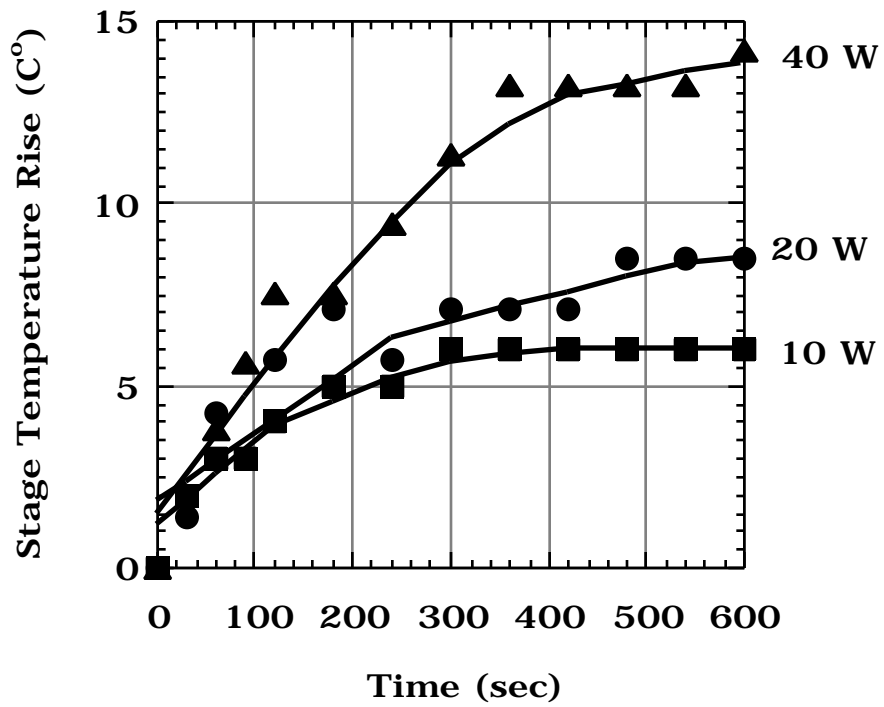


Figure 9. Measured heating of of a stainless steel specimen as a function power level for an inductively coupled plasma generator.

References:

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Appendix 1.

Commerical Suppliers of Plasma Cleaning Systems.

Inductively Coupled Systems:

South Bay Technology Inc.

**URL = <http://www.southbaytech.com>
1120 Via Callejon
San Clemente, CA 92672 USA
Email: sbt@www.southbaytech.com**

Capacitively Coupled Systems:

Structure Probe Inc.

**URL = <http://www.2spi.com>
569 East Gay Street
P.O. Box 656
West Chester, PA 19381-0656, USA
E-mail: spi3spi@2spi.com**

Dual Mode (Inductive and/or Capacitive Coupled)

E.A. Fischione

**URL = <http://www.fischione.com/>
9003 Corporate Circle
Export, PA 15632, USA,
Email: pef@fischione.com**