



Applications of Plasma Technology in Microscopy



Introduction

The cleanliness of specimen surfaces and the high vacuum electron microscope environments in which these surfaces are studied or processed has never been more critical than they are today with examination and fabrication nearing the atomic level. To achieve such accuracy, small

electron probes with high beam currents are needed. Routine manufacturing at the scale required for nanotechnology demands pristine and controlled surfaces in order to create the desired structures. Modern electron and ion microscopes are equipped with sophisticated vacuum systems and can provide these conditions, but maintaining cleanliness over time may be more difficult. One of the ways that scientists have been able to achieve these remarkably unadulterated surfaces has been to subject their samples and microscopes to cleaning by various plasma technologies.

One type of contamination is hydrocarbon molecules from the sample or vacuum chamber surfaces. Minuscule quantities can interact with the electron or ion beam to generate unwanted artifacts in images or data (Vane and Moore, 2014). Hydrocarbon contamination may come from several sources during the steps required for specimen preparation: inadvertent touching of the specimen or specimen holder or handling the samples without gloves, backstreaming if the microscope has an oil diffusion pump system, chemicals used during electrolytic thinning or layer removal, or through adhesives or solvents needed to fix the sample onto the sample stub. While contamination is often considered in terms of the examination of non-biological samples, it is useful to point out that exposure of biological and polymeric samples to ion and electron beams can create extensive carbon contamination and the tools used for this work are often in dire need of methods to clean them as well (Armbruster et al., 2017).

Carbon Contamination

The problem of hydrocarbon contamination inside the electron microscope is well documented and has been an issue from the earliest

days of electron microscopy (Sullivan et al., 2002, Postek et al., 2014). This artifact is often the result of the electron (or ion) beam striking unwanted contaminant molecules and promoting the growth of carbonaceous materials on the surface of the sample. Because reduced numbers of low energy, secondary electrons reach the detector from the contaminated surface, the contamination region often appears as a darkened area in the secondary electron image. Typically in a beam scanning instrument this contamination layer is in the shape of the rastered pattern on the sample, a rectangle (Figure 1). The effect is more pronounced at high magnifications and lower accelerating voltages, just the conditions under which smaller surface features are often analyzed. Cleaning the specimen before placing it in the scanning electron microscope (SEM) helps, but there is always a small amount of hydrocarbon in the system. Also, the source of these residual hydrocarbons is manifold as they can be left behind from the manufacturing of the tool, part of the vacuum or lubrication system, or derived from the sample handling, hence the requirement for periodic chamber cleaning.

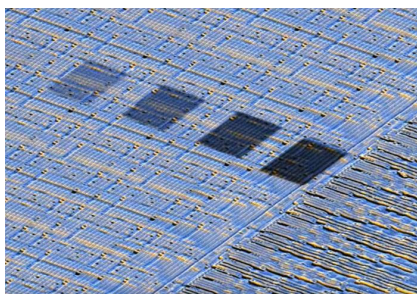


Figure 1. Four contamination rectangles were created on a patterned silicon wafer sample by rastering the beam for 1, 2, 4, and 8 hours (left to right respectively) at 2kV and a beam intensity of 18 in the MIRA3. To record this image a TESCAN

MIRA3 Field-Emission SEM was equipped with an Evactron® E50 plasma cleaner, a SmarAct 8 axes piezostage, and a multi-detector setup made by Pointe Electronic. The thickness of the hydrocarbon deposition layer on the darkest rectangle on the right is ~1000nm (Armbruster et al., 2019).

Historical Background

In 1999, XEI Scientific invented the Evactron De-Contaminator, a practical plasma cleaning system for Scanning Electron Microscopes (SEMs) that could be mounted on the chamber to clean in-situ (Vane. R., US patents). The original Evactron design used a simple manually operated micro-needle valve as a metering valve for the air entering the plasma radical source (PRS) to make oxygen radicals. This Evactron model used a constant rotational speed vacuum pump such as a rotary vane pump, and the pressure was only easily adjusted once when the system was installed. When open, the leak valve and roughing pump always came to the same equilibrium pressure. Newer SEM evacuation system designs use a turbo pump that accelerates during pump down. In response a servo-controlled flow valve was added to an Evactron model in 2004 to stabilize pressure. Control logic was switched to a microprocessor and time, power, and pressure became programmable in 2008. Evactron models were designed to operate at turbo pressures (Vane and Kosmowska, 2016 and Kosmowska et al., 2017). Some of these design advances are shown in Figure 2.



Figure 2. Three generations of Evactron plasma cleaners mounted on SEMs. 1) Evactron 10 PRS in 2004 with the first servo control of pressure, 2) Evactron 25 PRS with shroud over the valve manifold, and 3) Evactron

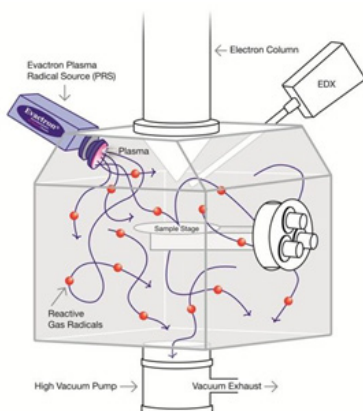
E50 PRS released in 2018 gives high performance cleaning at 50 watts, has an external cathode and lower cost.

Plasma cleaners are now common in the electron microscope suite with users in many disciplines cleaning both samples and sample holders prior to microscopy. Direct plasma cleaners are available from several manufacturers as desktop models. These vary both in sophistication and price. However, these instruments do not address the internal surfaces of the microscope. Although the amounts of mobile hydrocarbon contaminants contained by those internal surfaces might be miniscule, the scales at which observations are now being pursued are such that the issue requires an effective resolution if progress is to be maintained. Any proposed solution which rests upon a requirement for the disassembly and manual cleaning of components is unlikely to be practical and – even if pursued – would entail a level of manual intervention that would potentially place a disproportionate economic burden on any assessment of research costs and benefits.

Theory of Operation

The Evactron system generates plasma from which oxygen radicals are produced for removing hydrocarbons from vacuum systems. Because the vacuum portion of the Evactron, the plasma radical source (PRS), generates a remote plasma, the chamber and specimen do not experience direct plasma exposure.

The general principle shown in Figure 3 below is that the plasma generates active species that convectively flow into the chamber and react with hydrocarbon contaminants to produce volatile compounds that can be removed by the vacuum pumps. The system cleaning



pressures are determined by the pumping system in use. If the system has turbo pumps, the chamber pressure is typically in the 2 to 15 mTorr range (0.3 to 2 Pa). If the system uses a roughing pump, pressures are generally in the 200 to 400 mTorr range (26 to 54 Pa) in the chamber.

Experiments with different gases to create the plasma have shown room air to be an excellent source of oxygen to create reactive radicals and efficiently crack hydrocarbon molecules. It has the benefits of being available, free, and safe. Additionally, through the choice of other noncorrosive gases for producing radicals, different chemical etch processes may be selected while benign regimes for sensitive components and optimized chemistries may be obtained for the fast removal of unwanted contaminants.

The Evactron cleaning process is successful because the hydrocarbon oxidation products are volatile in vacuum. Oxygen radicals oxidize hydrocarbons and form volatile oxides. The oxidation generally begins with scission of carbon-carbon bonds or by hydride extraction (hydrogen atom removal) that creates reactive sites on the HC chain. Subsequent reactions with oxygen radicals further break down the chain, converting hydrocarbons into short chain ketones, alcohols, H₂O, CO, and CO₂, all compounds that are easily pumped away. Low pressures increase cleaning speeds by increasing mean free paths and reducing the recombination rates of the oxygen radicals by three body collisions (Vane and Cable, 2015). Residual gas analysis is effective in monitoring the removal of contaminating species (Vane and Cable, 2018).

The most thermodynamically favorable reactions are C double bond oxidation, followed by hydride extraction, followed by C-C single bond oxidation. C-C single bond oxidation is only slightly exothermic which accounts for the very slow degradation of polymers compared to single chain HC compounds. The C-C single bond is usually broken and oxidized after an adjacent bond is oxidized to create a reactive site. In fluorocarbons C-F bond oxidation is very endothermic and these compounds are essentially non-reactive. The effect of Evactron cleaning on other materials is predicted by the oxidation chemistry of the target material. If a stable oxide layer is formed, as found with most metals, Evactron plasma oxidation will stop.

The Evactron system produces a unique, low temperature plasma for generating oxygen radicals from air. In air plasmas, oxygen is ionized and disassociated in a series of reactions leading to the formation of oxygen radicals. Compared to plasma ions, these radicals are long-lived species and can leave the plasma excitation volume for use downstream. However, the radicals are reactive with nitrogen ions within the plasma and are easily destroyed.

As the ionization potential of oxygen is 12.1 eV and that of nitrogen is 15.6 eV, oxygen ionization is more likely in a low temperature or low energy plasma. The transition from an oxygen-dominated plasma to a nitrogen-dominated plasma depends on the plasma temperature. By lowering the temperature of the electron energy distribution, oxygen ionization is favored. When nitrogen ions are produced in air plasmas, two oxygen radicals are destroyed for every nitrogen ion produced. Since nitrogen is the major constituent of air, the destruction takes place rapidly. In addition, the reaction product NO^+ is a stable ion that is unable to react with neutral diatomic gases and reacts with hydrocarbons to form nitrogen oxide polymers. Such polymers are resistant to further oxida-

tion. The Evactron system optimizes the operating chamber pressure and plasma temperature so that the oxygen radical flux is maximized.

Photons in the plasma are in the vacuum UV (VUV) wavelengths, and VUV energy is very effective in breaking most organic bonds, that is, CH, CC, C=C, CO, and CN. Thus, high molecular weight contaminants are broken into smaller components. A second cleaning action is carried out by the various oxygen species created in the plasma (O_2^+ , O_2 , O_3 , O, O^+ , O, ionized ozone, metastably-excited oxygen, and free electrons), which combine with organic contaminants to form H_2O , CO, CO_2 , and low molecular weight hydrocarbons. Exhibiting relatively high vapor pressure, these compounds are easily pumped out of the microscope by the vacuum system. An illustration of the effects of plasma cleaning on a NIST reference sample is shown here in Figure 4, before (left) and after (right) treatment.

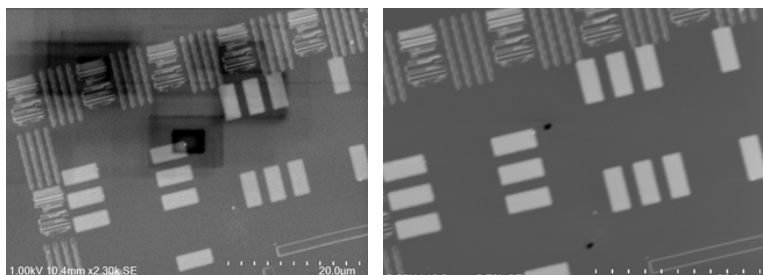


Figure 4. *The NIST contamination reference sample before (left) and after (right) plasma cleaning.*

This downstream plasma cleaning technique has proven to be extremely useful in electron and ion column instrumentation as the technique can remove unwanted hydrocarbon contamination from the inner surfaces of complex instrumentation without disassembly. This example in Figure 5 below is the Evactron® Model 25 Zephyr equipped

with a KF40 flange and impedance matching electronics configured for SEM or dual beam FIB use. The compact plasma radical source easily mounts onto an analytically-configured column where most ports are occupied by various spectrometers. The Zephyr models were developed to operate at pressures compatible with full speed turbopump operation between 10 and 25 mTorr and flow rates between 10-25sccm (Vane and Moore,

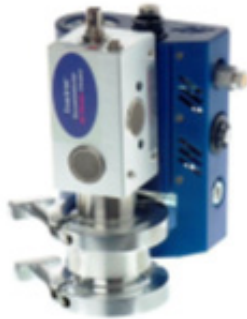


Figure 5. *Zephyr 25 PRS.*

Further studies by Vane and Cable (2015) led to the development of “Pop” ignition, which allows Evactron plasma cleaning to be started directly from very high vacuum chamber pressure and then operate with the turbo pump at full speed.

Cleaning Cycle

Cleaning is done at higher pressures than those that typically exist when the microscope is in operation. However, the process is quite fast and often can be accomplished immediately after a vent or sample exchange cycle. Once a system is initially cleaned, maintenance can usually be accomplished with a weekly cleaning of 10 minutes or less.

This obviously depends on the type and cleanliness of samples being inserted into the scope. The photos below show an example of improvement in the image quality of a gold-on-carbon SEM resolution sample. The image on the left was taken before cleaning with the Evactron process, and the image on the right is the result after plasma cleaning.

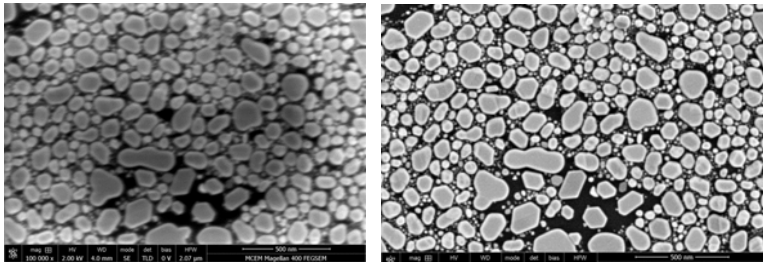


Figure 6. Images of a sputtered gold on carbon standard contaminated with hydrocarbons before (left) and after (right) Evactron plasma cleaning for 10 minutes at 20 watts power. The images were taken in a TFS/FEI Magellan 400 FEGSEM at 2kV and 100,000X indicated magnification.

A further benefit of this technique is that its benign nature has proven safe for common but sensitive materials found inside of electron microscopes such as x-ray detector windows. As an update to an earlier study (Vane et al., 2004), XEI Scientific and Moxtek performed window exposure test to show that Evactron plasma cleaning will not damage the thinnest Moxtek window, the AP3.3 EDS window (Kosmowska et al., 2018). The test consisted of exposing several AP3.3 windows to the oxygen radical flow from an Evactron Model E50 in an experimental vacuum chamber for over 200 hours. No damage was found after extended exposure equivalent to 11 years of daily cleaning.

Plasma radical sources are now available in a number of configurations for most makes and models of electron and ion microscopes. Standard PRS units commonly allow for air or oxygen and oxygen/

argon mixtures. These units have KF40 flanges adapted for most SEMs and Dual beam FIB/SEM. Further, because they are portable, these systems may be moved about cleaning a number of different electron microscopes in the laboratory. A high vacuum Conflat flange version is available for surface analysis tools or other high vacuum chambers and provides for the use of hydrogen gas.

Downstream Plasma Cleaning in Metrology

Workers at the National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland are strong believers in removing all contamination from both samples and chambers. As discussed by Vldar et al., (2001) and Postek et al., (2014), the work of the NIST nanoscale metrology group needs highly accurate SEM and helium ion microscopy down to the atomic level. Reproducible results require optimum cleanliness so that the sample does not change noticeably during observation. Cleaning regimes utilizing a liquid nitrogen trap, clean nitrogen gas purging, cryotechniques, special pump oil, oil free methods, and others had all been deployed at NIST without reaching the standards required by the Institute.

However, the downstream plasma cleaning method that is deployed at NIST has led to their adoption of the technology – using the XEI Evactron decontamination system – since it has been assessed as the only current mechanism that will allow the NIST contamination specifications to be met. NIST does not endorse a specific product or brand, but is a leading advocate of the use of plasma-based SEM cleaning. Implementation

and regular use of these methods has made it possible to eliminate the effects of electron beam induced contamination.

This set of images was generated by the researchers at NIST and illustrate carbon contamination on a sample in a scanning electron microscope (Vladar et al., 2001). The left images show the build-up after scanning for ten minutes at 5kV and 10pA. The upper image shows the effect of using a cryo trap. Contamination is reduced but is still clearly present. Contrast this with the lower pair of images. The right hand image shows the result of using downstream plasma cleaning with almost no contamination observed.

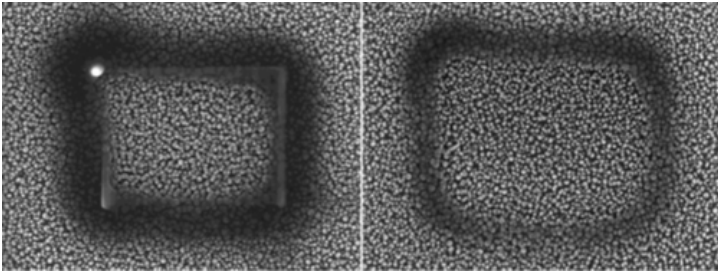


Figure 7a. Contamination build up (left) Contamination reduced with use of a cold trap (right).

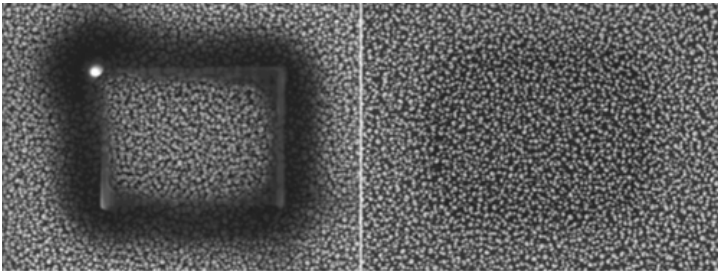


Figure 7b. Contamination build up (left) Contamination reduced after plasma cleaning (right).

Other Applications

Critical Dimension Measurements

Comparison imaging to examine the effects of contamination on critical dimension (CD) measurements has shown that these image artifacts can drastically alter dimensional measurements (Vladar et al., 2001). In CD work, modification of dimensions by the SEM imaging process causes a loss of precision in the measurement. Using a very clean SEM, the test pattern in Figure 8 (left image) began to show filling-in of the holes after a 20-minute scan. After in-situ cleaning of the chamber and the specimen, a repeat of the measurement showed no filling of the holes and a much-reduced scan mark (right image).

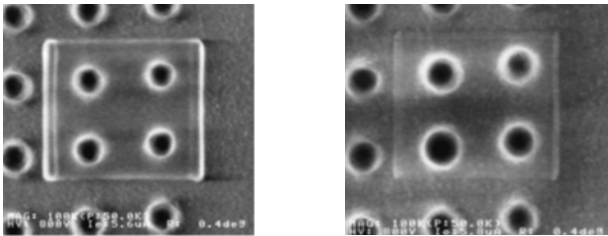


Figure 8. CD test pattern showing fill-in of the holes during scanning (left) while after in situ cleaning of the chamber and specimen, a repeat of the measurement shows no filling of the holes and a much reduced scan mark.

Artifact Removal

It is also well established that cleaner vacuum systems can assist in removing spurious analytical artifacts. Often, carbon analysis can contain contributions that do not originate from the sample but can be due to contamination. The image pair below illustrates carbon contamination peaks in EDS spectra that were removed after plasma cleaning.

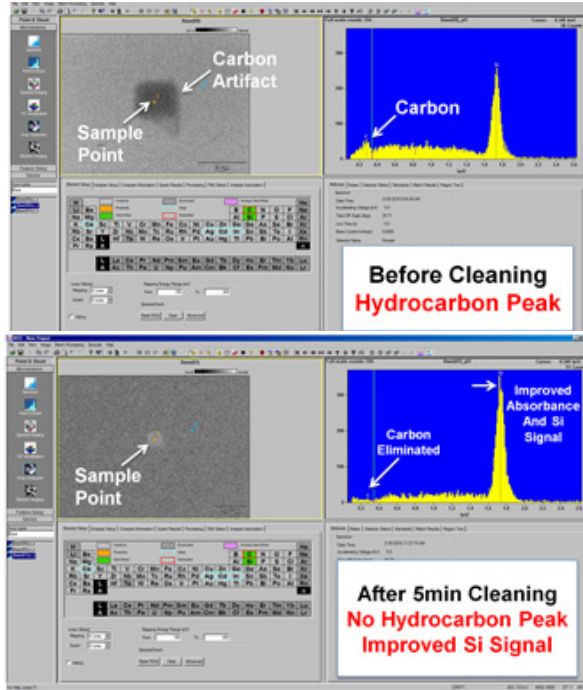


Figure 9. EDS spectra before and after plasma cleaning.

EBSD/TKD Applications

Improvement in pattern quality and enhanced measurement efficiency makes plasma cleaning an essential step before attempting any EBSD experiments (Fanta et al, 2018). Plasma cleaning improved pattern intensity with faster acquisition times, shorter sample exposure and minimal drift. Plasma cleaning is critical for dynamic experiments as well as high resolution mapping.

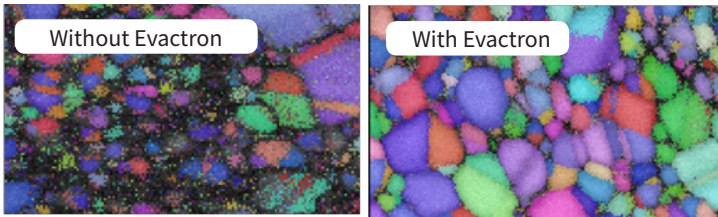


Figure 10 . Plasma cleaning improves TKD pattern quality which equals a better indexing rate, increased acquisition speed and improved effective spatial resolution. An 88% increase in hit rate on 20nm Au with a Bruker e-FlashFS and OPTIMUS™ TKD was achieved in this experiment.

Serial Block-face SEM

Serial Block-face SEM (SBFSEM) is an automated technique to obtain serial images in a SEM for a 3D reconstruction of resin-embedded specimens. Since datasets can include hundreds or thousands of images, loss of image quality due to contamination and charging can ruin an experiment. Excess contamination of backscatter detectors can lower sensitivity to the point where the detector must be replaced. Armbruster et al (2017) documented a 14% increase in BSE contrast after plasma cleaning cycles, justifying the need for routine cleaning as part of SBFSEM experiments.

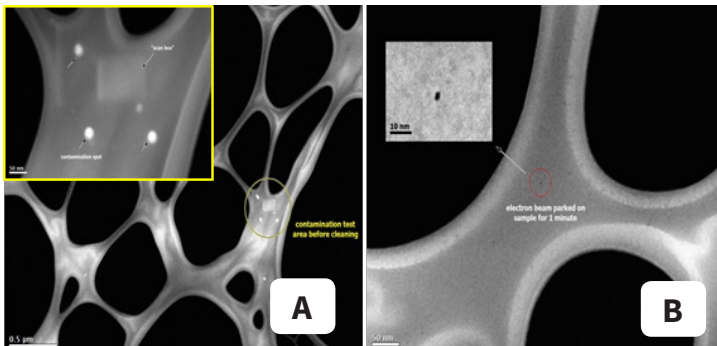
Nanoscale Applications

Having pristine surfaces is an absolute requirement for nanomanipulation and nanofabrication. The work by Mancevski (2011) has shown that downstream plasma cleaning was essential for successful vapor phase cutting of carbon nanotubes using a nanomanipulator system. Also, electrical measurements made by positioning minute probes on circuits, using nanopositioning systems located inside SEMs and FIBs, require that the probes be free of contamination in order to make good contacts. In situ cleaning of these devices is a requirement for accurate

measurements and plasma cleaners are considered almost an essential accessory for nearly all of these new tools.

TEM Applications

For TEM applications the efficacy of plasma cleaning is undisputed (Morgan et al., 2010). Placing the specimen holder and specimen into a plasma cleaner for minutes allows the user to hold a converged probe on the specimen for analysis without contaminating the viewing area. Contamination marks from prior TEM analysis can be removed from the specimen by plasma cleaning. The three STEM HAADF images of lacy carbon support films shown below illustrate this point. Image A is a low magnification overview of the sample before cleaning. The insert captures the same area at higher magnification to clearly document the contamination artifacts generated by spot and scanning modes. After a 15 minute cleaning in the Evactron SoftClean™ chamber, Image B shows that no contamination occurs even after one minute of stationary beam exposure.



Benchtop Systems

The fundamental technology associated with downstream plasma cleaning has been further developed to increase the practical utility and availability of the system. In its earliest forms, plasma cleaning

required separate systems for the cleaning of samples on the one hand and electron microscopes on the other. This was a result of the PRS unit typically being mounted only on the electron columns and not available for use on the desktop. As a consequence, market research indicated that many electron microscopists did not have ready access to a multi-purpose plasma cleaning system.

The natural solution was to combine both desktop and column cleaning in the same tool. Describing one such instrument, XEI created first the Evactron SoftClean™ Chamber. This is a small, versatile chamber which holds TEM sample holders, aperture strips, tweezers, specimen clamp rings, Wehnelts, SEM samples or small parts destined for examination in the microscope. This chamber allows users of existing systems to mount their Evactron plasma radical source onto the SoftClean chamber, delivering the same downstream plasma cleaning technique and achieved pre-cleaning without the need of another direct plasma cleaning tool. This way, sensitive samples can be chemically etched safely and without exposure to high energy ion bombardment and potential damage. It can also be used as a safe storage repository for clean samples when not in use as a cleaning chamber. However, the user is required to physically cable and un-cable the instruments as the controller can only support one PRS unit at a time.

Conclusions

Downstream plasma cleaning has evolved into a very effective method to get the best possible images and analytical data from sophisticated electron and ion column tools. Evactron plasma cleaners are reliable accessories to remove problematic hydrocarbon contamination from samples, holders and microscopes themselves. This downstream plasma

cleaning technology is allowing researchers in various fields to optimize performance from their microscopes and investigate, image, analyze, and manipulate materials. XEI Scientific can account for over 3000 installations of their tool on nearly all makes and models of SEM and Dual Beam FIB/SEMs. Today most high resolution tools come equipped with some form of downstream plasma cleaning upon delivery from the factory. Further, service personnel often bring an Evactron when they make service and preventative maintenance visits in the field in order to maximize SEM performance.

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