# Using beam chemistries with SEM, FIB and DualBeam™ for surface modification

Charged particle beams in scanning electron microscope (SEM) and focused ion beam (FIB) equipment are generally used for imaging and direct surface modification of samples held under vacuum. However, by introducing small quantities of gas near to the sample surface whilst the beam is scanning, the FIB or SEM can accurately deposit or preferentially etch material. Consequently, this allows FIBs, SEMs and DualBeams (a combined FIB and SEM instrument) to quickly and easily custom make and modify a wide range of structures on a micro and nanoscale.

## Beam Chemistry Basics

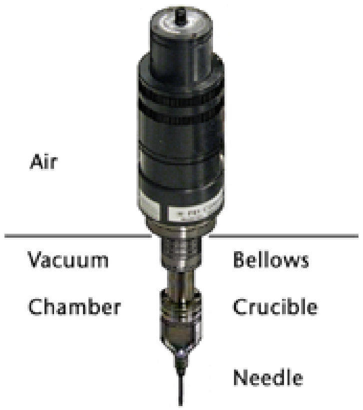


Figure 1: The Gas Injection System (GIS) allows gas precursor materials to be safely stored under vacuum and ready for immediate use in the system whilst still being easily accessible for servicing and exchange.

FEI has an extensive range and expertise of beam chemistries used in conjunction with charged particle beam microscopes. These gases are introduced close to the sample surface via the safe, versatile and easy to use gas injection system (GIS). The GIS essentially consists of a reservoir of precursor material attached to a fine needle which is accurately inserted, when required, to around 100 µm above the sample surface within the vacuum chamber of the SEM, FIB or DualBeam. Having the needle close to the sample surface means that gas flow can be kept to a minimum which ensures that there is no disruption to the system's vacuum and the effect of the gas remains very localized.

Beam chemistries are normally used with specialized scanning routines (patterns) to optimally steer the beam over the area to be modified. The microscope operator is free to define the position, area and shape of the patterns. For ease of use, a predefined set of scanning parameters (called application files) are provided for each kind of gas but, if necessary, the operator can define their own custom scanning parameters for special effects. The specialized digital patterning engine integrated into FIB, SEM and DualBeam instruments allows the operator to vary a number of parameters such as the time the beam dwells on any one point, the focus of the beam at that point, the overlap between beam points and many more. This enables the operator to fine tune the deposition or etching characteristics of a particular beam chemistry. Additionally, the pattern engine can import user defined patterns such as images or more specialized vector patterns (stream files). These special patterns allow the operator to etch or deposit complex shapes or even 3-dimensional structures. Since the GIS and patterning along with the rest of the microscope are centrally controlled by a computer, gas deposition and etching can be used as part of automated routines which the microscope can run unattended, such as making transmission electron microscope (TEM) samples or a complex series of structures.

## Beam Chemistry Mechanism

It is important for the operator to have some knowledge of the mechanism by which the beam chemistry takes effect as it will influence the choice of gas to be used for a particular procedure and perhaps also whether to use the ion or electron beam to achieve the best result.

The precursor gases introduced near to the sample surface by the GIS adsorb on to the sample surface and the ion or electron beam scanning over the defined area activates (or cracks) the adsorbed molecules either leaving a deposit of the required material or promoting etching of the underlying surface. Volatile components of the process then leave the surface and are pumped away by the vacuum system.

It is generally accepted that the main agent involved in the cracking of the adsorbed precursor molecules is the secondary electrons produced from the sample surface by the scanning of the ion or electron beam. These secondary electrons at < 50 eV have a similar energy to bond energies in molecules and so they are the most likely cause for the cracking of the precursor molecules. As both the ion and electron beams generate secondary electrons, both, in principle, can be used to perform beam induced deposition or etching. However, the fundamental differences between ions and electrons will mean that the result achieved with a given gas will vary widely depending on whether the FIB or SEM is used.

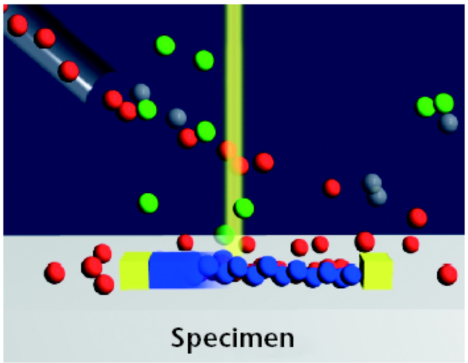


Figure 2: Schematic display of the beam chemistry process of deposition. It shows the supply of precursor molecules from the GIS (red). They (temporarily) stick to the surface and are decomposed by the ion/electron beam into a volatile component (green) and a non-volatile component (blue) that deposits on the surface. Some neutral gas molecules in the vacuum chamber are shown in gray.

## Deposition Process

The most obvious difference between ion beam induced deposition (IBID) and electron beam induced deposition (EBID) is the speed of deposition at a given beam current. The ion beam deposition is much faster than deposition with the electron beam. This is primarily due to the ion beam producing many more secondary electrons near the surface of the sample compared to the electron beam. The secondary electron yield of the electron beam can be increased by lowering the accelerating voltage but, in general, for standard accelerating voltages (30 kV for the ion beam and 5 kV for the electron beam) at a given beam current, the electron beam deposition is ~10 times slower than the ion beam when depositing platinum for example.

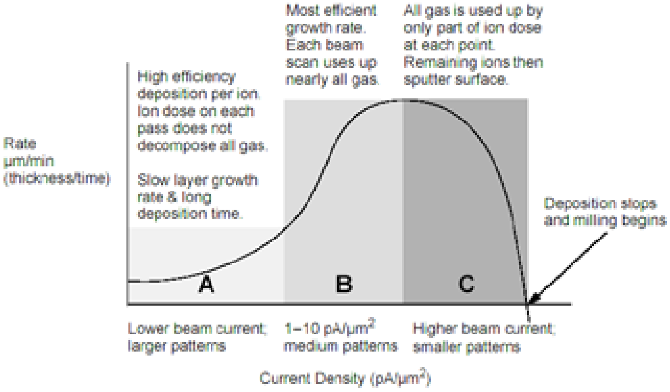


Figure 3: Ion Beam Current and Pattern Area
The deposition rate of a material (e.g. platinum) depends on a range of parameters. Generally, parameters such as sample orientation and distance to the GIS needle are fixed but, the ion beam current, the pattern area, pattern speed (dwell time and overlap) and refresh time (time allowed for each point to replenish with adsorbed gas) can be varied by the operator.
The most critical parameter with ion beam deposition is the beam current density on a given pattern. This can be influenced either by choice of beam current or by changing the size of the pattern area. At low beam currents with large pattern areas, deposition per incident ion is high, but thickness growth rate of the deposited layer (measured in µm/min) is low. See area A. At intermediate values, maximum growth rate occurs, but the exact conditions vary with current and other scan parameters. It is recommended that beam current into the pattern area be in the range of 1-10 pA per µm$^2$ for platinum, which results in about 1 µm thickness in 300 seconds. See area B. With high ion beam current and small pattern areas, the deposition efficiency falls until net milling, rather than deposition, occurs. See area C.

Physically, the other major difference between the ion and electron beams is the size, mass and amount of momentum that each ion carries compared to an electron. Gallium (Ga) ions used in most FIB systems are much larger than electrons and at 30 kV carry ~360 times more momentum, so that when it impacts the sample surface it has a much more obvious physical effect of sputtering away material. This has several consequences for the use of beam chemistry with the ion beam compared to the electron beam. When depositing material with the ion beam it has to be remembered that the impacting and sputtering action of the ion beam has not been removed but is merely over taken by the rate of deposition. So, when depositing layers on a sensitive surface care should be taken while the initial ~100 nm of deposition is built up. For some very sensitive surfaces the operator may prefer to use the electron beam to start deposition and then, once a layer of say 100 nm has been deposited continue with the ion beam. The sputtering action of the ion beam also means that to achieve an overall deposition the correct beam current should be chosen for the area of the feature being made. If the beam current density is too high then the net effect may actually be to mill a surface rather than to deposit material upon it ! If the beam current density is too low then the deposition rate will be slow, there will be an inefficient use of gas and the deposited material will contain a higher proportion of unreacted precursor material and carbon.

So, the correct choice of ion beam current density for a deposition (e.g. 2-10pA/μm$^2$ for platinum) will result in a in a good deposition speed, efficient use of gas and a good (e.g. highly conductive) composition of the deposition due to the sputtering action of the ion beam on the residual carbon species from the precursor gases.

Since the electron beam generally does not ablate material there is no restriction on the electron beam current density that can be applied while depositing material. So, although the secondary electron yield from a surface is much lower with the electron beam, the beam current can be increased to compensate. Therefore, if required very high rates of deposition can be achieved using the electron beam. In general as mentioned above the secondary electron yield from a surface is greater at lower electron beam accelerating voltages. So, the fastest deposition rates of material will be achieved by using high electron beam currents and lower (1-5 kV) accelerating voltages. The limit for the rate of deposition with the electron beam is usually determined by the flow rate of the precursor material to the deposition region and also, in practical terms, how accurate the deposition should be. High rates of electron beam deposition require large beam currents and with their larger spot size the deposition is spatially larger than would be achieved by using a smaller beam current over a longer time.

The absence of the sputtering action with the electron beam means that the deposition will contain a much higher proportion of carbon as a byproduct of the precursor material than a similar deposition with an ion beam. For depositions used for mechanical or protection purposes this may not be an issue but if the aim is to get as low a resistivity deposition as possible, then this is detrimental. So, generally the ion beam is used to deposit the best conducting depositions. Conversely, when depositing insulating material, the electron beam deposition gives the highest resistivity since there will be no Ga incorporated in the deposition, but electron beam deposition of the insulating material is much, much slower than with the ion beam.

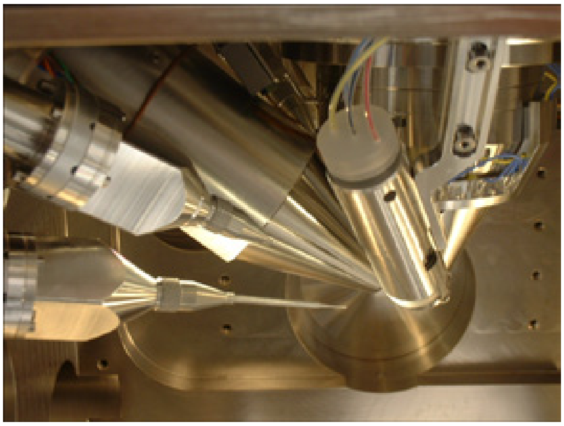


Figure 4 : The inside of a DualBeam chamber

In practice, where the FIB and SEM are both available in a DualBeam the FIB is generally used for the processing tasks such as milling, deposition and etching, while the electron beam is used for imaging and monitoring any ongoing process. This makes most sense as the FIB is usually faster at the processing than the SEM and the SEM imaging is non-destructive and has better resolution. However, the electron beam is preferable for some possesses, such as when making an initial deposition on a sensitive surface or when making minimum dimension depositions. Of course when the electron beam is being used for processing it cannot be used for imaging at the same time and so, once again, the ion beam would be used in preference for processing if possible, leaving the electron beam free to image the result. Furthermore, the conditions for processing with the electron beam are not generally the same conditions as would be chosen for imaging. For this reason and because the electron beam depositions contain more carbon, the ion beam is normally the preferred method for depositing material even at fast rates however, ultimately, the fastest deposition rates are achieved with the electron beam.

## Etching Process

The differences between the ion and electron beams also have an influence when using etching gases too. The mechanism by which etching gases achieve a result may be due to one or more effects. Etching gases adsorb to the sample surface. They may directly react with it (i.e. no activation from the beam is necessary). They may be activated by secondary electron emission from the surface of the sample. The adsorbed gas molecules may make it easier for material to be removed from the sample surface. The etching gas may react with sputtered material near to the sample surface preventing it redepositing.

Whichever process is most prevalent in the action of the etching gas, it is obvious that the physical sputtering process of the ion beam compared to the electron beam is going to have a major influence.

The FIB can mill any material without the need for any additional gas. So the gas assisted etching processes using the ion beam will always be faster (using standard conditions) than using beam chemistry with the electron beam. Despite the ion beam's ability to mill regardless of material, it is often used in conjunction with beam chemistry especially when low beam currents to speed up the rate of removal of material. Beam chemistry with the ion beam can also make the sputtered (and then reacted) material more volatile so that it does not redeposit. This not only means that very clean surfaces can be made (e.g. when cutting a conducting line in a semiconductor to prevent a leakage current) but it also allows the ion beam to be used in conjunction with an etching gas to achieve milled holes with a greater aspect ratio than using the ion beam alone.

Electron beams on the other hand have no physical sputtering effect at the beam energies used in a standard SEM and so must rely purely on the reactivity of the adsorbed gas and on the volatility of the reaction products.

If the reaction products are not volatile and produce a passivation layer then the electron beam etching will be ineffective. Whereas the same sample/gas combination processed with the ion beam may be etched successfully as the ion beam sputtering process is continually removing the surface and revealing fresh substrate for exposure to the gas. A good example of the differences between reactivity of gases and the effect of physical sputtering can be seen when attempting to delineate the different materials on a cross section through a microelectronic device. FEI's Delineation etch, when used with the ion beam, easily delineates the different layers but also gives some orientation to the etching due to the impinging angle of the ion beam. The same etch used with the electron beam has no visible effect as the reaction products from the etch are not volatile and so passivate the surface and prevent further etching. However, Insulator Enhanced Etch (IEE, xenon difluoride) can be used with both the ion and electron beams as the reaction products are volatile. Interesting, using IEE with the ion beam and electron beam shows up some differences. Not only does the electron beam etched surface not have such a strong orientation (due to the lack of sputtering) but also it tends to show up regions with different electronic properties. This effect has not been fully investigated to date but it probably highlights regions of different secondary electron emission which give an indication of the electronic properties of that region.

The other reason for using etching beam chemistry, especially with the ion beam, is that it can selectively etch different materials at different rates so that an etching process can be more readily controlled. For example, when milling a microcircuit using the enhanced etch (iodine) gas injector, the iodine will selectively mill Al faster than $SiO_2$. This preferential etching means that a conducting line can be cut quickly while minimizing the amount of protective dielectric which is removed.

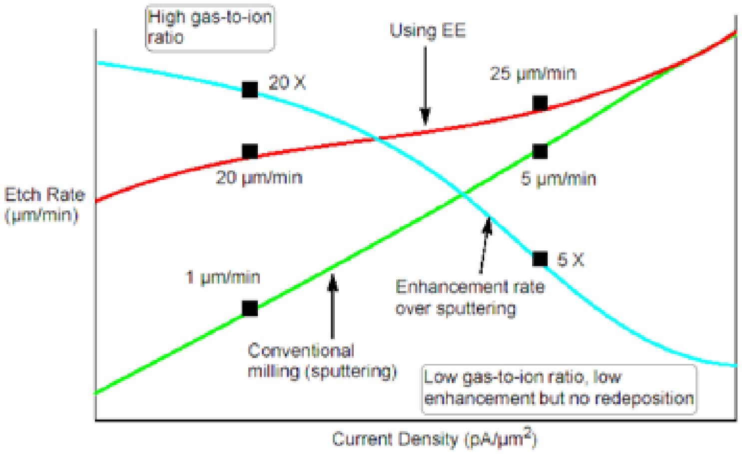
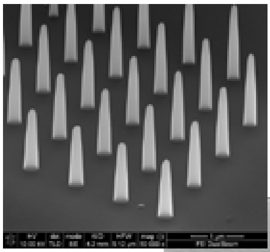


Figure 5: Ion Beam Enhanced Etching (here in a Log/Log scale). Rather than removing large amounts of material themselves, etching beam chemistries usually only assist the sputtering process caused by the ion beam (see igure 3). At low ion beam current densities the assistance of the gas is particularly strong as the ion beam removes the surface layer and there is enough gas to quickly adsorb on to the sample surface. As the beam current density increases the ion beam starts to remove material faster than the fresh gas can arrive at the surface. So, eventually at some beam current density, the gas no longer increases the etching rate above the ion beam by itself. However, even in this regime the beam chemistry can be useful as it often prevents redeposition of the sputtered material. The point at which there is no enhancement from the gas can be increased by promoting the gas flow to the sputtered area for example by using a coaxial needle with $XeF_2$ when milling $SiO_2$ or Si.

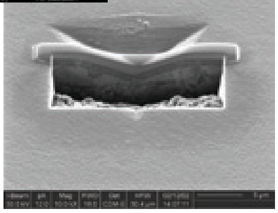
## Beam Chemistry Range

FEI has developed a wide range of beam chemistries for a number of different applications with both the electron beam and ion beam. These range from low resistivity metal depositions for Ohmic connections, materials for mechanical connections, protective capping layers for delicate sample preparation to etches for polymers, metals and glasses.

## Deposition Beam Chemistries



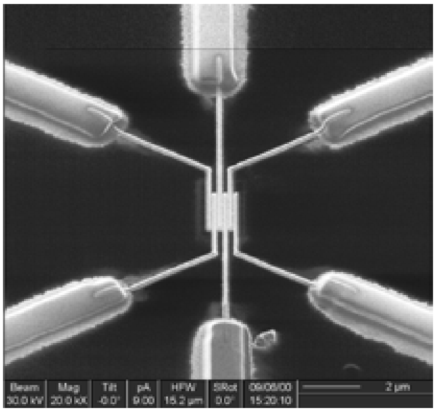
Left image: FIB deposited platinum pillars forming part of a photonic array each pillar is ~150 nm in diameter



Right image: Platinum deposition is often used as a protective layer over the material of interest whilst it is milled in preparation for cross sectional or TEM imaging. In this image a protective platinum layer has been used to enable the FIB to mill a clean cross section through a hardness indentation in TiN on steel.

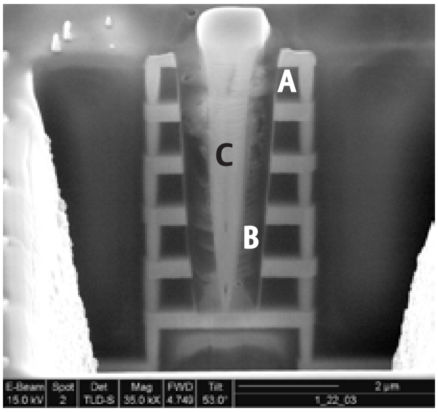
### Platinum (Pt) deposition

Pt deposition is probably the most versatile and commonly used of all of the deposition materials. It's easy to use and fast to deposit. It is often used for TEM sample preparation, to make electrical contacts, to deposit a thin conductive layer on an insulating sample, or to deposit a thick protective layer before cutting a cross section or a TEM foil. It is also used in nanoprototyping for creating 3D structures. It can be used with both electron and ion beam. It is the most commonly used gas with the electron beam as it deposits relatively quickly. However, the resulting electron beam deposit does have a much higher carbon content compared to a similar deposit made with the ion beam. So, for electrical purposes ion beam deposition is preferred but for delicate, damage sensitive samples electron beam deposition is a useful alternative.



### Tungsten (W) deposition

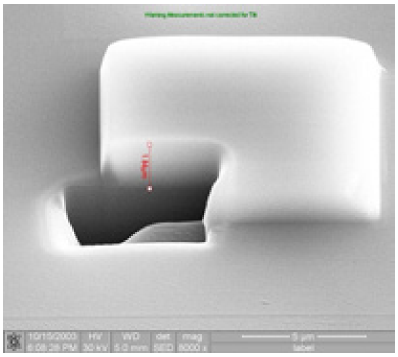
W deposition is in general able to fulfill the same use cases at Pt deposition, but for electrical applications where a deposit with good conductivity is required, W deposition is preferred over Pt deposition. However, the W deposition rate is slower and more care has to be taken when depositing it with the ion beam, so for applications like TEM sample preparation or sample surface protection, Pt is generally preferred. The W deposition is harder than Pt so it is useful for making mechanical structures such as probing tips and for using as the protective layer on very heterogeneous materials before cross sectioning to reduce the curtaining effect. W deposition also has a lower proportion of carbon in the final deposit when compared with Pt deposition.



### Insulator deposition

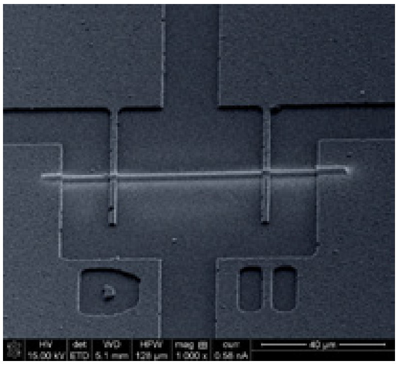
Insulator deposition is often used to produce insulating coatings (e.g. covering metal tracks), re-planarize an area after a FIB cut or isolate different metal layers from one another when making connections over multiple layers (see image) connecting buried or surface tracks. When making cross sections or TEM foils it is also sometimes useful to give a different contrast from the surface material if it is a conductor. The resistivity obtained is typically equal or superior to $10^{14}$ μΩ-cm with the ion beam. Higher resistivities can be obtained by using the electron beam for the deposition, however, this is a much slower process than with the ion beam.

**A** - Top metal layer
**B** - Large via milled through several metal layers with FIB and back filled with insulator deposition
**C** - Inner via milled with the FIB through the insulator deposition and back filled with tungsten deposition to form a contact between lowest metal layer and the surface



### Carbon deposition

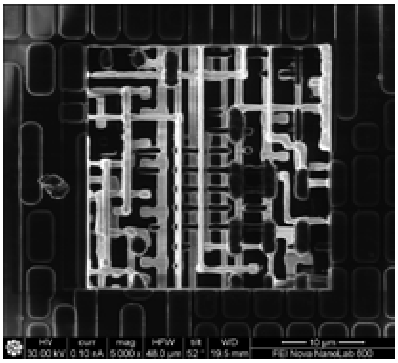
Carbon deposition is primarily used as a protective capping layer for cross sections and TEM sample preparation as it is deposited readily (at about the same rate as the Pt deposition) but its sputter rate when milled is less than Pt so it offers more protection during the preparation process. The grain size in the carbon deposition is also smaller than the grains in the platinum deposition. This smaller grain size helps to reduce curtaining artifacts when making a final polish on TEM samples or cross sections at low ion beam energies. Additionally, since carbon deposition has a low atomic number it is often useful when trying to identify other light elements near to a sample surface with TEM, X-ray analysis or with back scattered electrons. However, since the carbon deposition is very resistive (a typical deposition will be in the kΩ range) it is not as generally applicable as Pt deposition. Nevertheless, despite its resistivity, a coating of carbon deposition can still be used to reduce charging on samples. It can be deposited with either the ion or electron beam. However, the rate of electron beam deposition of carbon is rather slow when compared to deposition with the ion beam or with electron beam deposition of platinum.



### Gold deposition

Gold deposition is an attractive process for multiple applications in Optics, Biology (fixing proteins), as it has a high electrical conductivity and low chemical reactivity and combined with the patterning facility of the SEMs, FIBs and DualBeams it can deposit multiple small features in an automated way. Gold deposition is based on a precursor that is more expensive and more delicate to use than platinum or tungsten deposition, so should not be considered for mechanical structures or routine electrical contacting.

## Etching Beam Chemistries



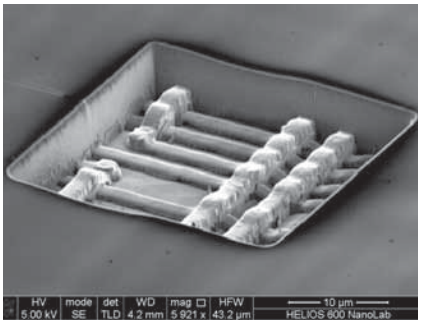
### Insulator Enhanced Etch (IEE)

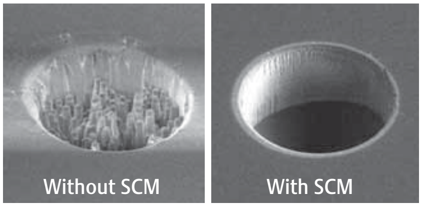
Insulator Enhanced Etch (IEE) allows rapid etching of many inorganic insulating materials using a halogen compound, Xenon Difluoride ($XeF_2$). As with all of the etching gases, at moderate ion beam currents the IEE process removes material faster than normal ion milling and so speeds up machining of glass, nitrides and other insulators. As well as speeding up machining rates, etching gases are particularly useful because they preferentially etch some materials at a faster rate than others. The IEE process generally etches insulators faster than conductors and so it is widely used to remove passivation from microcircuits leaving the underlying metal contact lines largely intact. Due to its high etching rates and its ability to prevent re-deposition IEE is the preferred method for making the highest aspect ratio holes in insulating materials and microelectronic devices. Its preferential etching capability also makes it very useful for highlighting different layers on FIB cut cross sections particularly in microcircuits. $XeF_2$ strongly etches silicon so it should be used sparingly when used to highlight layers where bulk silicon is present. IEE is primarily used with the ion beam but it can also be used with the electron beam to promote etching on some samples (e.g. Si, $SiO_2$).

### Selective Carbon Mill (SCM)

Selective Carbon Mill (SCM) is an FEI patented chemistry that uses water vapor to increase the removal rate of carbon-containing materials such as polyamide, PMMA (polymethyl methacrylate) and other organic materials by a factor of 20, and diamond by a factor 10 relative to normal FIB sputtering rates. In addition, SCM decreases the removal of some other materials (e.g., Si and Al). This effectively increases the etching of polymers over these other materials so making SCM a very effective preferential etch. The controlled release of small amounts of water vapor near to sample surface with SCM has also been shown to reduce surface charging, which helps to improve both milling and to some extent imaging on an insulator.

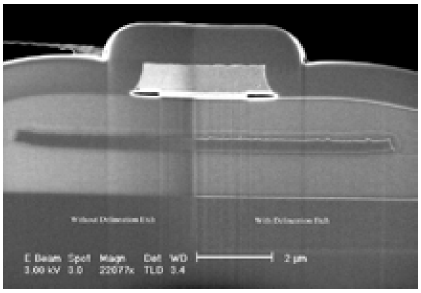
The horizontal field width of the two lower images is 26 µm.





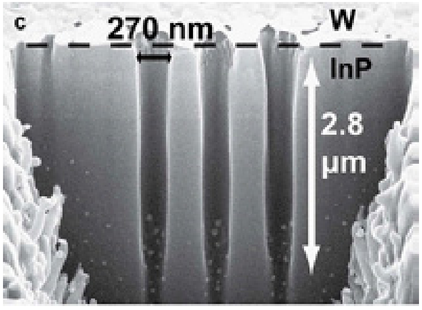
### Delineation Etch

Delineation etch provides variable etch rates on oxides to enhance structural detail. It only etches Si or poly-Si when used in conjunction with the ion (or electron) beam so it is easier to use than IEE but does not give such a strong etch. Contrast in a secondary electron images reflects primarily from the presence of topography, protruding edges allow more secondary electrons to escape, and therefore, appears brighter than recessed edges.



### Enhanced Etch™ (EE)

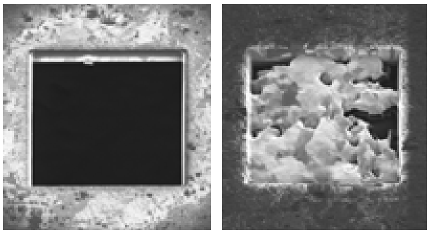
Enhanced Etch™ (EE) is an FEI patented chemistry that particularly etches metals and to some extent, silicon and some nitrides faster than normal ion beam milling. It also helps to prevent re-deposition of these materials which enables higher aspect ratio holes to be milled and by increasing etch rates and reducing redeposition has also. EE uses a halogen gas (iodine) directed toward the surface of the sample during milling. The use of halogens have been shown to improve etch rates of cross sections and vias milled in InP and GaAs whilst also improving the optical properties of the milled surfaces. (Left: high aspect ratio holes in InP using EE, Callegari *et al*, J. Vac. Sci. Technol. B, Vol. 25, No. 6, Nov/Dec 2007).



### CoppeRx™

CoppeRx™ is a stand-alone software application that uses tungsten (W) gas and an FEI patented milling process to cleanly remove surface copper from a sample. The pattern milled with CoppeRx produces a smooth, even box, free of copper debris. In contrast, milling without CoppeRx produces a rough uneven box with considerable copper debris.

The horizontal field width of the two images is 13 µm.



## Beam Chemistry Development

FEI has a dedicated group of scientists to investigate new beam chemistries and their applications for SEM, FIB and DualBeam systems. They collaborate with leading researchers around the world to develop and test deposition and etching gases for a range of applications in nanotechnology, biology, materials science and the semiconductor industry. For every gas that is investigated, the group not only assess its effectiveness, process optimization (including hardware and software), shelf life and cost, but also its safety. All the gases that are supplied must be safe for the user, the system and for the engineers that work on the system so introducing new beam chemistries is a meticulous process. In recent years this process has delivered selective carbon etch, delineation etch, CoppeRx, carbon deposition and most recently gold deposition. The beam chemistry group is constantly working on new products and improving existing gas processes such as deposition purity. Beam chemistry is often an important factor in developing new applications for FIB, SEM and DualBeam and so, FEI welcomes customer's inquiries and requests.

## Further Reading

- Review Article - "Gas-assisted focused electron beam and ion beam processing and fabrication" by Ivo Utke, Patrik Hoffmann, John Melngailis, J. Vac. Sci. Technol. B 26 (4), Jul/Aug 2008
- Book - "Introduction to Focused Ion Beams" Edited by L.A. Giannuzzi, F.A. Stevie, published by Springer, New York, 2005

## Recent beam chemistry-related FEI publications

- A. Botman, J. J. L. Mulders, C. W. Hagen (2009), Creating pure nanostructures from electron-beam-induced deposition using purification techniques: a technology perspective, Nanotechnology 20, 372001
- A. Botman, M. Hesselberth, J.J.L. Mulders (2008), Investigation of morphological changes in platinum-containing nano-structures created by electron-beam-induced deposition, J. Vac. Sci. Technol. B Volume 26, Issue 6, pp. 2464-2467
- A. Botman, D.A.M. de Winter and J.J.L. Mulders (2008), Electron-beam-induced deposition of platinum at low landing energies, J. Vac. Sci. Technol. B Volume 26, Issue 6, pp. 2460-2463
- A. Botman, J.J.L. Mulders, R. Weemaes and S. Mentink (2006), Purification of platinum and gold structures after electron-beam-induced deposition, Nanotechnology, 17, 3779-85