

Chemical Surface Modification with SEM, FIB and DualBeam

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, if small quantities of gas are introduced near the sample surface while the beam is scanning, the FIB or SEM can accurately deposit or preferentially etch material as well. This allows FIBs, SEMs and DualBeams (a combined FIB and SEM instrument) to quickly and easily create and modify a wide range of structures on a micro- and nano-scale.

Beam chemistry basics

Thermo Scientific™ charged particle beam microscopes allow for an extensive range of beam chemistries. For instance, the safe, versatile and easy-to-use gas injection system (GIS) introduces gases close to the sample surface in SEM, FIB and DualBeam™ vacuum chambers. The GIS essentially consists of a reservoir of precursor material attached to a fine needle, which can be accurately inserted down to ~100 µm above the sample surface. Having the needle this close results in minimal gas flow, ensuring that there is no disruption to the system's vacuum. The effect of the gas, therefore, 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 can 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 the operator is free to 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 beam dwell time, beam focus, overlap between beam points and many more. This enables them 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 even more specialized vector patterns (stream files), etching or depositing complex shapes or even three-dimensional structures. Since the GIS, patterning and the rest of the microscope are centrally controlled by a computer, these beam chemistries can be used as part of automated routines. These allow the microscope to run unattended, generating transmission electron microscope (TEM) samples or other complex series of structures.

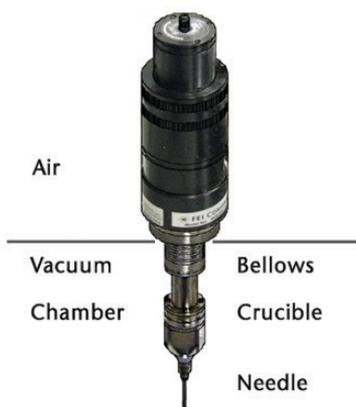


Figure 1: The Gas Injection System (GIS) allows gas precursor materials to be safely stored under vacuum, ready for immediate use in the system while still being easily accessible for servicing and exchange.

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 by the GIS adsorb onto the sample surface, and the ion/electron beam scanning over the defined area activates (or cracks) the adsorbed molecules. This either leaves a deposit of the required material or promotes etching of the underlying surface. Volatile components of the process are pumped away by the vacuum system.

It is generally accepted that the main agent cracking the adsorbed precursor molecules is the secondary electrons produced from the sample surface by the scanning of the ion/electron beam. (These secondary electrons, at <50 eV, have a similar energy to bond energies in molecules.) As both the ion and electron beams generate secondary electrons, either can be used, in principle, 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.

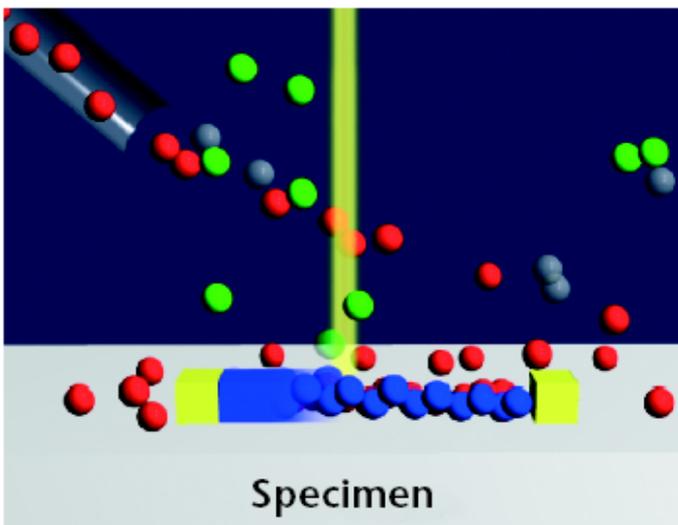


Figure 2: Schematic display of the beam chemistry process of deposition. It shows the supply of precursor molecules from the GIS (red). They (temporarily) stick to the surface and are decomposed by the ion/electron beam into a volatile component (green) and a non-volatile component (blue) that deposits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

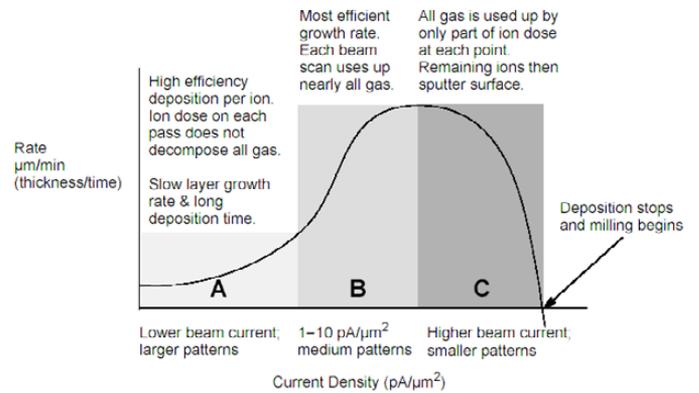


Figure 3: Ion beam current and pattern area

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 μm² 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 differences between ion and electron beams are 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. When they impact the sample surface, they have a much more obvious physical effect, sputtering away material. This has several consequences for the use of beam chemistry with the ion beam. When depositing material, the impacting and sputtering action of the ion beam has not been removed, but is merely overtaken by the rate of deposition. So, when depositing on a sensitive surface, care should be taken while the initial 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 ~100 nm has been deposited, continue with the ion beam. The sputtering action of the beam also necessitates that the correct beam current be chosen for the feature's area. If the beam current density is too high, 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, 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.

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

Since the electron beam generally does not ablate material, there is no restriction on the applied electron beam current density when depositing material. Although the secondary electron yield from a surface is much lower with the electron beam, the beam current can be increased to compensate. Additionally, the secondary electron yield from a surface is greater at lower electron beam accelerating voltages. Therefore, the fastest deposition rates of material will be achieved by using high electron beam currents and lower (1–5 kV) accelerating voltages. The rate of deposition with the electron beam is usually limited by the flow rate of the precursor material to the deposition region and by how accurate the deposition should be. High rates of electron beam deposition require large beam currents; with larger spot size, the deposition is spatially larger (less accurate) as compared to 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. Generally the ion beam is used to deposit the best conducting depositions. Conversely, when depositing insulating material, the electron beam gives the highest resistivity since there will be no Ga incorporated in the deposit. Note that 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, when both FIB and SEM are available in a DualBeam, the FIB is typically used for processing tasks such as milling, deposition and etching, while the electron beam is used for imaging and monitoring ongoing processes. Generally, this makes sense, as FIB is usually faster at processing than SEM, and SEM imaging is non-destructive and achieves better resolution. (The electron beam is preferable for some processes, such as making an initial deposition on a sensitive surface or making minimum dimension depositions.) Additionally, if the electron beam is being used for processing, it cannot simultaneously be used for imaging, and the conditions for processing with the electron beam are generally not the same as those used for imaging. Electron beam deposits also contain more carbon than those made with the ion beam. Overall, this means that the ion beam, even at fast rates, is still preferable for processing, particularly to leave the electron beam free to image the result. (However, it is important to note that, ultimately, the fastest deposition rates are achieved with the electron beam.)

Etching process

The differences between ion and electron beams also have an influence on how the etching gases interact with the sample surface. Generally, the gases may:

- React directly with the surface (i.e. no activation from the beam is necessary)
- Become activated by secondary electron emission from the surface
- React with the sputtered material near the surface, preventing it from redepositing

Additionally, the adsorbed gas molecules may make it easier for material to be removed from the sample surface.

The FIB can mill any material without the need for additional gas, so the standard, gas-assisted ion-beam etching processes will always be faster than 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 with low beam currents, in order to speed up the 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 means that very clean surfaces can be made (e.g. when cutting a conducting line in a semiconductor to prevent a leakage current) and that holes milled with added gas have a greater aspect ratio than those obtained with the ion beam alone.

Electron beams, on the other hand, have no physical sputtering effect at the beam energies used in a standard SEM. They must rely purely on the reactivity of the adsorbed gas and 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. The same sample/gas combination may be processed successfully with the ion beam because it continually removes the surface and reveals fresh substrate for exposure to the gas.

Differentiating the materials in a cross section of a micro-electronic device is a good example of this. Thermo Scientific™ Delineation Etch, when used with an ion beam, easily delineates the different layers and 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 are not volatile and therefore passivate the surface and prevent further etching. However, Insulator Enhanced Etch (IEE, xenon difluoride) can be used with both beams, as the reaction products are volatile. Interestingly, using IEE with the ion versus electron beam shows some differences. Not only does the electron beam-etched surface have weaker orientation (due to the lack of sputtering), but it also tends to show regions with different electronic properties. To date, this effect has not been fully investigated, but is likely the result of different secondary electron emissions, which give an indication of the electronic properties of that region.

The other benefit of etching beam chemistry, especially with the ion beam, is that it can selectively etch different materials at different rates, meaning that the 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 aluminum faster than SiO_2 . This means that, for example, a conducting line can be cut quickly while minimizing the amount of protective dielectric that is removed.

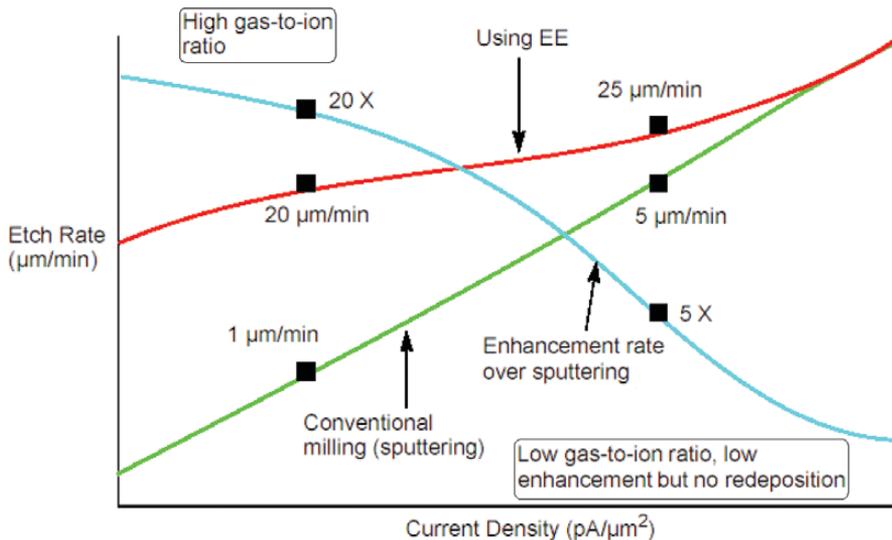


Figure 5: Ion Beam Enhanced Etching (here in a Log/Log scale). Rather than removing large amounts of material themselves, etching beam chemistries usually only assist the sputtering process caused by the ion beam (see figure 3). At low ion beam current densities, the assistance of the gas is particularly 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

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

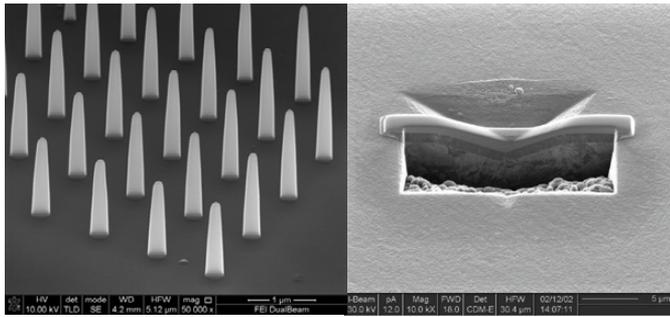


Figure 6. (left) FIB-deposited platinum pillars forming part of a photonic array. Each pillar is ~150 nm in diameter. (right) Platinum deposition is often used as protective layer over the material of interest while it is milled in preparation for cross-sectional or TEM imaging. In this image, a protective platinum layer has been used to enable the FIB to mill a clean cross section through a hardness indentation in titanium nitride on steel.

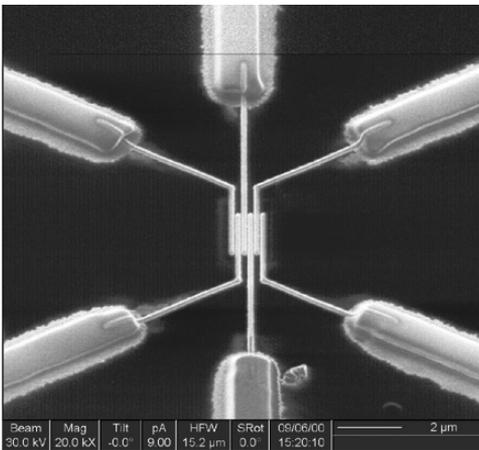


Figure 7. Tungsten deposition.

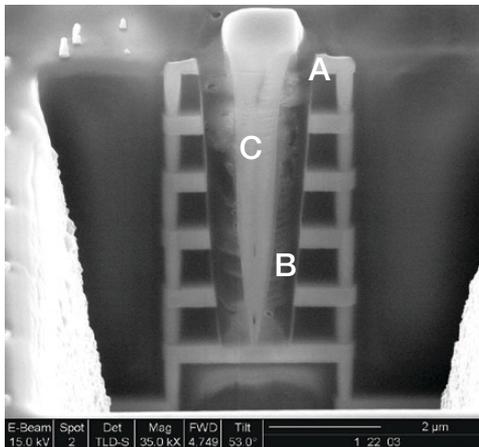


Figure 8. Insulator deposition.

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

Deposition beam chemistries

Platinum (Pt) deposition

Platinum (Figure 6) is probably the most versatile and commonly used of all of the deposition materials. It is easy to use and fast to deposit. It is often used for TEM sample preparation to make electrical contacts or to deposit a thin conductive layer on an insulating sample. It is also used in nanoprototyping for creating 3D structures. It can be used with both electron and ion beams and is the most commonly used gas with electron beams, as it deposits relatively quickly. The resulting electron beam deposit, however, 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

Tungsten deposition (Figure 7) is generally able to fulfill the same use cases as platinum deposition. For electrical applications, where a deposit with good conductivity is required, tungsten deposition is preferred. Even so, the tungsten deposition rate is slower, and more care must be taken when depositing it with the ion beam. So, for applications such as TEM sample preparation or sample surface protection, platinum is favored. Tungsten deposits are harder than platinum, so they are useful as the protective layer on very heterogeneous materials (to reduce the curtaining effect), and they are very useful for making mechanical structures, such as probing tips. Tungsten deposition also has a lower proportion of carbon in the final deposit versus platinum deposits.

Insulator deposition

Insulator deposition (Figure 8) 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). When generating cross sections or TEM foils, it can also be useful to give them a different contrast from the surface material, especially if it is a conductor. The resistivity obtained is typically equal or superior to $10^{14} \mu\Omega\text{-cm}$ with the ion beam. Higher resistivities can be obtained by using the electron beam for the deposition, but this is a much slower process.

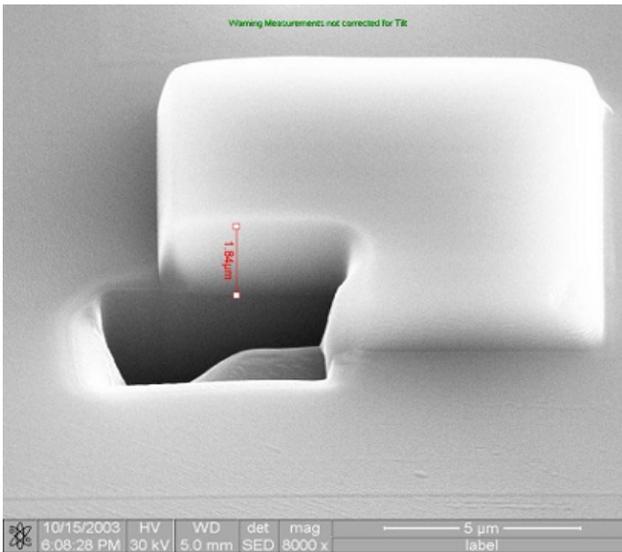


Figure 9. Carbon deposition.

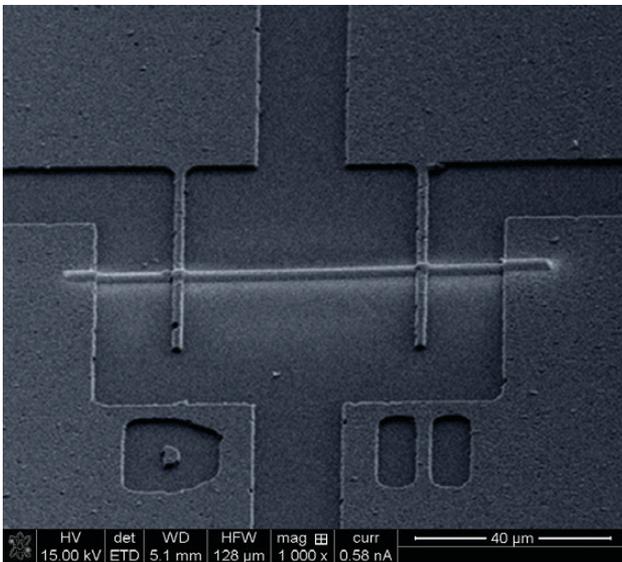


Figure 10. Gold deposition.

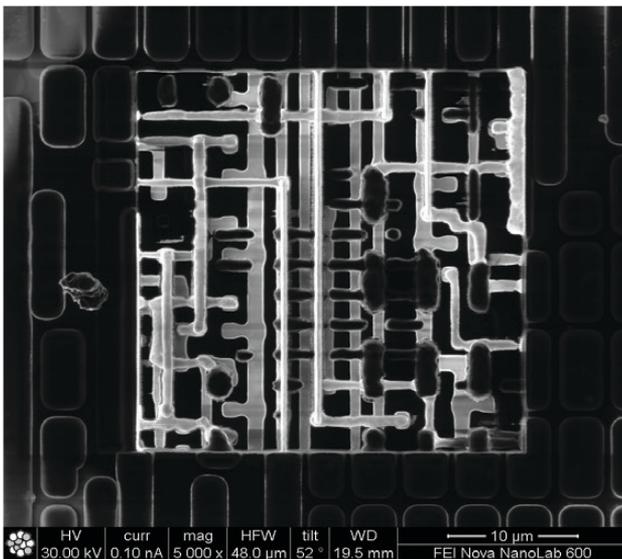


Figure 11. Insulator Enhanced Etch.

Carbon deposition

Carbon deposition (Figure 9) is primarily used as a protective capping layer for cross sections and TEM samples, as it is deposited readily (at about the same rate as platinum). However, its sputter rate when milled is less than platinum, 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 deposits. This smaller grain size helps to reduce curtaining artifacts when doing a final polish on TEM samples or cross sections at low ion beam energies. Additionally, since carbon has a low atomic number, it is often useful when identifying other light elements near the 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 $k\Omega$ range), it is not as generally applicable as platinum deposition. Nevertheless, despite its resistivity, a coating of carbon can still be used to reduce charging on samples and 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 either deposition with the ion beam or electron beam deposition of platinum.

Gold deposition

Gold deposition (Figure 10) is an attractive process for multiple applications in both optics and biology (fixing proteins). It has a high electrical conductivity and low chemical reactivity, and when it is combined with the patterning ease of the SEMs, FIBs and DualBeams, 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 it should not be considered for mechanical structures or routine electrical contacting.

Etching beam chemistries

Insulator Enhanced Etch (IEE)

Insulator Enhanced Etch (IEE) (Figure 11) 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 therefore speeds up machining of glass, nitrides and other insulators. As well as increasing 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 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 highlighting layers in the presence of bulk silicon. 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 a Thermo Fisher-patented technique that uses water vapor to increase the removal rate of carbon-containing materials. Polyamide, PMMA (polymethyl methacrylate) and other organic materials are removed 20 times faster, and diamond is removed 10 times faster 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, making SCM a very effective preferential etch (Figure 12). 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.

Delineation Etch

Thermo Scientific™ Delineation Etch (Figure 13) provides variable etch rates for oxides, enhancing 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 gives a weaker etch. Contrast in the secondary electron image primarily reflects topography, as protruding edges allow more secondary electrons to escape, and therefore, appear brighter than recessed edges.

Enhanced Etch (EE)

Thermo Scientific™ Enhanced Etch (EE) is our patented chemistry that specifically 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 (Figure 14) to be milled. 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 while also improving the optical properties of the milled surfaces.

CoppeRx

Thermo Scientific™ CoppeRx™ Software is a stand-alone software application that uses tungsten (W) gas and an our patented milling process to cleanly remove surface copper from a sample. The pattern milled with CoppeRx Software (Figure 15) produces a smooth, even box, free of copper debris. In contrast, milling without CoppeRx Software produces a rough, uneven box with considerable copper debris.

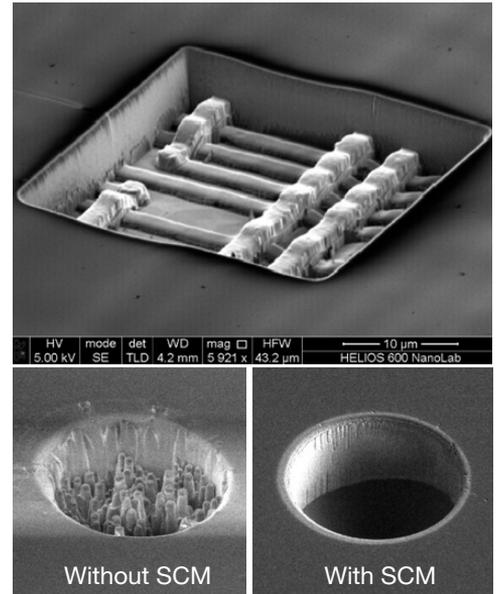


Figure 12. Selective Carbon Mill. The horizontal field width of the two lower images is 26 μm.

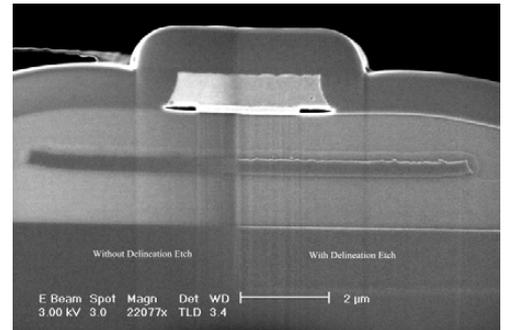


Figure 13. Delineation Etch.

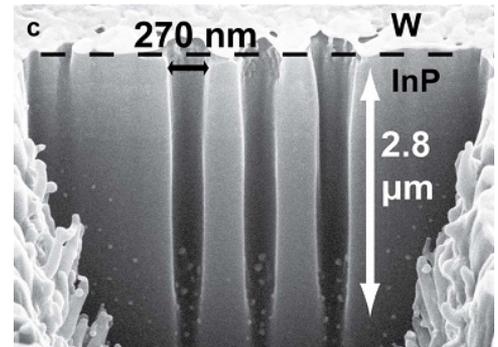


Figure 14. Enhanced Etch. High aspect ratio holes in InP using EE. Ref. Callegari et al, *J. Vac. Sci. Technol. B*, Vol. 25, No. 6, Nov/Dec 2007).

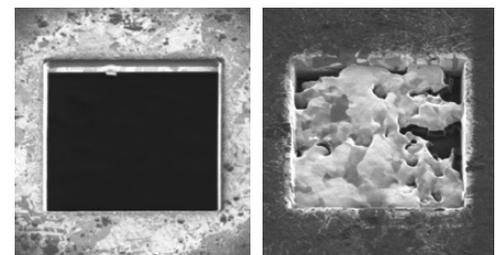


Figure 15. CopperRX Software. The horizontal field width of the two images is 13 μm.

Beam chemistry development

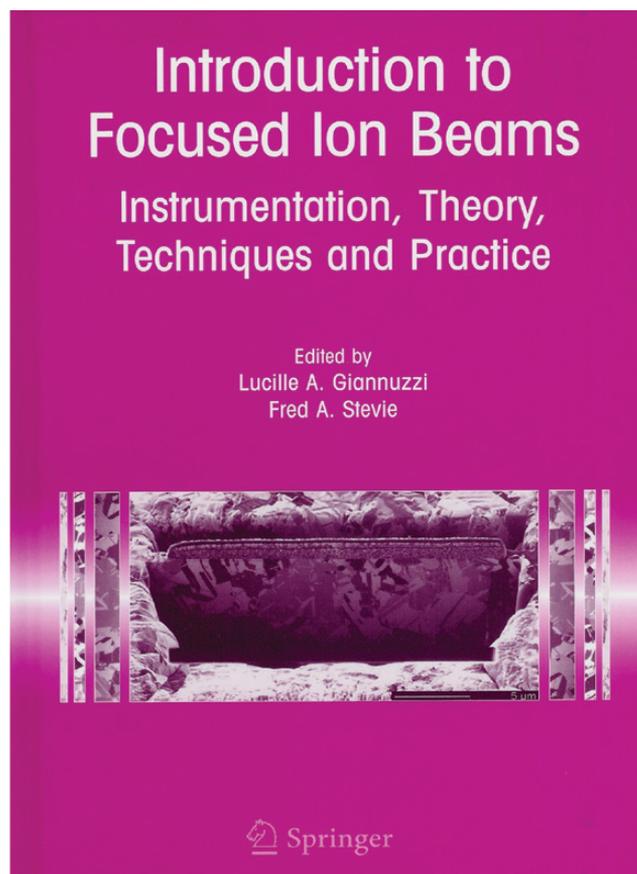
Thermo Fisher Scientific has a dedicated group of scientists to investigate new beam chemistries and their applications for SEM, FIB and DualBeam systems. They collaborate with leading researchers around the world to develop and test deposition and etching gases for a range of applications in nanotechnology, 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 Software, 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 Thermo Fisher Scientific welcomes customer 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

Thermo Scientific™ beam chemistry-related 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



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