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Teaching an Old Material New Tricks: Easy and Inexpensive Focused Ion Beam (FIB) Sample Protection Using Conductive Polymers

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Abstract: This letter describes an innovative spin-coating system, built from off-the-shelf components, that can easily and inexpensively be integrated into any laboratory environment. Combined with a liquid suspension of conductive polymer, such a "rotary coater" enables simple coating of planar samples to create a physical protective barrier on the sample surface. This barrier aids in charge dissipation during scanning electron microscope and focused ion beam (FIB) imaging and provides wide-scale protection of the sample surface from ion bombardment during FIB imaging and gas-assisted deposition. This polymer layer replaces the localized and time-consuming electron beam deposition step typically performed during transmission electron microscopy lamella preparation. After observation, the coating can be easily removed, if desired. The described spin-coating procedure has minimal cost while providing repeatable positive results, without the need for expensive commercial coating instrumentation.

Key words: focused ion beam, TEM lamella preparation, scanning electron microscopy, conductive polymers, sample preparation

Introduction

Focused ion beam (FIB) instruments have seen widespread adoption in industrial labs and academic user facilities around the globe because of their broad range of capabilities and the extensible nature of the platform. Frequently arranged in a "dual-beam" configuration with a scanning electron microscope (SEM), FIB/SEM instruments are versatile nano-inspection, fabrication, modification, and sample preparation tools (Giannuzzi & Stevie, 2005).

As with any charged particle imaging system, an electrically conductive specimen is required for images and patterning free of "charging" artifacts arising from an accumulation of charge on the sample surface. This surface potential can deflect the primary ion or electron beam and disturb the paths of emitted secondary electrons, causing distortion of the collected image or FIB pattern. Careful tailoring of the accelerating voltages used to form the electron beam may alleviate such artifacts in SEM (Joy, 1989), but such adjustments are not always practical. Alternatively, SEM imaging can be performed in a water vapor atmosphere to eliminate charging artifacts on dielectric substrates (Moncrieff et al., 1978), but FIB processing in wet environments is usually impractical. To control charging artifacts resulting from the build-up of positive charge during FIB processing, the SEM can be used to simultaneously supply a countering negative charge (Stokes et al., 2007), but this requires careful tailoring of exposure conditions. Oftentimes, the preferred solution to charging issues is a conductive coating of carbon or metal applied to the sample, typically requiring the use of an expensive sputter or evaporation system and precious metal sources. Metal coatings are difficult to remove without damaging the substrate and contaminate the sample, often limiting their application to sacrificial samples only.

In addition, one very common application of FIB/SEM instruments is the site-specific preparation of cross-sectional and planar transmission electron microscopy (TEM) lamellae. This procedure is well documented in the literature (Schaffer et al., 2012), and enables the highest-resolution TEM samples with unparalleled control of sample location and thickness. When preparing a foil with a thin film near the surface, however, great care must be taken to protect the surface of the sample from the destructive effects of the ion beam. Without a protective coating, even just a few seconds of imaging with the FIB could damage material within the ion penetration range, destroying the subsurface area of interest and rendering the sample useless.

Such damage can be prevented by the use of sacrificial material deposition within the FIB/SEM using a gas-assisted process. Typically, this involves the sequential deposition of a thin layer of material (C, Pt, or W) using the electron beam (deposited thickness of ~0.2 μm) and then ion beam (a further 2-μm thickness). The electron-beam-induced

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deposition is performed first as it does not cause any structural damage to the surface at typical SEM accelerating voltages and current densities, whereas ion beam deposition at an energy of 30 keV may result in ~20–30 nm of damage (McCaffrey et al., 2001). Although effective, deposition of material in the FIB/SEM using the electron beam is quite slow, and the protection is limited to only a small patterned area on the sample, even though widespread protection is often desired.

In a busy multi-user environment (such as commercial analytical labs and university microscopy centers), there is a strong incentive to reduce the time needed by users on the equipment, while budget constraints often limit the purchase of expensive sample preparation equipment. Thus, an inexpensive and reversible means to protect samples from FIB damage during observation and lamella preparation could be useful in these facilities. Such a technique making use of inexpensive components combined with liquid conductive polymers has been implemented with great success and is described in the following sections.

Materials and Methods

Conductive Polymers

An obvious candidate material for charge distribution, physical protection, and easy removal is the class of organics known as conductive polymers. First synthesized in 1862 (although their significance was not known at the time) (Letheby, 1862) and earning a Nobel Prize in 2000 (Shirakawa, 2001), these electrically conductive organic materials have inspired widespread applications, including organic light emitting diodes, organic photovoltaics, and antistatic coatings, among others. In the microfabrication community, conductive polymers have long been used in electron-beam lithography (EBL) to enable ultra-high-resolution patterning on nonconductive substrates, and likewise can have similar benefits for FIB patterning (Dylewicz et al., 2011). Indeed, conductive polymers have been previously used to reduce the negative impacts of FIB charging during circuit edit, mask repair, and lithographic applications (Talbot & Trexler, 1994; Alias et al., 2015; Janeiro et al., 2016). This letter is the first report, however, extending their application to physical TEM lamella protection (to the authors' knowledge).

A number of conductive polymers can be used for this purpose, ranging from inexpensive generic polymers to more expensive commercial formulations designed specifically for EBL applications. Among the generic formulae available from most chemical suppliers are polymers such as polyaniline, polypyrrole, and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), whereas examples of commercial products include aquaSAVE (Mitsubishi Chemical Corporation, Tokyo, Japan) (Mitsubishi Chemical Corporation, 2004) and ESPACER (Showa Denko, Tokyo, Japan) (Showa Denko, 2008). Generally, films of these polymers are cast onto planar samples using dedicated (and expensive) spin-coating systems designed for lithographic applications. The properties of these films are dependent on the angular velocity used during casting (see Fig. 1), allowing both the film thickness and its conductivity to be controlled. Any of the polymers mentioned here should be expected to work well for the dual purposes of charge mitigation and physical protection, but the specific polymer used in this work was aquaSAVE-53za. If desired, the polymers can be easily removed using a warm bath of deionized (DI) water (optionally performed in an ultrasonic cleaner).

The top portion of Figure 1 demonstrates the higher resistance of the conductive polymers when compared with two thin film materials commonly used to reduce charging in the SEM. Although not nearly as conductive as a metal film, the resistivity of the conductive polymers is low enough to be effective in eliminating charging artifacts.

Besides the film's resistance, of particular interest for physical protection of the sample surface from ion beam damage is the total film thickness. To be effective in protecting the surface against a Ga^+ ion beam accelerated to an energy of 30 keV, the film must be at least 30 nm thick (McCaffrey et al., 2001). Greater thicknesses will provide an additional buffer against implantation damage during prolonged ion beam imaging and deposition of protective material during TEM lamella preparation. In general, the

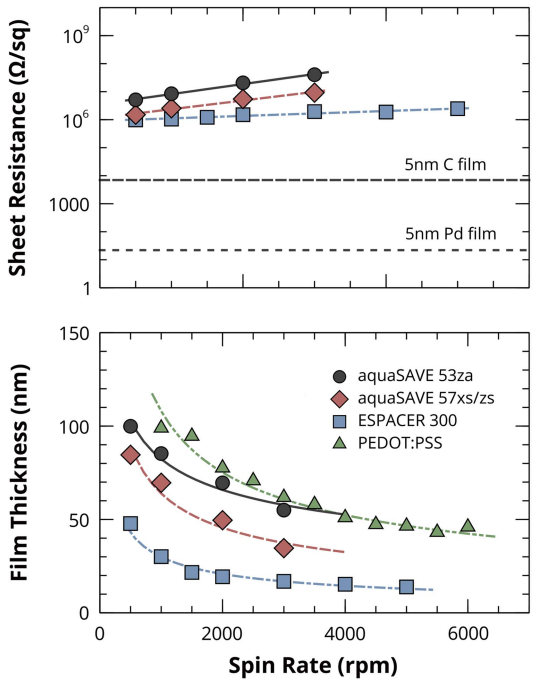

Figure 1. Sheet resistance and film thickness resulting from spinning three commercial conductive polymers, along with a generic PEDOT:PSS formulation. For resistivity comparison, the expected sheet resistance for C and Pd films (thickness of 5 nm) is plotted, showing the higher resistance of the conductive polymers compared with traditional coating films. The bottom pane shows that any of the polymers would result in a sufficiently thick protective film. Polymer data compiled from Mitsubishi Chemical Corporation (2004), Showa Denko (2008), Greco et al. (2011); C and Pd film data from Goldstein et al. (2003). PEDOT:PSS = poly (3,4-ethylenedioxythiophene) polystyrene sulfonate.

thickness of a spin coated film t will have an inverse power law relationship with the speed of revolution Ω

$$t \propto \Omega^{-N},$$

where typically, $0.5 \leq N \leq 1.0$ (Sukanek, 1991). The spin curve in Figure 1 provides typical film thicknesses for a single coating of various conductive polymer formulations, demonstrating that films >50 nm in thickness can be easily cast by selecting the correct rotational speed, thus allowing one to bypass the time-consuming step of electron-beam-induced deposition during TEM lamella preparation.

Rotary Coater

While very effective at casting polymers onto planar substrates, dedicated spin coater systems are typically expensive, bulky, and (if available at all) located in a microfabrication facility rather than in a convenient microscopy sample preparation laboratory. A convenient, and very cost-effective solution, built from simple off-the-shelf components, is presented in this work. This "rotary coater," as shown in Figure 2, is quickly and easily assembled from a benchtop vise, a rotary tool, and a plastic shield. With just these three pieces, samples can be coated in a matter of seconds, just before FIB/SEM observation.

Assembly of the rotary coater is simple. On a stable lab bench, a rotary tool (preferably with variable speed control) is clamped into a fixed vise such that its axis of rotation is normal to the bench. A plastic shield can be easily fashioned from a recycled CD or DVD container with a removable cover, that has had a hole drilled in its base to allow attachment to the rotary tool. With the collar nut of the rotary tool removed, the base of the shield is slipped over the shaft of the rotary tool, and the collar nut reattached to affix the shield base to the tool. Use of a level to verify the angle of the assembly is helpful, but not strictly necessary. For further convenience, a foot pedal switch may be added to apply power to the rotary tool.

Coating a sample is also very straightforward. First, the specimen is mounted onto a standard SEM stub holder. With the plastic shield cover removed, the specimen and stub are placed into the chuck of the rotary tool, which is then tightened securely. Using a dropper, a small amount of conductive polymer is placed in the center of the sample and spread to wet the entire surface. The plastic cover is reaffixed and power to the rotary tool is supplied, spinning the sample for about 10 s. The polymer will dry into a thin film almost instantaneously, making the sample ready for FIB/SEM observation. Selecting an appropriate speed for the rotary tool is often an iterative process, but Figure 1 may be used as a guide.

To obtain the results presented in the following section, aquaSAVE-53za was spun onto two different samples using a (nominal) 30,000 rpm spin rate (the fixed operating speed of the rotary tool used in this work). Compared with the speeds plotted in Figure 1, casting at a higher speed does not fundamentally alter the mechanics of the casting process or the behavior of the film, and results in a thinner (and moderately more resistive) film. A high-speed deposition represents the "worst-case" scenario, meaning an effective coating at these speeds guarantees that a slower speed procedure will also succeed. The first coated sample was an insulating quartz substrate with Au metallization deposited on the surface, used to test the charge dissipating capabilities of the film. The second was a 4H–SiC substrate with a 60-nm thick SiO_2 oxide layer, used to demonstrate the behavior of the conductive polymer during TEM lamella preparation. In this process, the conductive polymer can replace the often time-consuming electron beam deposition step, protecting the sample surface from the 20 to 30 nm of damage that occurs during the ion beam deposition of the thicker protective layer. In this study, however, an extra thin layer of Pt was deposited using the electron beam so as to enable an accurate measurement of the polymer's thickness via TEM. After this layer, a thicker 2 μm layer of carbon was deposited with the ion beam to provide the majority of the protection during the subsequent thinning of the lamella.

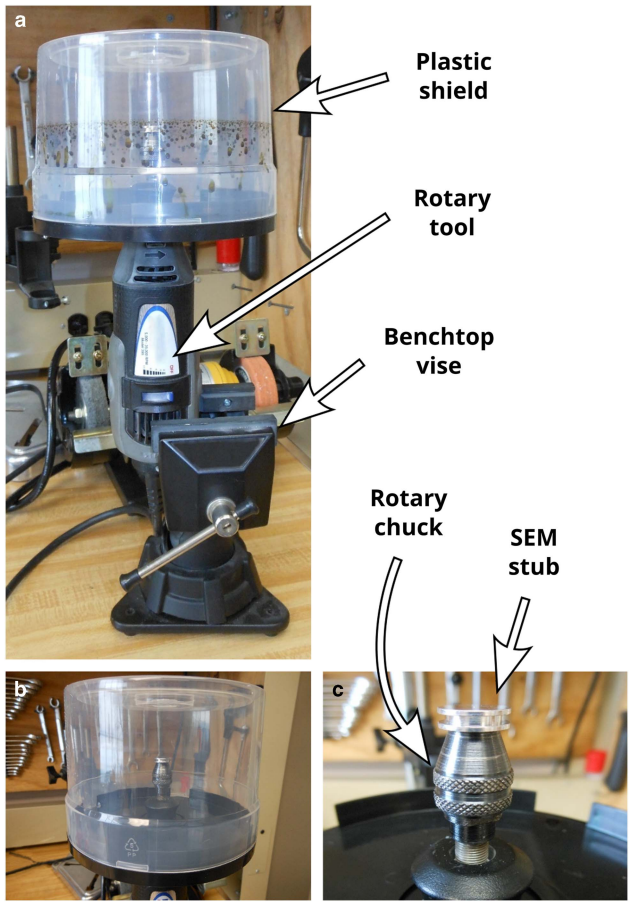

Figure 2. Pictorial depiction of the "rotary coater" described in the text. **a:** Full view of the entire coater assembly. **b:** Detail of the coating chamber, showing a typical scanning electron microscope (SEM) sample stub contained within. **c:** Additional detail of the stub fastened to the rotary tool using the included tool chuck.

Results

Charge Reduction

Figure 3 illustrates the positive effects of a conductive polymer coating when attempting to image and pattern on a nonconductive specimen in the FIB/SEM. In Figure 3a, two identical quartz substrates are imaged with a 30 keV energy primary electron beam. As evident in the figure, the sample that received a thin conductive polymer coating (~30 nm in thickness) has greatly reduced charging artifacts, which facilitates imaging, and will drastically improve the quality of patterning on the sample using either the electron or ion beam.

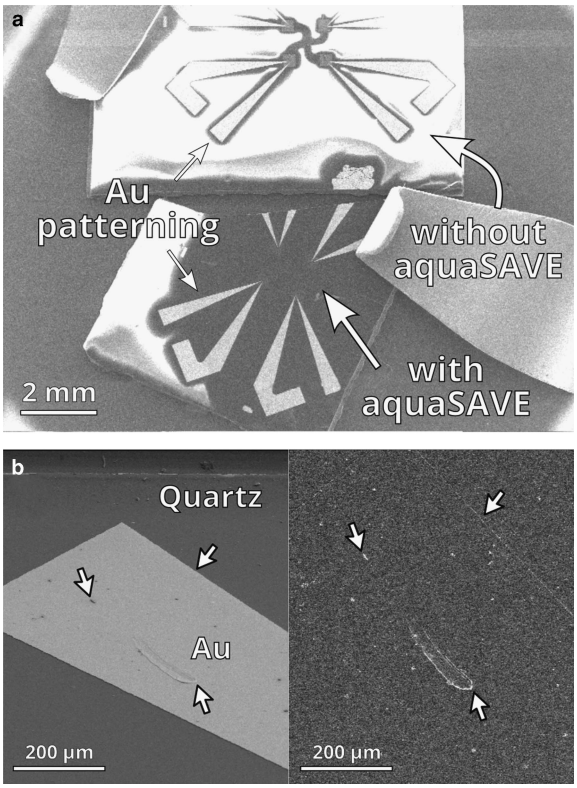

Figure 3. Focused ion beam (FIB)/scanning electron microscope (SEM) images showing the beneficial effect of using a conductive polymer coating on a nonconductive sample. **a:** Low-magnification $U = 30$ kV SEM comparison of two quartz substrates with thin Au patterned deposition, with and without a 30,000 rpm "rotary coating" of aquaSAVE. The coated sample exhibits greatly reduced charging artifacts, although due to the limited conductivity of the thin film (compared with metals), some charging does remain on the left-hand side of the coated sample. Use of a lower energy electron beam, or simply using another grounding clip on that side of the sample would alleviate the problem. **b:** Two higher magnification images using (*left*) $U = 10$ kV SEM at 52° inclination and (*right*) $U = 30$ kV Ga^+ FIB at normal incidence. The small arrows indicate the same sample features present in each image. The material contrast of the Au is lost in the FIB image because the Ga^+ ions do not penetrate through the polymer layer. Topography contrast remains, however, as evidenced by the edge of the Au area and outline of the scratch on the Au surface.

In Figure 3b, higher magnification electron (10 keV) and ion (30 keV) images reveal further effects of the polymer coating. In the SEM image, the sample appears as if completely conductive, with no charge buildup and high contrast between materials, meaning that the primary electron beam easily penetrates the polymer film and the secondary electron signal is collected from the underlying material. In the FIB image of the same location, however, there is no discernable contrast between the Au metallization and the quartz substrate. Due to the shallow interaction volume of Ga^+ ions, the ions do not penetrate through the conductive polymer layer to reach the substrate, and almost the entirety of the detected secondary electron signal originates from within the thin polymer. This causes a substantial loss of material contrast and leaves only topographical contrast as a navigational guide. This is a potentially undesirable consequence of the coating method, but the prevalence of dual-beam FIB/SEM tools almost guarantees an SEM image will be available as well to mitigate this effect.

In addition, it is important to note that the charge mitigation effect is limited only to the surface of the sample (like all conductive surface coating techniques). This is not an issue in typical SEM analysis, but charging artifacts may still arise during sub-surface imaging of nonconductive materials, as performed during FIB cross-section analysis or serial tomography applications. In such cases, metal intrusion or vacuum epoxy impregnation (for porous samples), or embedding of the material in another conductive medium would be more appropriate.

TEM Lamella Protection

To evaluate the effectiveness of the polymer coating as a FIB protective layer, a TEM lamella was prepared using standard techniques (Schaffer et al., 2012) from a thin film specimen. TEM images from the resulting lamella are shown in Figure 4. In the lower magnification image (Fig. 4a), the damage caused by ion beam deposition of a carbon layer is plainly visible, and extends (as expected) for about 30 nm into the electron beam deposited Pt layer, meaning the polymer layer must be at least this thick to provide complete protection from the ion beam during deposition. In the higher magnification image (Fig. 4b), the polymer coating is revealed to be about 27-nm thick and extremely flat. While thinner than initially desired, the layer was deposited with a very high spin rate of 30,000 rpm, and could be thickened substantially through the use of a variable speed rotary tool, which would allow spinning at a lower speed comparable with traditional spin-coater tools (such as 5,000 rpm). Even at 27 nm however, this layer would have likely been enough to protect the SiC/SiO_2 interface from damage, due to the thickness of the SiO_2 film, illustrating how different samples will have unique requirements for protection layer thickness.

The rotary coater system has proven to be very effective in the authors' laboratories, but does have some limitations, which are important to consider when evaluating it as an alternative to the more expensive traditional techniques. First, like any coating technique, the surface of the sample

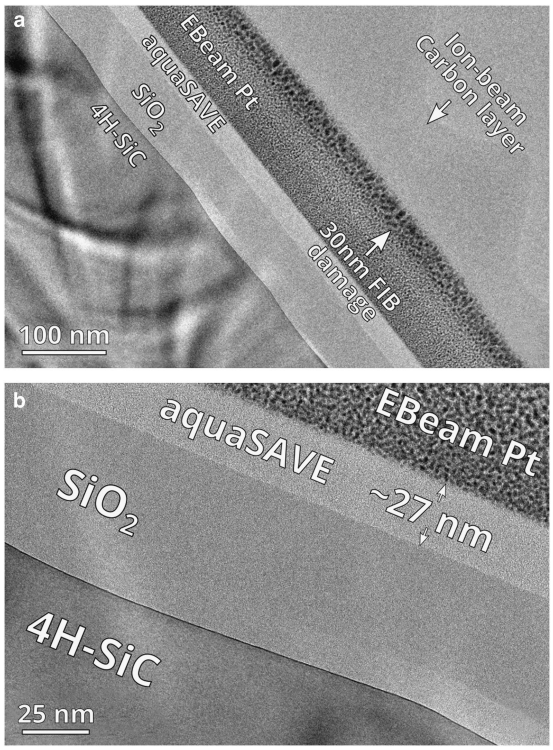

Figure 4. Cross-sectional transmission electron microscopy (TEM) images of a SiC/SiO_2 interface after spin coating a layer of aquaSAVE conductive polymer in the rotary coater, using 30,000 rpm. In (**a**), the 30 nm of ion beam implantation damage is clearly visible within the electron beam deposited Pt layer. The ion beam deposited protective carbon layer is faintly visible above this damage layer. (**b**) A higher magnification view of the aquaSAVE reveals an even coating of about 27 nm, sufficient for eliminating charging artifacts and protecting the subsurface SiC/SiO_2 interface from focused ion beam damage.

will be obscured by the casted film. Details of the smallest features (i.e., smaller than the 30–75 nm thickness of the film, depending on coating speed) may be hidden, especially when imaging with the ion beam. As such, a polymer coating may not be the best choice for ultra-high-resolution imaging or TEM lamella preparation. As shown in Figure 3b however, the electron beam can easily penetrate these polymer films, and can often provide sufficient navigational cues, even at high magnification. Another important limitation is that the rotary coater system is effectively limited to the protection of planar samples only. For nonplanar samples, an ultrasonic atomizer could be used to "spray coat" the sample. Finally, as with traditional carbon coating, the use of the polymer layer will introduce additional elemental species to the sample, which need to be accounted for in any sort of analytical study (such as energy dispersive x-ray spectroscopy).

Although deceptively simple, the rotary coater has proven itself as a remarkably effective tool in the authors' laboratories. It has numerous advantages over evaporative and sputter coaters, as well as more dedicated spin coater installations. The coating is applied in mere seconds, without the need to prepare sputter targets or waiting for a vacuum system to pump. There is little laboratory infrastructure (power, water, gas, etc.) needed to implement the rotary coater, and the tool can often be built from components already present in a typical laboratory environment. If not, the individual components are exceedingly inexpensive (the authors' system was built for under $50). With the rotary coater, the entire sample is coated and protected while remaining transparent to the electron beam, and the entire coating can be easily removed with a DI water bath, if needed.

Conclusion

Sample preparation is often critical to obtaining the best results from an electron or ion beam microscope, but the techniques used to prepare nonconductive samples are often time-consuming and irreversible. The use of conductive polymers is presented in this article as a solution not only to improve imaging and patterning on difficult samples, but as a practical protective barrier against FIB implantation damage. A simple, yet effective coating system dubbed a "rotary coater" enables quick and easy conductive coating of planar samples. Results from coated samples are positive, proving the technique's effectiveness as both a charge mitigation strategy and ion beam protectant during TEM lamella preparation. The rotary coater can be implemented into any laboratory environment and should be of great use to the microscopy community as a whole.

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