Contamination Cleaning of TEM/SEM Samples with the ZONE Cleaner

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Introduction

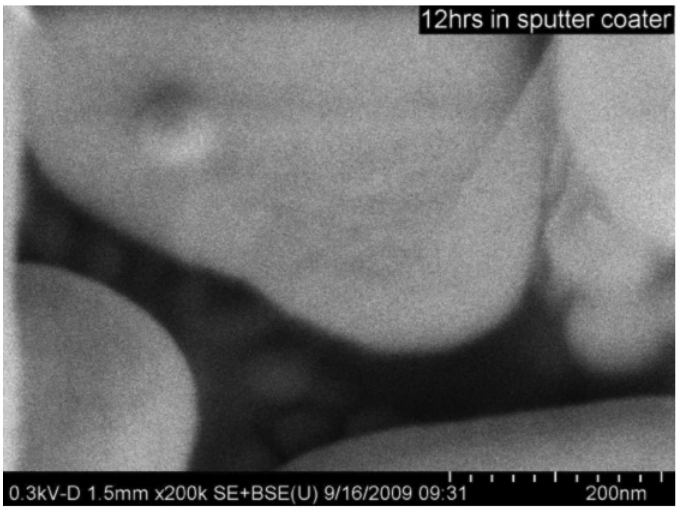
Microscopists demand better performance from their electron microscopes with every new instrument. With the advancement of new instrument technologies, better images, higher resolution, more precise analysis, and faster throughput are all benefits that are expected of expensive purchases. Still, in many cases, a well-known problem detrimentally affects the quality of results: specimen contamination.

Contamination in electron microscopy refers to the deposition of carbonaceous material on the sample surface exposed to electron bombardment in a process known as electron beam induced deposition (EBID) [1]. This occurs when there are carbon species present on the sample surface or in the vacuum system. Through interaction with the electron beam, the carbon species crosslink and form physical structures on the sample. The buildup of this carbon layer can be seen in SEMs as the well-known "black box." In both SEM and TEM, this contamination results in a reduction of clarity of sample features. In addition to obscuring surface morphology, contamination interferes with focusing and astigmatism correction; it causes the generation of additional signals that are not representative of the sample. Figure 1A illustrates a typical sample with its surface covered by carbon deposits through EBID, making it difficult to discern the underlying surface morphology. When present, sample contamination directly and negatively affects the collection of useful data, and in many cases it will pose a limit to the microscope's performance. Three areas where even a small amount of hydrocarbon contamination can have a severe impact on the test results are the following: (a) ultra-high resolution microscopy, (b) low-kV "surface" microscopy, and (c) long-duration mapping such as with EDS, EELS, and EBSD. The increasing popularity of these and other operating modes elevates the importance of clean samples.

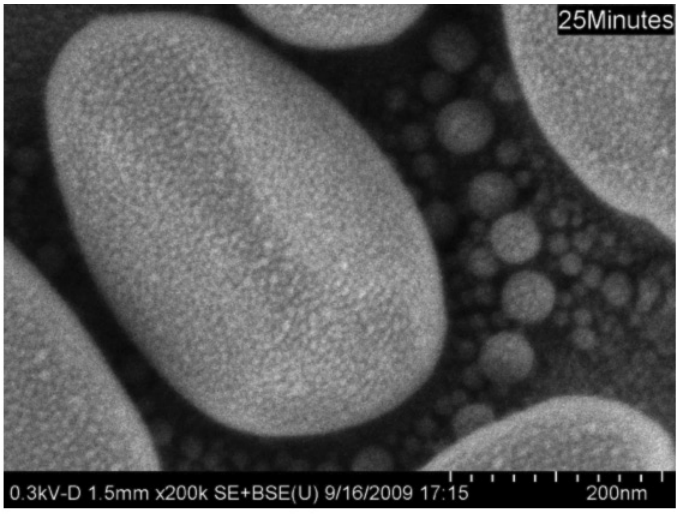
Although it is known that contamination molecules can come from the microscope vacuum or the sample itself, specimen-borne hydrocarbon is still the main contributor in most cases [2, 3]. Sources of sample contamination are numerous and can be introduced at various stages of sample preparation and sample transfer. Careful, clean sample handling practice such as the use of gloves and chemical cleaning of tweezers can minimize one source of hydrocarbons, but they have no effect on the cleanliness of the sample itself. Common cleaning methods such as solvent rinsing, heating, vacuum heating, and plasma etching all have limitations. Rinsing the sample with organic solvent such as isopropyl alcohol and methanol can remove the majority of organic contamination, but this method leaves behind a thin film of residue that itself contaminates the specimen. Heating and vacuum heating are limited in effectiveness and cannot be applied to heat-sensitive materials. Plasma cleaning involves numerous operating parameters and can often damage the sample or redeposit elements.

ZONE Sample Cleaners

Hitachi High-Technologies Canada recently developed the ZONE cleaning systems—ZONE-SEM (Figure 2A) and ZONE-TEM (Figure 2B)—as stand-alone, one-stop sample



(A)



(B)

Figure 1: Gold particles (small) on tin particles (large) on a carbon substrate. (A) Before ZONE cleaning. (B) After 25 minutes of ZONE cleaning. Surface features can be seen clearly on the after picture, including smaller particles on the substrate below.

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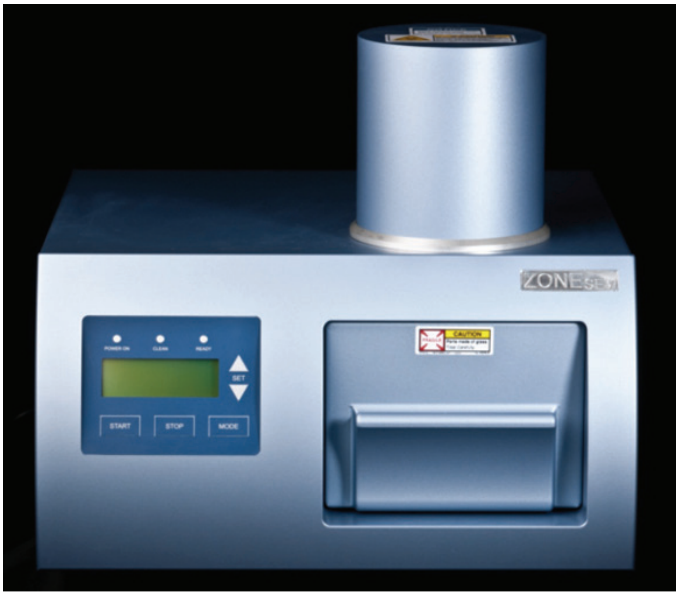

Figure 2: ZONE cleaning systems. (A) ZONE SEM unit. (B) ZONE TEM unit.

cleaning tools to effectively remove specimen hydrocarbon contamination for both bulk SEM samples and thin TEM samples. The ZONE system employs ultraviolet (UV) radiation and ozone in a simple, dry process at ambient temperature to produce clean surfaces within minutes, and with minimal etching of specimens containing carbon structures.

The ability of UV with ozone to decompose organic molecules has been known and applied for a long time, and it has been shown to be particularly effective in the removal of hydrocarbon contamination [4, 5]. Figure 3 illustrates the main principles in the cleaning process—a sequence of reactions that in reality all take place simultaneously. A medium- or low-pressure discharge lamp generates the required UV radiation at specific wavelengths. Because only the wavelengths that are absorbed can induce photochemical

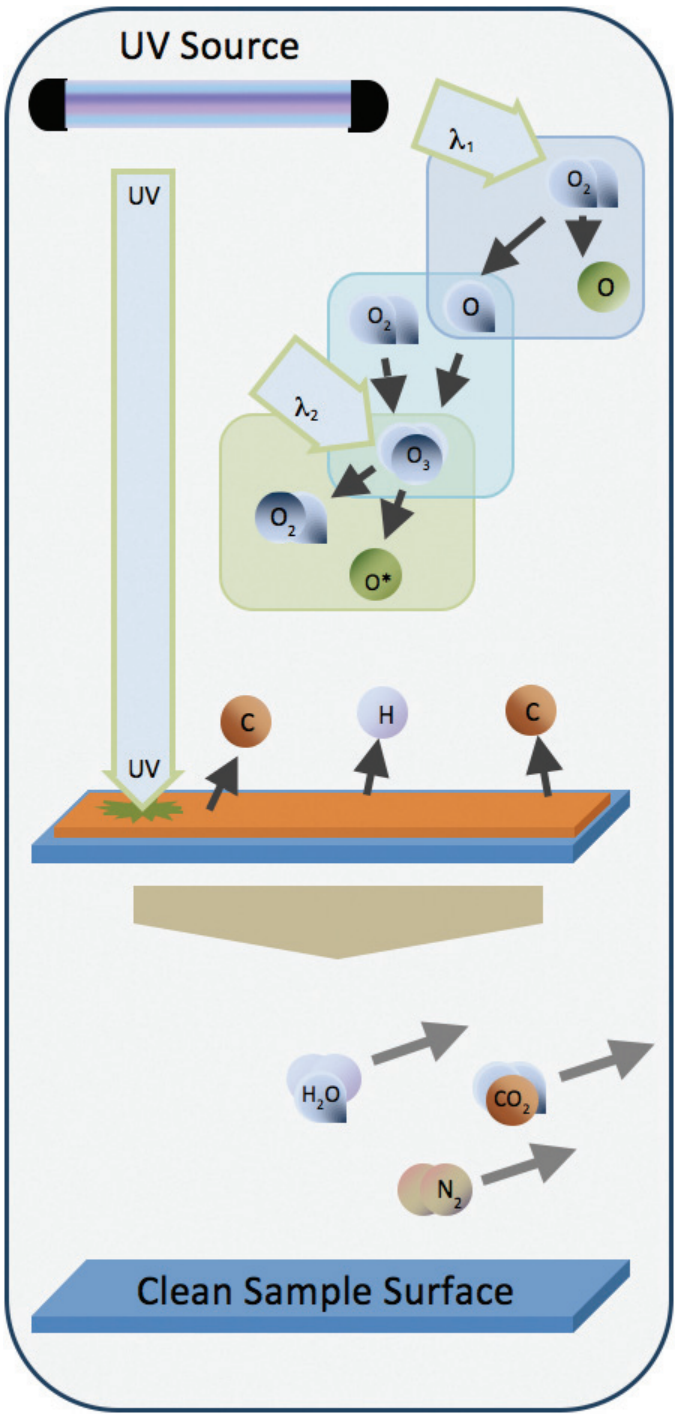

Figure 3: UV/ozone cleaning process. Two wavelengths of UV radiation generate and destroy ozone. This creates oxygen atoms in the process, which oxidize decomposed organic molecules to form CO_2 and H_2O to be removed by the vacuum system.

changes, two wavelengths are of particular importance: 189 nm and 254 nm. The short wavelength is absorbed by oxygen and leads to the generation of ozone. The longer wavelength is absorbed by most hydrocarbons [6] as well as by ozone. The process of continual generation and destruction of ozone also produces atomic oxygen, which is a very strong oxidizing agent. Meanwhile, hydrocarbon molecules on the sample surface and on the sample holder absorb both wavelengths,

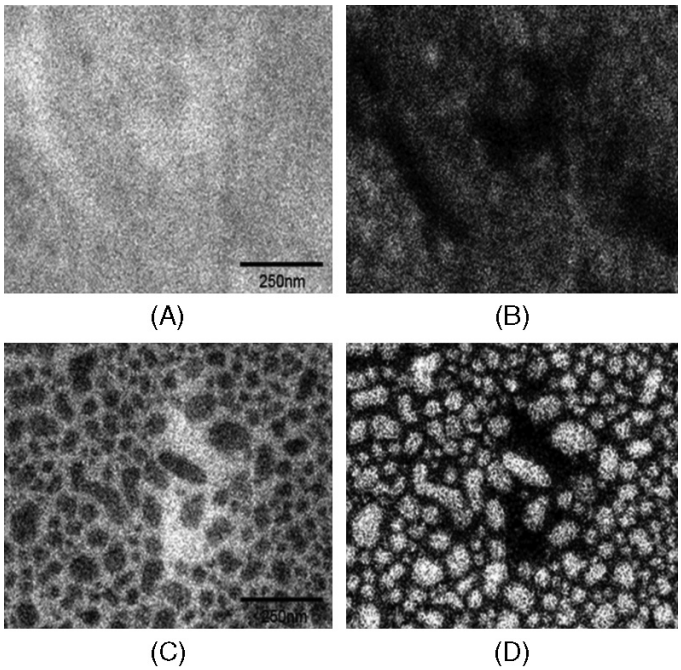

Figure 4: Energy-dispersive spectrometry (EDS) X-ray maps of a resolution sample of gold on carbon. (A) Carbon Kα peak before cleaning. (B) Au Mα peak before cleaning. (C) Carbon Kα peak after cleaning. (D) Au Mα peak after cleaning.

decomposing the hydrocarbons and making them susceptible to oxidation. The typical by-products are carbon dioxide (CO_2) and water (H_2O). Finally, the product gasses exit the system through the vacuum pump.

A sample that has been UV/ozone cleaned may present a highly reactive surface. If this is the case, the clean surface may adsorb contamination more readily than a dirty one. It is therefore important to minimize contact and handling of the sample. The ZONE cleaning systems take this into account by cleaning the sample holder along with the mounted sample, so that the sample holder or sample rod can be inserted into the microscope directly after the cleaning process to minimize recontamination.

One side benefit for many applications is the surface modification that happens once the hydrocarbons have been removed. Many surfaces will change from a hydrophobic to a hydrophilic condition. This helps the user disperse many of the nano and quantum samples that are of interest today.

Results

Among the several operating modes that are affected by sample contamination and EBID are high-resolution SEM (Figure 1), low-kV "surface" SEM (Figure 1), and long-duration analytical mapping (Figure 4). Figure 4A shows that prior to cleaning, the carbon X-ray signal was emitted from the entire area, obscuring the true X-ray signals from the specimen. After ZONE cleaning, carbon X rays from the support film and gold X rays from the deposited gold particles can be clearly distinguished (Figures 4C and 4D).

Several additional factors are shown here as well. Although the UV radiation effectively targets hydrocarbon molecules, it causes less damage to various carbon structures such as graphite and graphene. Figure 5 shows a sample of carbon nanotube seen in STEM mode on a Hitachi SU9000 SEM. The red box shows an area of contamination buildup, deposited prior to ZONE cleaning. The same beam condition was applied to the blue box area after cleaning, and no hydrocarbon was observed. More importantly, carbon lattice patterns can still be clearly observed at sufficiently high magnification, indicating that the carbon structure was not damaged by the UV cleaning process. Similar non-damaging results have been noted in graphene samples as well (not shown here). Most important for TEM carbon film users, this process is useful for cleaning times of over 2 hours without removing the carbon film, whereas a typical cleaning time is only 10 minutes.

Unlike bulk SEM samples, TEM samples are made to allow the electron beam to pass through them. This means that the TEM sample contaminates differently from SEM samples. Figure 6 shows a nanopillar sample that was imaged in the

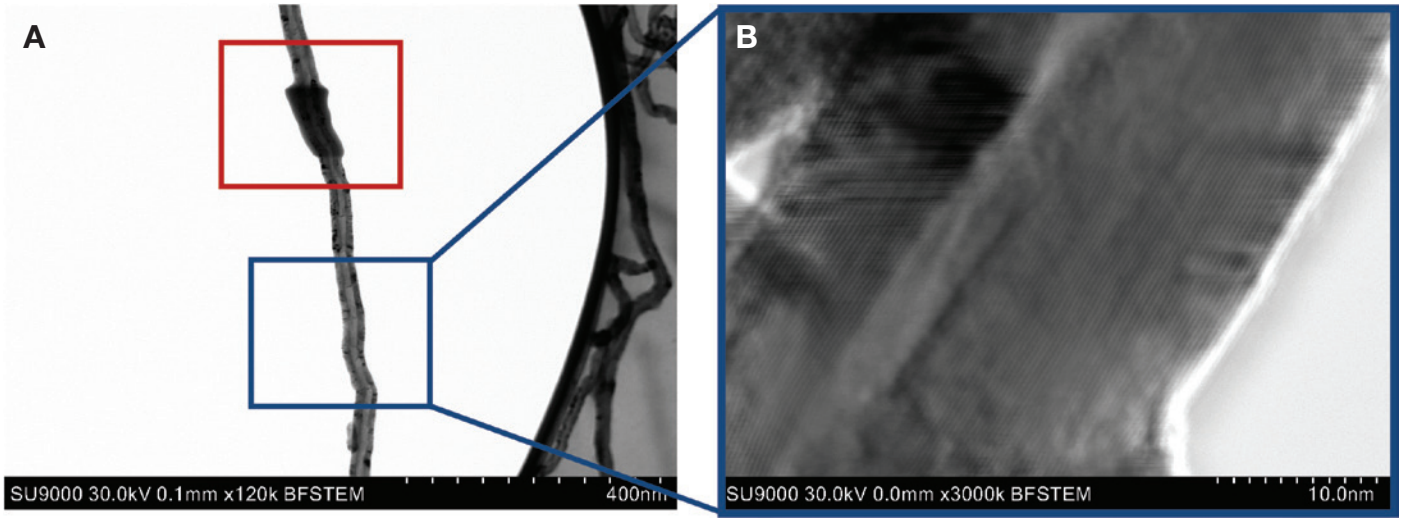

Figure 5: STEM micrograph of a carbon nanotube with electron beam exposure on two areas. (A) Red box indicates area exposed prior to ZONE cleaning. Note the buildup of hydrocarbon contamination. Blue box indicates area exposed after ZONE cleaning with no contamination. (B) Magnified view of the blue box area shows that the carbon nanotube structure was not damaged by ZONE cleaning.

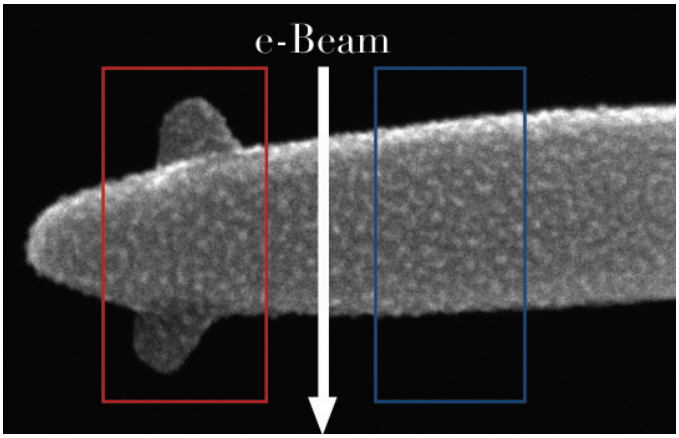

Figure 6: A nanopillar rotated 90° after beam exposure to two areas in TEM. Red box indicates the area of exposure prior to ZONE cleaning, and the blue box indicates the area of exposure after ZONE cleaning. Note the contamination deposit on both the top and bottom of the sample within the red box.

STEM before (red box) and after (blue box) ZONE cleaning using the same beam conditions. The pillar was then rotated 90° on its axis to illustrate the nature of EBID in the TEM: contamination builds up on both sides of the sample. Taking this into consideration, the TEM sample and sample rod are cleaned on both sides in the ZONE TEM unit.

ZONE systems were designed primarily as sample cleaning tools, but the UV/ozone cleaning process also lends itself to sample storage. A dry, oil-free vacuum system and the presence of residual ozone preserves the clean sample surface in storage mode as a convenient desiccator.

Conclusions

Although proper clean handling practices still play an important role in obtaining a clean sample during sample preparation, an effective instrument has been developed to allow microscopists to see the true details of their specimen. This specimen-contamination-removal system uses a gentle, non-destructive cleaning method to minimize the effect of electron beam induced deposition and to reveal fine surface features. The ZONE cleaning systems, for SEM and TEM, clean both the specimen and specimen holder.

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