A 200-kV STEM/SEM Produces 1 Å SEM Resolution

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Introduction

"Second best no more" was the title of an article written by David C. Joy for *Nature Materials* [1]. The article was for highlighting a breakthrough made by a team formed between Brookhaven National Laboratory (BNL, USA) and Hitachi High Technologies Corporation (HHT, Japan). Sub-angstrom secondary electron (SE) images were obtained on a Hitachi HD-2700, which is a combined scanning electron microscope (SEM) and scanning transmission electron microscope (STEM) operating at a maximum accelerating voltage of 200 kV. For the first time, single atoms and atomic lattices on crystal surfaces are unambiguously presented in SE images.

Like any standard 30 kV SEM, the 200 kV HD-2700 STEM/SEM probes the specimen with an electron beam focused into a tiny spot on a specimen. The electron probe scans across a specimen area, and SE signals emitted from the illuminated specimen area are collected by a high-sensitivity SE detector installed above the specimen position, resulting in images that carry structural information of material surfaces. In terms of the image formation process, the 200 kV SE imaging is similar to the conventional 30 kV SE imaging—the most popular imaging mode for SEM. The difference is the resolution power. The 200 kV HD-2700 delivers sub-angstrom (0.8 Å) SE imaging resolution; whereas, the best achievable resolution on a conventional 30 kV SEM is about an order of magnitude worse. The BNL/HHT team received a 2010 Microscopy Today Innovation Award because this team, according to the award statement, was the first to observe isolated single atoms with secondary electron imaging, and these observations point to a new mechanism for secondary electron emission. This article describes the high-voltage, high-resolution STEM/SEM and shows its benefits for secondary electron microscopy applications.

HD-2700: A Spherical Aberration-Corrected Field-Emission STEM/SEM

The HD-2700 is a 200 kV, field-emission STEM/SEM [2] equipped with an SE detector above specimen position to collect secondary electrons, while a bright-field (BF) detector and a high-angle annular dark-field (HAADF) detector below specimen position collect electrons transmitted through the specimen (Figure 1). To achieve an ultrahigh resolution in SEM or STEM, a spherical aberration corrector (Cs corrector) is employed in front of the objective lens (Figure 1). The Cs corrector provides a large flux of electrons in the incident electron probe that is focused into a fine spot at the back focal plane of the objective lens. This allows 10 times higher probe current and 2 times finer probe size compared to non-Cs-corrected microscopes. The fine probe size provides high resolution for all scanning electron probe-based imaging modes (SE, BF-STEM, HAADF-STEM), while the high probe current generates sufficient signals for image formation and chemical analysis at each pixel in the scanned specimen area.

For the HD-2700 equipped with a Cs corrector, a cold-field-electron emitter, and a high-resolution pole piece (the one at BNL), an electron probe of 0.8 Å (0.08 nm) diameter can be formed. This probe size is small enough to be placed on individual atoms, which is what the BNL/HHT team was doing. They held such an electron probe on single uranium atoms and collected HAADF-STEM and SE images simultaneously. Quite unexpectedly, the team found that the SE images showed the same resolution as that of the HAADF images. In other words, the image profile of single uranium atoms was revealed in both SE and HAADF-STEM images [3]. In another observation, a Si (110) surface was imaged as shown in Figure 2. The well-known Si dumbbells with a 1.4 Å distance between the two projected neighboring Si columns can be clearly distinguished in the SE image.

Applications of High-Voltage, High-Resolution SE Imaging

Having achieved SE imaging resolution on an atomic level, the BNL/HHT team immediately applied the HD-2700 to various materials characterization problems. Figure 3

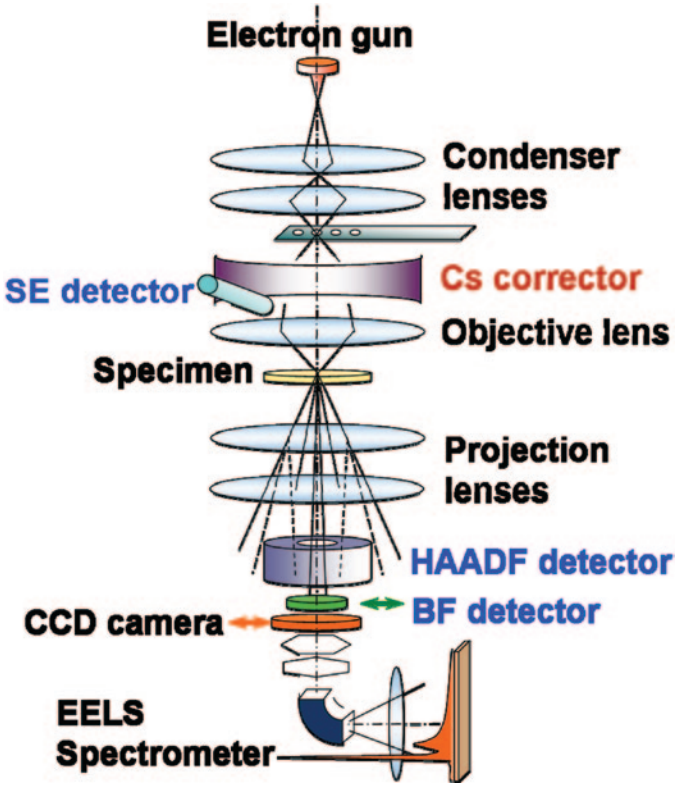

Figure 1: Schematic illustration of the electron optical system for a Cs-corrected HD-2700 STEM/SEM. A probe-forming Cs corrector is positioned above the objective lens. The SE detector is located above, and the BF and HAADF detectors are located below the specimen position.

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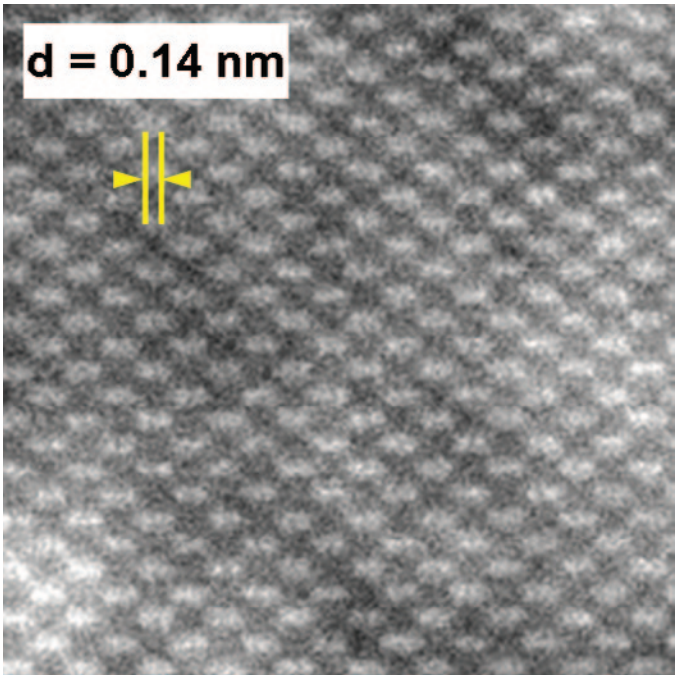

Figure 2: SE image of a Si (110) surface. The Si dumbbells, composed of two projected Si columns separated by a distance of 1.4 Å, can be clearly resolved.

shows simultaneously collected BF-STEM, HAADF-STEM, and SE images of a gold nanoparticle. The capability of simultaneously collecting images in multiple imaging modes is an important advantage of STEM/SEM systems. The BF-STEM image is similar to the TEM phase contrast image, which gives the morphology and atomic lattice information of materials. The HAADF-STEM image is a dark-field image that carries chemical information because the image contrast is proportional to $Z^{1.7}$ (Z denotes atomic number) [4]. This is often called the Z-contrast image. The heavier the atom, the brighter the contrast is in HAADF-STEM images. It should be emphasized that both BF- and HAADF-STEM images are formed by electrons transmitted through the specimen so the images reflect a projection of the interior structure of specimen. The SE image is formed by secondary electrons emitted from the specimen surface, revealing surface structural characteristics. The simultaneous atomic resolution imaging using both surface-generated secondary electrons and transmitted electrons provides correlative information for understanding what is happening on the surface and inside the sample.

The advantage of acquiring SE and STEM images simultaneously is also shown in Figure 4, which contains an SE and an HAADF-STEM image for polymer-coated Au nanoparticles. The images were obtained using a Hitachi HD-2300A filed emission STEM/SEM operated at 200 kV [5]. The sub-80 nm diameter Au nanoparticles were coated with cross-linked polymer shells. Under the SE imaging mode, a group of the Au/polymer core-shell nanoparticles appeared as close-packed spheres. However, the simultaneously acquired HAADF-STEM image shows up to 20 nm gaps among the Au nanoparticles. Obviously, the gaps should not be empty as they appear to be in the STEM image; they were actually filled with polymer shells coating the Au particles. Because of the weak scattering power of the polymer, these polymer shells did not have sufficient contrast in the transmitted Z-contrast images. On the other hand, the SE imaging is more sensitive to low-Z elements than HAADF imaging and good topographical view [6], therefore it could image the polymer shells.

The 3-D visualization effect of SE imaging may be combined with *in-situ* heating electron microscopy to study the migration of nanocatalysts on a support surface. Using the SE detector on a Hitachi 300 kV field emission HF-3300 TEM/STEM/SEM, 1 nm diameter gold nanocatalysts supported on an iron oxide substrate were observed at elevated temperatures. When heated *in-situ* in the microscope, Au nanoparticles became mobile. Figure 5 shows a sequence of SE images taken at 700°C, the two gold nanoparticles indicated by arrows moved toward each other and finally merged to form a single particle. Terraces on the support surface are also visible [7]. Combined information about support surface and the behavior of nanocatalysts, as well as structural evolution in catalysts upon heating as imaged using the transmitted electrons (not shown), can be valuable for the study of catalysts.

Discussion

Shortly after its commercial introduction, the designers of SEMs settled on a maximum electron accelerating voltage of 30 kV to balance the demands of resolution, X-ray excitation, manufacturing cost, and engineering aspects. However, it was also noticed from theory that higher electron beam energy would improve the spatial resolution and reduce the effect of lens aberrations. Figures 2–5 show that 200–300 kV TEM/STEM/SEM can provide atomic-resolution characterization of both interior and surface structures of materials.

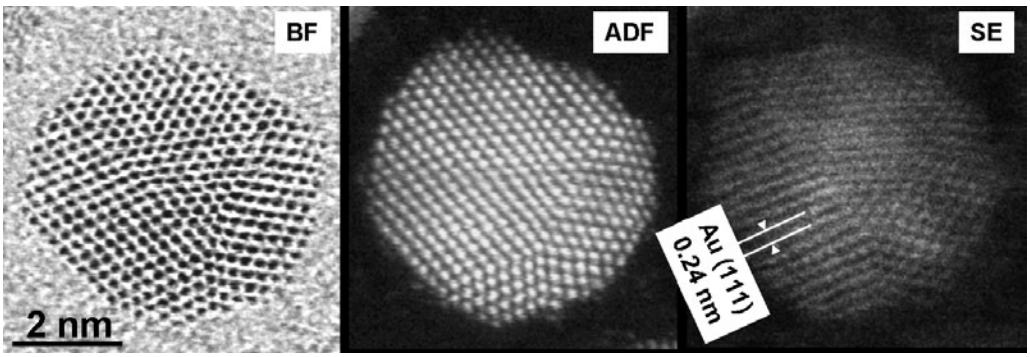

Figure 3: BF-, HAADF-STEM, and SE images of a gold nanoparticle. The three images were collected simultaneously on a Cs-corrected HD-2700 STEM/SEM. Accelerating voltage of 200 kV and a 0.1 nm diameter electron probe were used. Au (111) lattice fringes with a 0.24 nm lattice spacing are marked in the SE image.

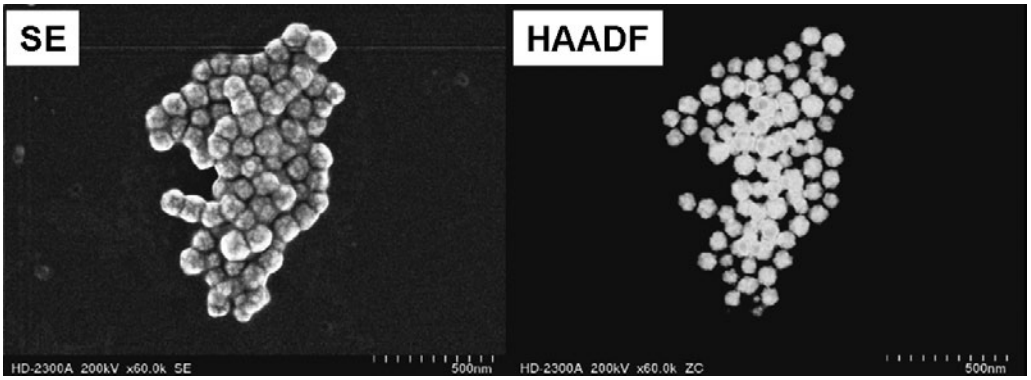

Figure 4: Simultaneously acquired SE and HAADF-STEM images of a cluster of Au nanoparticles with cross-linked polymer shells on the particle surfaces. The close-packed Au nanoparticles are well imaged in the SE mode, whereas the HAADF-STEM image does not show visible contrast for the polymer shells, therefore gaps appear among the nanoparticles. The images were taken on a Hitachi 200 kV field emission HD-2300A STEM/SEM. (Courtesy of Kvar C.L. Black of Northwestern University)

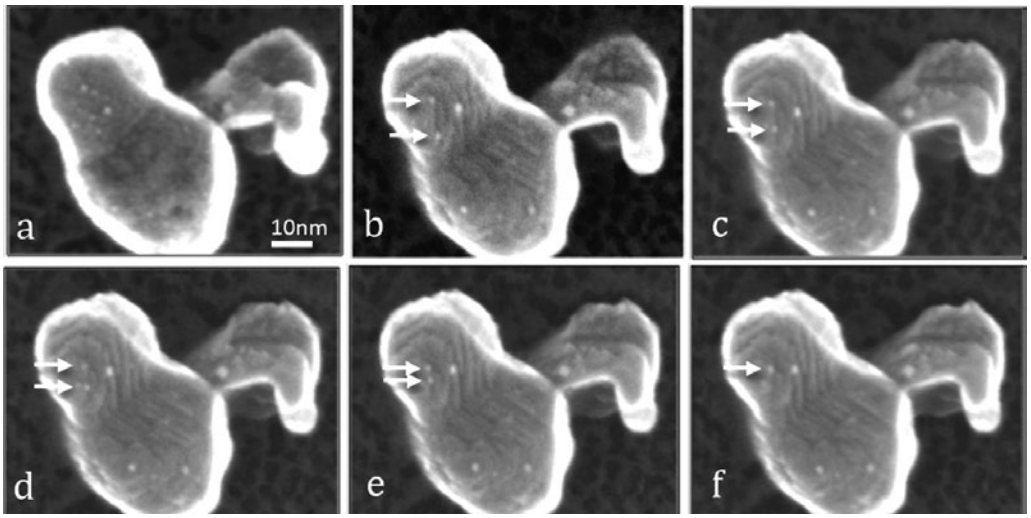

Figure 5: A sequence of SE images recorded using a Hitachi 300 kV HF-3300 TEM/STEM/SEM correlative electron microscope. Gold nanoparticles of 1 nm diameter can be seen on an iron oxide support surface. When heated to 700°C, Au nanoparticles became mobile on the support surface. The two particles indicated by arrows in (b) moved toward each other and eventually coalesced. Terraces on facets of the support surface are also seen. (Courtesy of Dr. Jane Howe of Oak Ridge National Laboratory)

For industrial users, atomic-resolution SEM and sub-surface metrology are attractive if high sample throughput is feasible at the same time. For example, conventional 30 kV SEMs have been used for metrology and defect inspection in semiconductor device industry because of the easy operation, use of bulk samples, and rapid sample throughput. With the shrinking size of electronic device features, the demand for sub-nanometer resolution could reduce demand for 30 kV SEMs in this field. Thin specimen analysis in TEM or STEM is desirable for its atomic resolution but undesirable for the tedious sample preparation process and the operational complexity, which can slow throughput. Now specimens that are too thick to be imaged by 200 kV or 300 kV transmitted electrons are still useful for atomic-resolution SE imaging in high-voltage, high-resolution STEM/SEM instruments because secondary electrons are emitted only from the surface layers of specimen.

The fact that the individual atoms were clearly imaged using secondary electrons challenged the traditional way of understanding SE imaging, which is attributed to the decay of collective electron excitation that is delocalized. A new mechanism has been proposed in which the image width of an atom is ascribed to a point-spread function that is dominated by inelastic scattering with large momentum transfer [6].

Conclusion

High-resolution 200 kV or 300 kV correlative TEM/STEM/SEM systems have been developed to simultaneously characterize interior and surface structures at atomic resolution. In particular, sub-angstrom-resolution SE imaging has been achieved on the 200 kV Cs-corrected HD-2700 STEM/SEM. This breakthrough in resolution challenges the existing SE imaging mechanism. There is no doubt that high-voltage, high-resolution SEM will find value in materials science and industrial applications, especially when used correlatively with the STEM or TEM imaging modes.

Acknowledgments

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