Imaging single atoms using secondary electrons with an aberration-corrected electron microscope

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Aberration correction has embarked on a new frontier in electron microscopy by overcoming the limitations of conventional round lenses, providing sub-angstrom-sized probes1–8. However, improvement of spatial resolution using aberration correction so far has been limited to the use of transmitted electrons both in scanning and stationary mode, with an improvement of 20–40% (refs 3–8). In contrast, advances in the spatial resolution of scanning electron microscopes (SEMs), which are by far the most widely used instrument for surface imaging at the micrometre–nanometre scale9, have been stagnant, despite several recent efforts10,11. Here, we report a new SEM, with aberration correction, able to image single atoms by detecting electrons emerging from its surface as a result of interaction with the small probe. The spatial resolution achieved represents a fourfold improvement over the best-reported resolution in any SEM (refs 10–12). Furthermore, we can simultaneously probe the sample through its entire thickness with transmitted electrons. This ability is significant because it permits the selective visualization of bulk atoms and surface ones, beyond a traditional two-dimensional projection in transmission electron microscopy. It has the potential to revolutionize the field of microscopy and imaging, thereby opening the door to a wide range of applications, especially when combined with simultaneous nanoprobe spectroscopy.

Our knowledge of the role of individual atoms in nanotechnology and energy-related research is strongly influenced by our ability to visualize them, not only in the bulk but also on the surface of a sample. In SEM, the resolution of an instrument depends on the fineness of the focused electron probe and the contrast arises from signals detected as the scanning probe interacts with the specimen. Among the multitude of simultaneously generated signals, two of the most important ones are the elastic scattering of transmitted electrons used in scanning transmission electron microscopes (STEM) and secondary emission from the surface used in SEMs. Spherical-aberration correction allows a reduction of the probe diameter and an increase in the probe current concurrently by increasing the numerical aperture of the lens. Aberration-corrected STEM instruments now routinely achieve a resolution of better than 0.1 nm (refs 2–6). With SEM instruments, the best resolution is 0.4 nm (Hitachi S-5500 operating at 30 kV; refs 10, 12) without aberration correction and 0.6 nm at 5 kV (JEOL JSM-7700F; ref. 11) with it.

SEM, using secondary electrons and backscattered electrons (BSEs), has distinct advantages over other high-resolution imaging techniques. It is surface-sensitive and can provide depth information. In contrast, images made with transmitted electrons (STEM) are projections and thus, give little information in the direction of the beam’s trajectory. To demonstrate this difference, Fig. 1a shows a pair of images of Pd particles on a carbon support. The image using secondary electrons clearly gives rich depth information about the particles’ locations, much of which is lacking in the transmission image. In the past decade or so, high-resolution SEM has proven an indispensable critical-dimension-metrology tool for the semiconductor industry. The semiconductor nanotechnology road map identifies the need for ultrahigh-resolution SEM in the quest for ever-decreasing device sizes9,13.

We attempted to achieve the highest possible SEM resolution and to determine whether it is limited by the basic physics of secondary production or by the instrumentation. We explored well-defined samples (single uranium atoms) in an instrument capable of producing both elastic scattering and secondary signals simultaneously in a single scan of the probe over a small area of the sample. Our instrument was the first Hitachi aberration-corrected electron microscope, HD-2700C, with a pole piece similar to the ‘in-lens’ design used in the S-5500 SEM (ref. 10), recently installed at Brookhaven National Laboratory (detailed in the Methods section). The elastic scattering was measured with a high-angle annular dark-field (ADF) detector and the secondary signal from low-energy electrons spiralling back in the lens magnetic field to a proprietary detector (Fig. 1b). We use the ADF image as a reference because it has a higher signal-to-noise ratio and provides quantitatively the ‘weight’ of all atoms in the path of the beam, thus identifying isolated single atoms on a thin support.

The spatial resolution, or probe size, of a modern electron microscope is often tested against and defined by the periodic structure of a crystal sample with a certain atomic spacing. This is not ideal because the results often strongly depend on the sample, including its thickness, surface condition and orientation during imaging due to the channelling effect. In this study, we select samples with UO2 clusters and individual uranium atoms on a thin (~2 nm) carbon film.

Figure 2a,b shows a pair of SEM/STEM images of uranium individual atoms and clumps. Quantitative intensity analysis of the ADF image clearly indicates the areas marked by small circles are individual atoms. The standard deviation in atom intensity (see the histogram in Fig. 2b) is larger than expected from the counting statistics owing to atom motion between successive scan lines causing distortion (stretching and gaps) in some spot profiles. Figure 2c,d shows the averaged images of the 50 spots aligned and summed for both images. The full-width at half-maximum (FWHM) of the intensity profiles as a function of distance from the centre of each spot is less than 0.1 nm for both signals.

Although clearly visible, the SEM contrast of the corresponding individual atoms is weak, largely because very limited numbers of secondary electrons (or BSEs) are generated from the individual atoms compared with the number of electrons transmitted through when the fast incident electrons hit them. The image quality can be significantly improved if an unsharp mask is used to reduce noise and variation in the background signal (see Supplementary Fig. S1). The spots that are missing from the SEM image, but which are
clearly visible in the STEM image, are probably the uranium atoms located on the bottom surface of the carbon support (more details are described in the bias experiments below). Some of the differing contrast of the individual atoms can be attributed to the atoms being at different depths, thus having different collection efficiencies.

To assess whether the SEM image intensity is a result of BSEs or secondary electrons, or both, we applied a bias (±50 eV) to the sample by modifying a Faraday-cup sample stage. Secondary electrons (defined as <50 eV energy) are considered to be produced mainly through interactions between energetic beam electrons and weakly bound conduction-band electrons in metals, or outer-shell valence electrons in semiconductors and insulators. Most secondary electrons are emitted with less than 10 eV energy; thus, a positive bias on the specimen will suppress the emission to be collected by the detector. In contrast, the BSEs are those incident electrons that underwent elastic scattering from the sample and changed their direction while losing little energy; therefore, the bias will not affect the image intensity.

Figure 3a shows the change in intensity of the SEM image of uranium on carbon film as a function of applied bias. To quantify the measurement, we used the simultaneously acquired ADF image intensities as a reference because they are independent of the bias. Supplementary Tables S1, S2 and Figs S2, S3 detail the measurements at each bias. The plot reveals that both for uranium and carbon, the normalized SEM image intensities decrease exponentially with the increase in bias. At +10 eV bias, the intensity drops nearly 80%. At +50 eV, only 10% intensity remains, suggesting that 90% of secondary electrons and 10% of BSEs contribute to the image, independent of the atomic number Z. Figure 3b,c illustrates another example, where the STEM image shows a thick holey carbon film located on top of a Ti grid and covered with thin carbon. We note that where the thin film is intact, it blocks the signal from the underlying thicker holey film. When a small bias is applied, the contrast of the thin carbon film generated by secondary electrons disappears almost completely, whereas the contrast of the thick grid stays the same. On the basis of many measurements, we found that the ratio of secondary electrons and BSEs is in the range of 85–90% to 15–10% for 200 kV electrons.

The ultrahigh-resolution SEM method was also used to image the periodic atomic structure of crystals. After optimization, we routinely achieved 0.1–0.15 nm atomic resolution in imaging with secondary electrons and BSEs. Figure 4a,b shows a pair of SEM/STEM images of a YBa$_2$Cu$_3$O$_{7-x}$ superconducting sample. Power spectra of the images indicate that spatial frequencies were transferred down below 0.14 nm. The ADF image reveals the atomic arrangement of the sample through its entire thickness, whereas the SEM image allows us to evaluate the atomic arrangement of the few top layers of the sample including the surface quality and condition. A few angstrom-thick amorphous patches greatly reduce the contrast in a SEM image while not affecting the ADF image. Image averaging (Fig. 4c,d) reveals dark lines in the SEM image (not seen in the ADF image) corresponding to CuO chain planes with reduced oxygen occupancy in the perovskite structure, suggesting that secondary-electron imaging may be sensitive in
observing light atoms. Our image analysis and bias experiment suggest that, for the sample in Fig. 4, only the top 4–5 atomic layers contributed to the SEM image and that the first and second surface atomic layers of the sample are, respectively, the Cu–O and Y–Ba–O layer.

The SEM resolution we demonstrate here is better than many would predict on the basis of the postulated delocalization of the secondary production process. We find equally sharp images in SEM and ADF (Figs 2 and 4), suggestive of negligible delocalization. The physical mechanism of secondary-electron generation is
traditionally ascribed to inelastic scattering and decay of collective electronic excitations with the transmitted electron giving up, for example, 20 eV, to produce a secondary electron of 20 eV minus the work function of the surface (or energy needed to escape from the atom). As the momentum transfer (scattering angle) of such a scattering event is small, the transfer should be delocalized. Electrons emerging from the surface can also be generated by localized processes, including backscattering. However, our bias experiment indicates that most electrons detected have low energies, not the 100–200 keV expected for backscattering. BSEs striking objects in the specimen holder or the column can also produce secondary electrons that are affected by the applied bias. Although possible, we believe that these are not a main contribution, given the high magnetic field in the specimen area that would trap electrons close to the beam axis.

The generation of secondary electrons responsible for the high-resolution SEM images can best be attributed to large-momentum-transfer inelastic scattering events such as inner-shell excitation (related to stopping power) and knock-on collision \(^{14}\) (causing thermal emission; a single adatom bound to the surface by relatively weak forces with 2 eV of kinetic energy would have an apparent temperature of 24,000 K, so thermal emission is also a possibility). The low signal levels in the SEM images result from the rarity of large-momentum-transfer events. Although electron energy-loss imaging demonstrates that electrons losing lesser amounts of energy give lower spatial resolution \(^7\), the low energies of secondary electrons we measure do not necessarily correspond to low momentum transfer. For single atoms, inner-shell excitation is the most likely source of large-momentum-transfer events. Secondary-electron emission requires electronic stopping, although electronic stopping is not always accompanied by secondary-electron emission. Electrons in the inner orbitals must overcome an energy barrier for the excited electron to escape from the atom. Therefore, the electron would emerge from the atom with considerably less than the mean excitation energy. For crystals, the underlying mechanism for atomic secondary-electron images might be different from that of single atoms. The incident and secondary electrons can be decomposed into Bloch waves \(^{15}\) and their interaction with the lattice is strongly influenced by channelling. Besides the inner-shell excitation, further momentum transfer can be introduced by electron–phonon interaction (the so-called Umklapp processes, where momentum conservation is fulfilled by a contribution from the lattice and the processes are fundamental consequences of transport properties such as thermal conductivity). Investigations of secondary-electron resolution on MgO and MoO\(_3\) (refs \(^{16, 17}\)) and coincidence measurements of carbon \(^{18}\) and silver islands on a thin carbon film using a VG STEM at 100 kV showed that 20-eV secondary electrons are produced efficiently by kiloelectronvolt-energy-loss events that are very localized \(^{19}\) and that there was no significant difference in spatial resolution between simultaneous SEM and STEM images \(^{20}\). Although no mechanism was proposed, these observations agree with ours, but at a lower resolution than we achieved.

We have achieved, for the first time, a 0.1 nm spatial resolution in SEM imaging using secondary electrons. We attribute our accomplishment to several factors, including the better design of the instrument’s electro-optics (including ultrahigh electric and mechanical stabilities) and the detector, aberration correction that reduces the probe size and increases its probe current and the higher operation voltage, which confers the benefit of a very small volume of beam interaction for a thin sample. Although we demonstrated unprecedented resolution in a SEM/STEM instrument, we consider that the same electro-optics design can be applied to a dedicated SEM instrument. However, the ability to use SEM and STEM simultaneously to image samples at atomic resolution in real space using secondary electrons generated from the surface and transmitted electrons from the bulk is particularly appealing and is unparalleled in comparison with any existing techniques in microscopy and imaging. Furthermore, information from the surface can complement the bulk information obtained, not
only in imaging but also in diffraction and spectroscopy. We expect synchronized SEM and STEM image acquisition (combined with electron energy-loss spectroscopy (EELS)) will become an emerging quantitative imaging technique, producing atomic-resolution information beyond a traditional two-dimensional projection and offering data on atomic species, their bonding environment and the local electronic structure of a selected area of interest. Undoubtedly, having the ability to concurrently obtain such detailed information will bring a new dimension to materials research. Therefore, the ultra-high-resolution SEM phenomenon warrants further research and development.

Methods

Instrumentation. The instrument, Hitachi HD2700C, is located in a specially designed laboratory in the Center for Functional Nanomaterials with significantly minimized mechanical vibration, temperature variation and electromagnetic field. It is equipped with a cold-field-emission electron source (ΔE = 0.3–0.4 eV), a CEOS hexapole aberration-corrector and a high-resolution electron energy-loss spectrometer. The system’s spherical aberration (third order) is adjusted to about 0.3 μm. Below the sample stage, there are five detectors designed for nano-diffraction and for simultaneous acquisition of transmission imaging including ADF imaging and EELS (and spectroscopy imaging). Above the sample, there is a positively biased Hitachi detector to collect low-energy electrons generated at the surface of the specimen for ultra-high-resolution SEM imaging. It is a highly efficient detector with a high amplifier gain and low noise, consisting of a Faraday cage, a scintillator, light tubes and a photomultiplier. The CEOS probe corrector, located between the condenser lens and the objective lens, has two hexapoles and five electromagnetic round lenses, seven dipoles for alignment and one quadrupole and one hexapole for astigmatism correction. In a spherical-aberration-corrected electron microscope, the probe size d (measured in FWHM) as a function of the beam convergence half-angle α is an incoherent sum of contributions from the source size, diffraction limit and chromatic aberration and is given by:

\[ d = \left(1/2 \left( \lambda/\alpha \right)^2 + (0.635/\alpha)^2 + (C_1 \alpha/\Delta E)^2 \right)^{1/2}, \]

where \( \eta \) is the probe current, \( \beta \) is the source brightness, \( \lambda \) is the electron wavelength at beam energy \( E \), \( \Delta E \) is the energy spread and \( C_1 \) is the chromatic aberration constant of the probe-forming lens. The calculated minimum probe size for the instrument is 0.075 nm (C1 = 1.5 mm), whereas the experimentally obtained value using single uranium atoms is 0.08 nm.

The samples. The uranium sample is typical of negative staining used in biological studies except that the uranyl acetate is 100 times more dilute. Tobacco mosaic virus was included to give a thickness gradient with a higher concentration of uranium atoms near the tobacco mosaic virus, sometimes forming small clumps. UO2, clumps (cubic crystals with a 0.34 nm spacing) and individual uranium atoms are located on a thin (2 nm) carbon film. The high contrast of uranium relative to carbon and its characteristic energy loss (24 eV at 100 eV) in atomic EELS allow us to identify single uranium atoms as test objects for SEM. The samples are particularly useful for measuring the probe size from typical individual atom images, wherein the single atom’s electrostatic potential can be considered as a delta function, eliminating the drawbacks of a crystal sample. The sample support images, wherein the single atom’s electrostatic potential can be considered as a delta function, eliminating the drawbacks of a crystal sample. The sample support images in a scanning transmission electron microscope.

Image analysis. In the combined SEM and STEM imaging mode, the SEM images were used to identify whether the individual atoms we see in the STEM images are on the top or at the bottom of the carbon support because a 2 nm carbon film blocks considerably the emission of secondary electrons from the sample surface. In our studies, no detectable etching or contamination of the carbon was observed. Quantitative intensity measurements were carried out with custom software (PCMass30, available from ftp.stem.bnl.gov) routinely used for mass measurement of unstained biological molecules. Atoms were selected in the ADF image by an automatic algorithm that fits isolated bright spots to a Gaussian profile with variable amplitude and width. The spots were summed using (x, y) coordinates determined from the ADF image. The FWHM corresponds to 0.08 nm for the ADF profile (0.025 nm pixel spacing). The SEM curve is noisier, with a FWHM < 0.1 nm.

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References


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Author contributions

Y.Z. initiated and coordinated the project and wrote the letter with J.W. H.I. and K.N. were involved in instrument development, H.I. carried out the experiment and collected the data, J.W. and Y.Z. analysed and interpreted the data.

Additional information

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