Atomic-Resolution Imaging and Analysis with C_s-Corrected Scanning Transmission Electron Microscopy

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Advances in nanotechnology and electronic device miniaturization are making atomic-level control of structure and composition increasingly important. To promote research and development in this field, it is essential to develop technology for measuring the structures, compositions, and properties of materials and devices with atomic resolution. Scanning transmission electron microscopy (STEM), which is a high-spatial-resolution imaging technique, combined with analytical equipment has been used in various fields such as research and development. However, conventional STEM equipment suffers from probe size limitations and a drop in electron-beam current due to the effects of spherical aberration (C_s) in the magnetic lens. Recently, though, C_s-correction technology has been developed, and the C_s corrector has been mounted on commercial STEM equipment. This technology is proving to be exceptionally effective in enabling imaging and analysis at even higher resolutions. In this paper, we describe the principles for increasing resolution by applying C_s-correction technology and present examples of atomic-resolution STEM measurements.

1. Introduction

Advances in nanotechnology and the increasing miniaturization of electronic devices are making it essential to control structures and compositions at the atomic level. To facilitate research and development in this field, technology for measuring the structures, compositions, and properties of materials and devices at this level must be developed. Transmission electron microscopy (TEM) is an imaging technique having high spatial resolution, and when combined with analysis equipment, it can provide a powerful technique available for direct atomic-level observation for target materials and devices. This technique is therefore taking on increasing importance in a variety of fields including research & development and quality control of devices. One particular form of it, scanning transmission electron microscopy (STEM), is now attracting attention as a method of achieving high-spatial-resolution imaging and analysis. In particular, annular dark field STEM (ADF-STEM), which makes use of an annular detector, can provide an image intensity that is dependent on atomic number (Z) by utilizing thermal diffuse scattering (TDS) electrons in the sample. Thus, such techniques are commonly called high-angle annular dark field STEM (HAADF-STEM) or Z-contrast techniques.[1] STEM can also be combined with electron energy loss spectroscopy (EELS) by passing the transmitted electron beam through a hole in the STEM's annular detector, thereby enabling EELS analysis and HAADF-STEM image acquisition at the same time. This method, called STEM-EELS, is a powerful tool for analyzing and evaluating atomic and electronic structures. The principle behind STEM-EELS is shown in **Figure 1**.

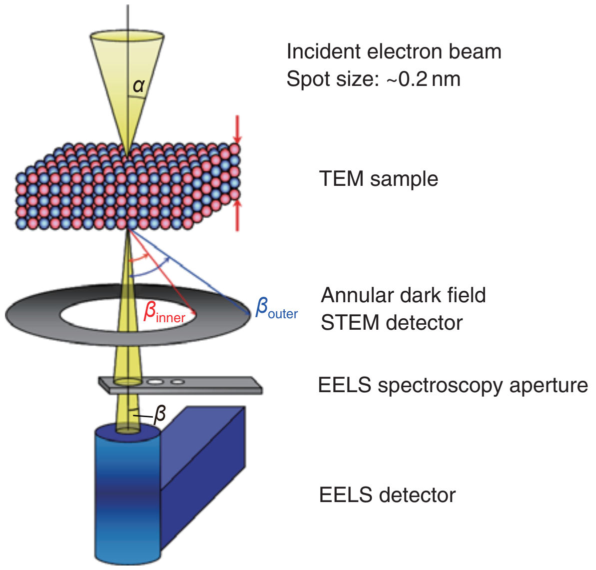


Figure 1
Principle of STEM-EELS.

A long standing issue for TEM is performance limitations on probe size and electron-beam current density due to the effects of spherical aberration (C_s) in the magnetic-field-type electromagnetic lens. Recently, however, C_s-correction technology has been developed and it has become possible to mount it in commercial STEM equipment. This combination is demonstrating atomic-resolution imaging and analysis. At Fujitsu Laboratories, we are using C_s-corrected STEM equipment to develop cutting-edge evaluation techniques at the atomic level with the aim of contributing to the development of novel materials and devices.

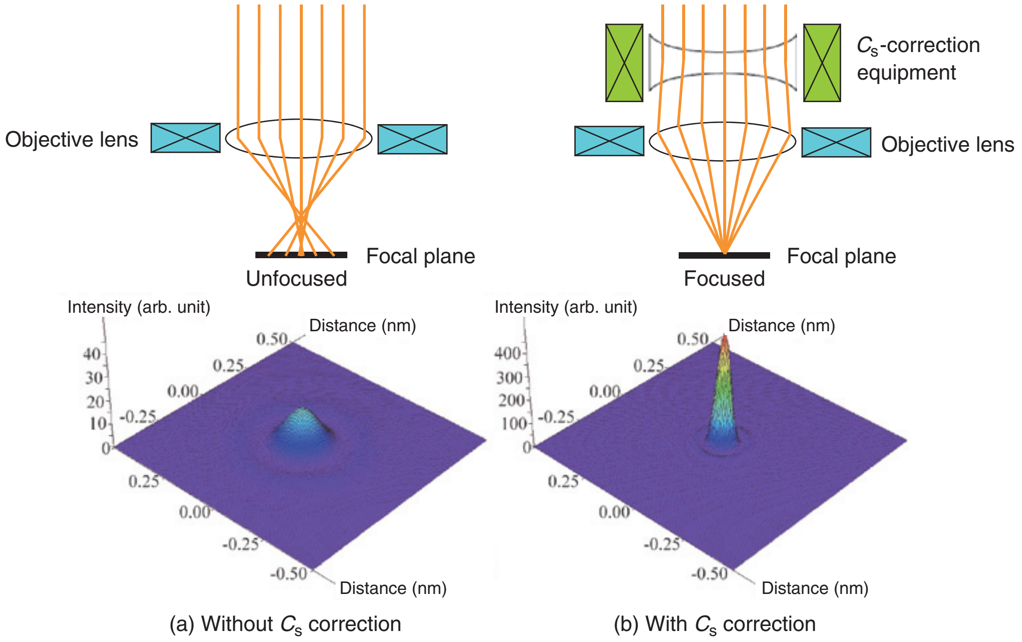
This paper begins by describing how resolution is increased through C_s-correction technology. It then presents an example of atomic-resolution Z-contrast evaluation by HAADF-STEM and an example of new materials evaluation by STEM-EELS.

2. C_s correction in magnetic-field-type electromagnetic lens

Spherical aberration in an objective lens has the following effect (here, we discuss optics for simplicity, but the same is true for electron beams and electromagnetic lenses): When light rays parallel to the optical axis of an objective lens pass through the lens, the focal position of rays from the edge of the lens shifts toward the lens compared with the focal position of rays near the axis. Thus, the focal points do not all coincide. The reduction in spatial resolution caused by spherical aberration and the effect of C_s correction are illustrated in **Figure 2**. As shown in Figure 2 (a), a point image affected by spherical aberration has worse point resolution because the electron beam probe spreads out at the focal plane and flares out around the image as a result of paraxial light. Spherical aberration can be reduced or cancelled out by combining a convex lens and a concave lens. In the case of a magnetic-field type of electromagnetic lens, however, spherical aberration in a cylindrically symmetric magnetic-field lens is always positive according to Sherzer's theorem, so C_s correction is limited if only a cylindrically symmetric magnetic-field lens is used.[2)]

C_s-correction theory and technology targeting magnetic-field-type electromagnetic lenses has been researched since the 1940s, and in recent years, the utility of hardware for this purpose has been demonstrated through the generation of negative spherical aberration using hexapole C_s-correction equipment (C_s corrector) developed by Haider et al. of CEOS.[3)] This C_s-correction equipment produces the same effect as the concave lens shown in Figure 2 (b). Specifically, it makes the electron beams located away from the optical axis diverge outward so that they also focus on the focal plane after passing through the system's objective (spherical) lens.

Below, we present the results for simulating the shape of the probe before and after applying C_s correction to a STEM objective lens. The calculation parameters were accelerating voltage of 200 kV, convergent semi-angle of 12 mrad before correction and 20 mrad after correction,



(a) Without C_s correction (b) With C_s correction

Figure 2
Reduction in spatial resolution caused by spherical aberration of objective lens and effect of C_s correction on probe-forming lens.

and a C_s coefficient of 1.0 mm before correction and 0.1 μm after correction. In theory, C_s correction in a STEM should produce spatial resolution about four times the electron-beam probe size before correction (0.05 nm instead of 0.2 nm) and an electron-beam probe current about ten times that before correction.

In this way, spherical aberration in a magnetic-field-type electromagnetic lens can be corrected and maximum performance for a transmission electron microscope is achieved. As a result, performance for the analysis of structure, composition, and physical properties on the atomic scale can be improved and evaluation time can also be shortened.

HAADF-STEM images of Si (011) and their power spectra obtained by conventional STEM equipment and C_s-corrected STEM equipment are shown in **Figure 3**. In the HAADF-STEM images, bright contrast corresponds to the positions of silicon atoms: pairs of atoms in a dumbbell configuration can be distinguished owing to the characteristic arrangement of atoms in Si (011).

Without C_s correction, however, the effects of probe broadening result in the appearance of high-intensity spots even in sections where no silicon atoms exist. Many noise components are included as well, and the end result is an unclear image. With C_s-correction, it is easy to distinguish the regions where silicon atoms exist and those where they do not, and the increase in electron-beam current results in a picture with a high signal-to-noise ratio. In addition, the spots representing silicon atoms are much smaller than in the case without C_s correction, indicating that the adverse effect of probe broadening has been reduced.

The power spectra obtained by Fourier transformation of the HAADF-STEM images reveal that spatial resolution has been improved from 0.14 nm without C_s correction to 0.085 nm with C_s correction, indicating that the information limit has been raised.

In the above way, the appearance of C_s-correction equipment has improved spatial

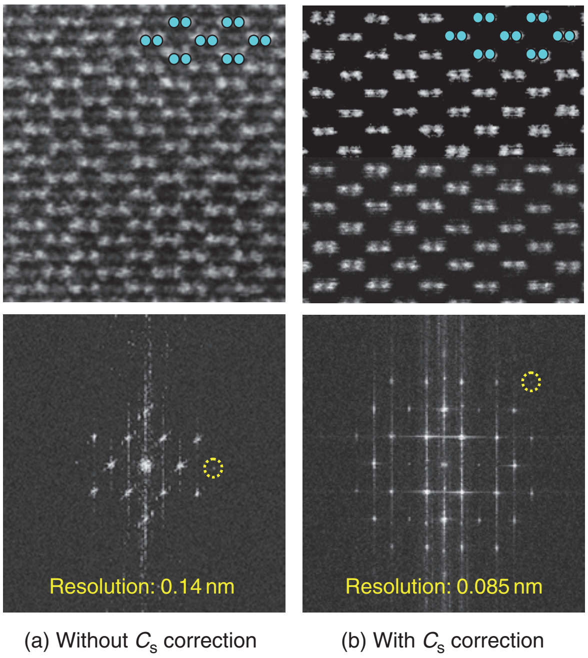


Figure 3
Atomic-resolution HAADF-STEM images of Si (011).

resolution dramatically and the increase in probe current has enabled high-sensitivity STEM imaging and analysis. These developments represent a dramatic leap toward atomic-resolution evaluation of materials and devices.

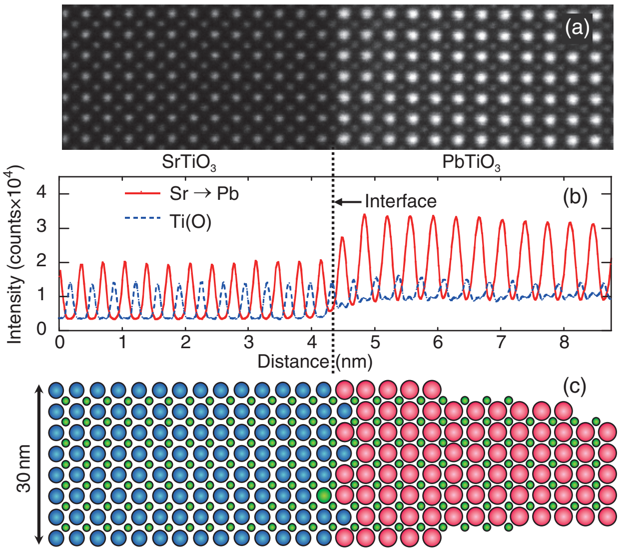
3. Evaluation of ferroelectric thin films by HAADF-STEM

Ferroelectric thin films are expected to be applicable to nonvolatile memory, piezoelectric generators, and other devices, so it is important to make them thin to reduce the size and increase the integration density of such devices.[4] However, when their thickness is reduced to the nanometer level, the structure of the interface between a ferroelectric film and a substrate or electrode material on which the film is to be formed can significantly affect the ferroelectric characteristics. For this reason, we formed $PbTiO_3$ on a $SrTiO_3$ (001) substrate by metalorganic chemical vapor deposition and, through the use of C_s-corrected HAADF-STEM images, evaluated the structure of that interface on the atomic level by the Z-contrast technique using the difference in atomic number between $SrTiO_3$ and $PbTiO_3$.

The results of atomic-resolution HAADF-STEM imaging of the $PbTiO_3/SrTiO_3$ interface section for a 20-layer $PbTiO_3$ film are shown in **Figure 4**. The HAADF-STEM imaging conditions were accelerating voltage of 200 kV, convergent semi-angle of 20 mrad, annular-dark-field-detector angle of 70–185 mrad, and sample thickness of 30 nm. In the image in Figure 4 (a), the atomic column intensity decreases with decreasing atomic number in the order Pb (Z=82), Sr (Z=38), and Ti (Z=22). In HAADF-STEM images, image intensity is dependent on the strength of TDS and atomic number, so if the atomic-number difference with neighboring atoms is large, a light element like oxygen will be difficult to distinguish, as is the case for the image presented here. If the atomic-number difference is relatively large, interpretation of Z-contrast is intuitive, but if atomic numbers are too far apart, it may be difficult to distinguish between the two elements in question, although this also depends on the inter-atom interval. In basic experiments, carbon nanotubes and diamonds have been observed as light elements, and in terms of atomic-number difference, it has been reported that the atomic-intensity difference between Ga (Z=31) and As (Z=33) in gallium arsenide could be observed.[5), 6)]

In the atomic arrangement at the $PbTiO_3/SrTiO_3$ interface, the lattice constants are relatively similar, so there is no periodic offset in the A [Sr, Pb] and B [Ti (O)] sites in the perovskite structure and it is compatible with epitaxial growth.

An atomic-column intensity profile taken in the (001) direction is shown in Figure 4 (b). It can be seen that the atomic intensity of the first $PbTiO_3$ layer from the $PbTiO_3/SrTiO_3$ interface in the intensity profile along A sites is low relative to that of the second and subsequent layers. This indicates mixing with the $SrTiO_3$ substrate at the time of $PbTiO_3$ film formation: the amount



1st layer: 30.0 nm Pb65%+Sr35% or defects, 2nd to 4th layers: 30.0 nm, 6th to 13th layers: 28–26-nm pure PbTiO$_3$

Figure 4
Quantitative Z-contrast analysis of PbTiO$_3$/SrTiO$_3$ interface by HAADF-STEM. (a) HAADF-STEM image, (b) Atomic-column intensity profile, and (c) Model obtained by simulation.

of mixing calculated from atomic intensities gave the Pb and Sr concentrations in the first layer as 65% and 35%, respectively. From the second layer on, the atomic intensity decreased gradually. This reflects the fact that the sample thins out in a tapered manner toward the thin-film surface with TEM sample preparation. Simulations were performed by HAADF-STEM calculations based on the Bloch wave method.[7] A model of the PbTiO$_3$/SrTiO$_3$ structure obtained from these calculations is shown in Figure 4 (c). The atom sizes and lattice constants in this model are ten times actual values. The first layer from the interface has a mixture of Sr and Pb in the atomic column, which accounts for its low Z-contrast intensity relative to the second layer, and the drop in intensity toward the thin-film surface can be understood from the decrease in the number of atoms in that direction.

By comparing atomic intensities by using C_s-corrected HAADF-STEM images, we can understand atomic compositional ratios in materials or at interfaces at the atomic level. This technology is expected to lead to major innovations in the development of novel materials and devices.

4. Evaluation of gate insulation film by STEM-EELS

Gate oxide thin film plays an important role in the performance of silicon integrated devices. It can affect various characteristics including device operating speed, power saving, and reliability. In silicon devices, the reduction in feature scale is accelerating and the thickness of gate oxide thin film has already broken through the 1-nm level. There is therefore a need for a method that can evaluate gate oxide thin film at the atomic level. Gate oxide thin film consists of materials like SiO_2, Si_3N_4, and HfO_2, most of which are in an amorphous state. The HAADF-STEM method described above can perform atomic-resolution imaging of crystal structure, but since no crystalline materials are present in an amorphous state, it cannot observe atomic structures in such a state. It is therefore necessary to investigate a method based on an analytical approach rather than imaging. With this in mind, we attempted to evaluate the structure and state of electrons in ultrathin gate oxide thin film at high spatial resolution by the C_s-corrected STEM-EELS method. This method has mainly been used to analyze material valence number and other states by detecting core-loss electrons scattered and absorbed by the atom's inner shell. In such a case, a certain amount of electron-beam current is needed, which means that either the current must be increased or the sample must be subjected to electron-beam irradiation for a long time. The C_s-corrected STEM-EELS method features a dramatic increase in electron-beam current, which makes it advantageous for EELS analysis, but such high-current-density atomic-resolution STEM-EELS measurements can damage to the sample. To solve this problem, we are investigating electronic structure evaluation by detecting energy loss (low-loss electrons) originating in plasma oscillations caused by valence-electron excitation. This information can be obtained relatively quickly in comparison with core loss evaluation.

The results of low-loss spectrum-line analysis of poly-Si/SiO_2 (1 nm)/Si-substrate by C_s-corrected STEM-EELS are shown in **Figure 5**. STEM-EELS measurements were performed at a total of 50 points (spread over 5.86 nm) with the spatial resolution of one point being 0.12 nm. Total acquisition time was 1 ms.

These low-loss spectrum measurements revealed a peak near 17.4 eV for Si and another near 20 eV for SiO_2. The EELS spectra obtained from these atomic-spatial-resolution STEM-EELS measurements could be identified by various type of analysis equipment. The design value of the SiO_2 film thickness was about 1 nm and the value observed by high-resolution transmission electron microscopy (HRTEM) was similar. In this experiment, however, STEM-EELS analysis showed that the effective film thickness was 1.87 nm when the mixing of poly Si, Si substrate, and SiO_2 film was taken into account.

Since low-loss measurements enable EELS analysis at very high speeds, we next applied it to spectrum mapping, as shown in **Figure 6**. Measurement conditions were the same as for the abovementioned spectrum-line analysis and the measurement area was 50 pixels × 25 pixels (5.86 × 2.93 nm^2). Spectrum analysis could process the 1250 analysis points rapidly, so we prepared Si and SiO_2 low-loss spectra from first-principles calculations and used them for reference to perform multivariate analysis.[8] In the figure, the Si and SiO_2 distribution intensities can be understood as follows: regions with bright

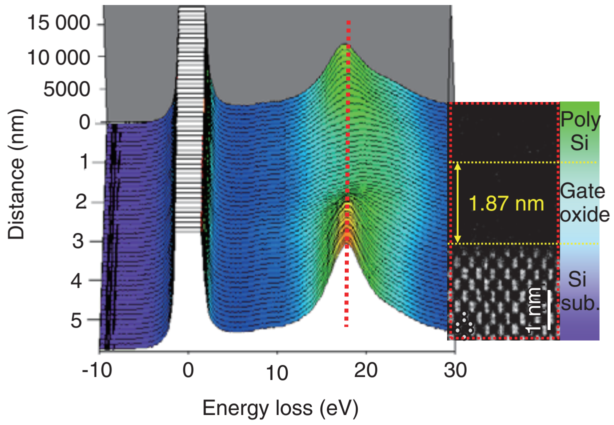
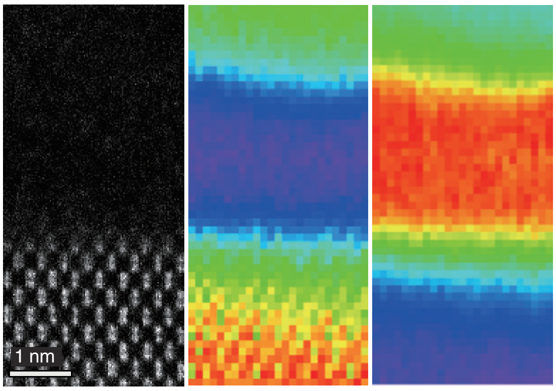


Figure 5
Low-loss spectrum of poly-Si/SiO_2 (1 nm)/Si-substrate by STEM-EELS.



(a) HAADF-STEM image (b) Si distribution (c) SiO_2 distribution

Figure 6
Low loss spectrum mapping of poly-Si/SiO_2(1 nm)/Si-substrate by STEM-EELS spectrum imaging.

contrast correspond to a high concentration while dark regions correspond to a low concentration.

The spectrum mapping results show that several layers of atoms on the surface of Si substrate were somewhat oxidized and that the interface on the poly-Si side was clearly rough. It has thus been shown that the effective thickness of gate oxide thin film can be measured with high spatial resolution by low-loss measurements using C_s-corrected STEM-EELS. Compared with this method, conventional core-loss measurements would require more than ten times the time per analysis point to perform measurements with good accuracy. C_s-corrected STEM-EELS is therefore expected to be a useful evaluation technique that speeds up measurements and avoids sample damage.

5. Conclusion

This paper described the principle of resolution improvement in TEM through technology for correcting spherical aberration in a magnetic-field-type electromagnetic lens and introduced techniques for evaluating materials and devices at the atomic level by C_s-corrected STEM.

TEM is expected to become increasingly important as an essential evaluation tool in the development of nanotechnology and advanced devices. To support this, we are promoting its C_s-correction technique and are working to achieve technical innovations in equipment, including STEM stabilization. Here, it is important not to simply use equipment in its present form but to understand the operating principles behind electron microscopes and analysis equipment and to extract maximum performance from them. It is also necessary to understand material properties and devices functions to support various types of evaluation. Although TEM is a superb technique for conducting evaluations, it does have many weak points. To meet complex and varied needs effectively, TEM should be combined with other analysis techniques to produce even more robust evaluation tools and drive the expansion of this field.

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