Ultra-high spatial resolution better than 0.5 Å has been achieved in aberration-corrected scanning transmission electron microscopy (STEM). By combining such an ultra-high resolution STEM with a differential phase contrast (DPC) imaging technique, we can now directly visualize the electric field distribution inside individual atoms in real space. The atomic electric field, i.e., the field between the nucleus of the atom and the electron cloud that surrounds it, contains information about the atomic species and charge redistribution due to chemical bonding. In this review, the current status of the development in atomic-resolution DPC STEM and its future direction is discussed.

Key-words : STEM, Electromagnetic field, DPC, Atomic resolution

1. Introduction

The spatial resolution of transmission electron microscopy (TEM) has dramatically been improved since the beginning of this century, mainly because of the spherical aberration correction technology for magnetic objective lens realized at the end of the 20th century. Since then, the spherical aberration of the objective lens has been effectively made correctable by hardware, and a spatial resolution better than 1 Å (1 Å = 0.1 nm) is commonly achieved on a daily basis. With the advent of such aberration correction technology, scanning-type TEM (scanning TEM: STEM) has become widely used in material and device research fields. In STEM, a narrowly focused electron beam is scanned on a sample, and electrons transmitted and/or scattered at each raster are detected with an annular or circular detector placed below the sample. The detected intensity is plotted on a monitor to form images. The spatial resolution is determined by the size of the electron probe. Now, as aberration correction technology has advanced, the electron probe has been narrowed to be 50 pm or less, and as narrow as 40.5 pm. In other words, the spatial resolution of aberration-corrected STEM has become smaller than the size of the hydrogen Bohr radius (≈53 pm).

On the other hand, in the history of STEM development, many studies have been devoted to how to detect transmitted/scattered electrons by detectors to form an image. Among them, the detection method currently used in the mainstream analysis is the method of selectively detecting high-angle scattered electrons by a donut-shaped detector called the annular dark field (ADF) imaging method. This method has a useful feature in which the obtained images become an incoherent image. This feature enables us to directly and robustly observe atomic columns and single atoms in materials and devices, and should extend the application of STEM to various research fields requiring direct observation of atomic structures. On the other hand, there should also be many other possibilities to use other detection methods to form STEM images. Now that aberration correction technology has matured, there is the possibility of acquiring new information on the atomic scale by reconsidering the signal detection method in STEM.

Our research group has developed a segmented detector for STEM that can undergo atomic-resolution observation. Recently, using this segmented detector, we have focused on the development of the differential phase contrast method (DPC) which can directly observe electromagnetic fields inside materials with high spatial resolution. This method greatly expands the current atomic-resolution STEM and should be expected to provide extremely useful information in the research field of materials and devices. In this review, we introduce the outline of the DPC STEM method, demonstrate its development for atomic-resolution observation, and discuss its future prospects.

2. Principles of DPC STEM imaging method

A schematic diagram of STEM is shown in Fig. 1(a). In general STEM, in addition to the above-mentioned...
ADF imaging, bright-field (BF) imaging\(^8\) using a circular detector, and the annular bright-field (ABF) method\(^9\), which allows direct observation of light elemental atoms, have been used. These images can be acquired simultaneously by introducing multiple annular/circular detectors. Figure 1(b) shows a schematic diagram of DPC STEM. In DPC STEM, the optical system for forming the electron probe is the same as that in normal STEM; however, the difference is that segmented detectors or pixel-type detectors need to be introduced into the electron detection system. In the present review, we explain DPC STEM using the segmented detector case. A detailed explanation of DPC STEM using pixelated detectors is reported elsewhere.\(^10\) First, the optical axis is adjusted so that the BF disk is projected onto the segmented detector. Here, on the sample plane, the vacuum region without the sample or the area for which it can be assumed that the field variation is uniform should be selected. Then, the BF disk position is precisely adjusted such that each segment of the detector detects the same electron signal strength. If an electric field or magnetic field with a component perpendicular to the incident electron beam direction is present inside the sample, the incident electron beam is subjected to Coulomb or Lorentz forces, and deflected at an angle proportional to the magnitude of the electric/magnetic field. In the case of a TEM thin film sample, because the deflection angle is only a minute deflection angle of several $\mu$rad to several hundred $\mu$rad, it is extremely difficult to detect such small deflection using normal circular or annular detectors. On the other hand, if we use a segmented detector, a slight unbalance occurs in the signal strength detected in each detection segment when the incident electron beam is deflected by the electric field or magnetic field inside the sample. Thus, it will be possible to quantitatively estimate the electron deflection by calculating the difference in the signals detected by the opposing detector segments. By sequentially calculating the difference in the signals at each sample raster during beam scanning, the deflection amount and deflection direction of the electron beam can be mapped. This information can be used to display the projected electric/magnetic field vector inside the sample. This is the essential mechanism of DPC STEM imaging.

One advantage of DPC STEM is that the DPC image can be observed simultaneously with the ADF image. Therefore, simultaneous observation of both structural information (ADF image) and electric/magnetic field information (DPC image) can be performed in the same field of view. This feature can be used to directly correlate the local structure with its properties one-by-one in materials and devices, such as at interface regions.

It should be noted that the explanation here is based on the assumption that the spatial distribution of the electric field and magnetic field is sufficiently large with respect to the size of the electron probe. Using a more generalized expression, “averaged” electron-beam deflection caused by the electromagnetic field is quantitatively estimated by detecting the center of mass of the electron diffraction pattern on the detector plane.\(^10\)-\(^14\) When the size of the electron probe and the spatial variation of the electromagnetic field is comparable (especially when observing the atomic electric field described later), it is necessary to consider not only the simple shift in the BF disk but also the intensity distribution change inside the BF disk. In the case of quantitative evaluation of DPC images, the detec-
tion accuracy of the center of mass is improved as the number of detector segments is increased, and ultimately, it can be said that the pixelated detector should be optimal. The quantification of DPC imaging is discussed more in detail in Ref. 14).

3. Atomic-resolution DPC STEM

It has been well demonstrated that medium-resolution DPC STEM is useful in the characterization of electromagnetic field structures inside materials and devices.\(^{15)-17}\) If we use an atomically sharp electron probe to perform DPC STEM, it is possible to directly visualize the electric field distribution, even inside atoms.\(^{19}\) Here, we introduce the results of quantitative observation of the atomic electric field in SrTiO\(_3\) crystal using a segmented detector. Next, we make use of high-sensitivity and high-speed detection ability, which are the advantages that segmented detectors provide, to observe the electric field inside single atoms. Finally, we introduce an example of the visualization of the total charge density distribution at the atomic level based on atomic electric field imaging.

In the STEM optics, the wave function on the detector plane can be obtained by Fourier transform of the wave function of the sample exit surface. Thus, observing the electron diffraction pattern on the detector plane means measuring the probability density of the wave function of the incident electron in the momentum space affected by the electric/magnetic field inside the sample. If the spatial distribution of the electric field in the sample can be assumed to be sufficiently uniform relative to the electron probe diameter, the BF disk will simply shift on the detector plane, as discussed before. In such a case, it becomes possible to measure the beam deflection from the difference between the intensities of the detection segments arranged diagonally in the segmented detector. On the other hand, when trying to visualize the electric field inside an atom using an atomic-size probe (when the electric field distribution to be observed is comparable to the diameter of the probe used), the above approximation does not hold.

**Figure 2** shows the schematic illustration of the BF disk when the probe position is very close to the center of a single atom.\(^{19}\) In the vicinity of the atom, the electric field intensity changes drastically, resulting in a large change in the intensity distribution inside the BF disk. In such a situation, it is not possible to define a “deflection angle” in a simple sense. However, because the incident electron is attracted by the electric field from the atomic nucleus, the probability density of momentum transfer is biased to the right, and it appears that the electron is “deflected” on average. Under the phase object approximation, the electric field inside the sample and the center of mass of the electron intensity distribution on the detector plane can be quantitatively correlated.\(^{11}\) Thus, to measure the electric field distribution inside the atom quantitatively, it is necessary to measure the center of mass of the electron diffraction pattern on the detector plane at each probe position with high accuracy. Although pixelated detectors that can precisely detect a two-dimensional electron intensity distribution at each probe position should be optimal,\(^{10}\) the problem of detection speed still limits their application to atomic-resolution DPC STEM for material studies. Although it is difficult to accurately measure the center of mass of the electron diffraction pattern with the segmented detector, with the combination of a method to approximately determine the center of mass\(^{12}\) and a recently proposed filtering method that uses a phase contrast transfer function,\(^{20}\) quantitative atomic electric field observation has become possible using segmented detectors. Next, we introduce the results of direct observation of atomic electric field in SrTiO\(_3\) crystal using a segmented detector.

**Figure 3** shows an atomic-resolution DPC STEM image of SrTiO\(_3\) observed from the [001] direction.\(^{19}\) For this observation, a 300-kV aberration-corrected STEM (ARM-300 CF, JEOL Ltd.) with a spatial resolution of 40.5 pm\(^2\) and a 16 segmented detector\(^5\) were used. Figure 3(a) shows an ADF image and (b) an electric field
vector color map constructed from the DPC image. Both images were acquired simultaneously. The bright spots in (a) correspond to the positions of atomic columns, and the image contrasts are ordered by averaged atomic number along the columns (O columns have less scattering power and almost no contrast). In the image of (b), it is observed that the electric field points radially outwards from the center of the atomic columns at each atomic position. This indicates that the electric field inside atoms is generated radially in all directions from the positively charged nuclei. The image contrast decreases at the atomic center because the incident electron and atomic electric field are parallel to each other, and the incident electron beam becomes insensitive to such a parallel field. Furthermore, by performing a quantitative comparison between an experimental atomic electric field strength and simulation, it has been shown that the atomic electric field may be sensitive to the ionicity of atoms. In other words, the atomic electric field contains information on the positively charged nucleus and negatively charged electrons distributed around it. Next, the observation of a gold (Au) single atom was performed using atomic-resolution DPC STEM. In the observation of SrTiO$_3$ crystal, the atomic electric field was observed by projecting many atoms located on the atomic column. In this case, the visualization of the internal electric field of a single Au atom is attempted. Figures 4(a) and 4(b) show the simultaneously acquired ADF and electric field vector color map of Au atoms dispersed on an amorphous carbon thin film. In the ADF image, Au single atoms and clusters can be directly observed as bright spots; however, in the electric field vector map, the image contrast is complicatedly formed everywhere, not necessarily corresponding to the ADF image. This is because this observation is in projection; thus, even the electric field variation derived from the amorphous carbon thin film supporting the Au single atom is inevitably detected with high sensitivity. However, when the DPC image is magnified, where the presence of Au single atoms is confirmed by the ADF image, the same rotating color contrast is observed as seen in the case of SrTiO$_3$ atomic columns, as shown in Fig. 3. This result clearly shows that the atomic-resolution DPC STEM is sensitive enough to directly observe the electric field distribution, even within single atoms. The experimental intensity profile and the simulated one across an Au atom are compared in Fig. 5. Although the low-dose condition, background noise, and the movement of Au single atoms during beam scanning severely affected the quality of the profile, the experimentally obtained profile and simulated one are quantitatively in good agreement. Thus, atomic-
resolution DPC STEM is sensitive to quantitative visualization of the internal electric field distribution of a single atom.

Figure 6 shows the results of atomic-resolution DPC STEM observation of monoatomic layer graphene. For this observation, an acceleration voltage of 80 kV is used. Figures 6(a) and 6(b) show ADF images, 6(c) shows the electric field strength map, and 6(d) shows the electric field vector color map, respectively. The carbon (C) atom in graphene is a single atom along the observation direction, and it is an element whose atomic number is much smaller than that of the previously shown Au atoms. However, as apparent from this observation, it can be seen that the atomic electric field of C single atom can be observed with high sensitivity. Unlike the case of SrTiO3, observed with a 300-kV accelerating voltage, the radially rotating color contrast at the atomic position is not clearly observed. This is considered to be because of the probe size of the 80-kV accelerating voltage. Interestingly, the atomic electric fields of adjacent C atoms cancel by partially overlapping each other, and in particular, the atomic electric field strength map shows the local minimum value of the electric field strength at the middle point in the direction of bonding (indicated as B). Thus, it can be seen that a large anisotropy occurs in the electric field distribution at the atomic level, depending on the structure and bonding environment. Furthermore, the electric field map may also be viewed as a two-dimensional force field map for any charged particle. From the DPC observation results, by only considering the electrical interaction, positive ions and negative ions (assumed point charge of infinitely small size) can be predicted to adsorb at the H6 site and B site, respectively. This prediction roughly agrees with the stable adsorption site predicted from DFT calculation. Thus, atomic-resolution DPC STEM visualizes the information on the atomic-level force field distribution.

4. Towards real-space imaging of local charge density

The fact that the electric field distribution inside the atom can be quantitatively observed should mean that this image can be converted into the charge density distribution according to the Maxwell equation. That is to say, we may be able to directly image the charge density distribution inside the atom or in between the atoms in real space. Figure 7 shows the result of the observation of the charge density distribution by atomic-resolution DPC STEM with a GaN single crystal. Figure 7(a) shows the simultaneous ADF, 7(b) shows the electric field vector color map, and 7(c) shows the charge density map converted from 7(b). While only the Ga atom columns can be observed in the ADF, both the Ga and N atom columns are clearly imaged in the electric field map. In the charge density map, the positive charge is concentrated at the center of each atomic column position (Ga and N), which should correspond to the positively charged atomic nucleus. In addition to such positive charge contrast, a negative charge contrast surrounding the positive charge at the Ga atom center is

**Fig. 6.** Atomic resolution DPC STEM observation of monoatomic layer graphene. (a), (b) show ADF images, (c) shows the electric field strength map, and (d) shows the electric field vector color map, respectively. Adopted from Ref. 21) with permission.

**Fig. 7.** GaN unit-repeated-averaged images of (a) ADF, (b) projected electric field, and (c) projected total charge density map calculated from (b). Adopted from Ref. 22) with permission.
observed. To clarify its presence, line profiles along the dotted line in Fig. 7(c) are shown in Fig. 8. For comparison, the result of simulating the charge density map is determined by multi-slice calculation (DPC calculation was initially performed including the dynamical effect and then the result was converted into the charge density map) and directly calculating the charge density from the potential model used for the image simulation. The experimental profile shows quantitative agreement with the multi-slice simulation and the direct charge density profile calculated from the potential. In particular, in both experimental and theoretical profiles, a negative charge contrast around the positive charge at the atomic center was observed. It has been shown by detailed model simulations that this negative charge is not an artifact due to dynamical electron scattering effects. It can be concluded that the negative charge contrast observed experimentally is the visualization of the electron cloud around the atomic nucleus in real space. Thus, the charge density distribution even inside atoms can be imaged by atomic-resolution STEM. By STEM, using normal annular or circular detectors, even if the probe diameter becomes much smaller than the size of atoms, only the presence or absence of atoms can be imaged because of the restrictions of the imaging principle. On the other hand, beyond the limit of normal STEM imaging, DPC STEM has the possibility of directly observing subatomic structure, such as the bonding electron distribution between atoms. However, spatial resolution, system noise, high-order aberration, and detector performance needs to be further improved to visualize intra- and inter-atomic charge density structure sensitively and precisely. In the future, it may be possible to directly map the charge density distribution in localized structures such as interfaces and surfaces, which should enable the fundamental understanding of material and device properties originating from nanostructures.

5. Conclusions and outlook

DPC STEM is considered to be a powerful material/device analysis technique because it enables the direct observation of local electromagnetic fields making use of high spatial resolution and the multi-analytical capabilities of STEM. By combining DPC with atomic-resolution STEM, the direct imaging of the atomic electric field that exists in between the positively charged nucleus and surrounding negatively charged electron cloud is realized. Thus, atomic-resolution DPC STEM should enable direct observation of internal and interatomic structure of atoms as a local electric field or charge density distribution. In other words, while atomic-resolution electron microscopy has focused on fine atomic structure observation for many years, atomic-resolution DPC STEM has the potential to observe a more microscopic world, i.e., the interior structure of atoms. In addition, atomic-resolution electron microscopy under a magnetic-field-free environment is finally achieved by the development of a novel objective lens system. Combining this new lens system with DPC, atomic-resolution magnetic field imaging may become possible in the near future. Thus, atomic-resolution DPC STEM has the potential to significantly evolve current atomic-resolution electron microscopy.

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