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10-kV diffractive imaging using newly developed electron diffraction microscope

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ABSTRACT

A new electron diffraction microscope based on a conventional scanning electron microscope (SEM), for obtaining atomic-level resolution images without causing serious damage to the specimen, has been developed. This microscope in the relatively low-voltage region makes it possible to observe specimens at suitable resolution and record diffraction patterns. Using the microscope we accomplished 10-kV diffractive imaging with the iterative phase retrieval and reconstructed the structure of a multi-wall carbon nanotube with its finest feature corresponding to 0.34-nm carbon wall spacing. These results demonstrate the possibility of seamless connection between observing specimens by SEM and obtaining their images at high resolution by diffractive imaging.

1. Introduction

Carbon nanomaterials and organic semiconductors are expected to be applied in various fields. Although their physical properties are closely linked to their atomic structures, their radiation-sensitive nature has been an obstacle to analyzing their structures. High-energy, i.e., high acceleration voltage (of more than 100 kV), electron microscopes are presently used to analyze the atomic structures of these materials. However, knock-on damage to specimens is a serious problem, especially for the light-element materials. Knock-on damage is a function of the acceleration voltage [1], and the threshold voltage of knock-on damage depends on the specimen used. The damage can be decreased using a beam with relatively low (or medium) voltage, i.e., several to a few tens of kilovolts. However, the scanning electron microscopes (SEMs) that are usually used in this range of acceleration voltage have insufficient resolution owing to lens aberrations. For the radiation-sensitive materials, a new high-resolution-imaging tool that does not cause damage to specimens is therefore urgently required [2,3].

Diffractive imaging with iterative phase retrieval [4,5] is one of the most promising methods of high-resolution imaging. With this method, the structure of an object (specimen) is reconstructed from diffraction intensities by retrieving phases via iteration procedures. It is possible to avoid lens aberrations because the diffraction pattern can be recorded in the far-field (without using an objective lens). In addition to the results obtained with X-ray beam [6–9], the results obtained with electron beam have recently been increasingly reported [10–14].

We are developing a method of diffractive imaging that causes little damage to the specimen, thanks to the use of a low-acceleration–voltage electron beam for analyzing atomic structures. Recently, we confirmed the validity of low-voltage electron-diffractive imaging using a prototype microscope with a fixed 20-kV acceleration voltage [12]. However, the microscope has only one simple illumination lens with low excitation, so the resolution is insufficient to observe a fine structure of the specimen (e.g., small carbon nanotube). Therefore, to execute the diffractive imaging, we previously selected the specimen using a transmission electron microscope (TEM) [12]. Moreover, fixed acceleration voltage prevents application of this imaging method to various materials at suitable acceleration voltage, which varies for each material. Considering these issues, the prototype is regarded not to be suitable for general use.

2. New electron diffraction microscope

The new diffraction microscope is based on conventional SEM (Hitachi High-Technologies Corp. S-5500) (see Fig. 1(a)). Its acceleration voltage can be varied from 0.5 to 30 kV and its illumination optics consists of a cold field emission gun, two condenser lenses, and an in-lens-type objective lens. It features a

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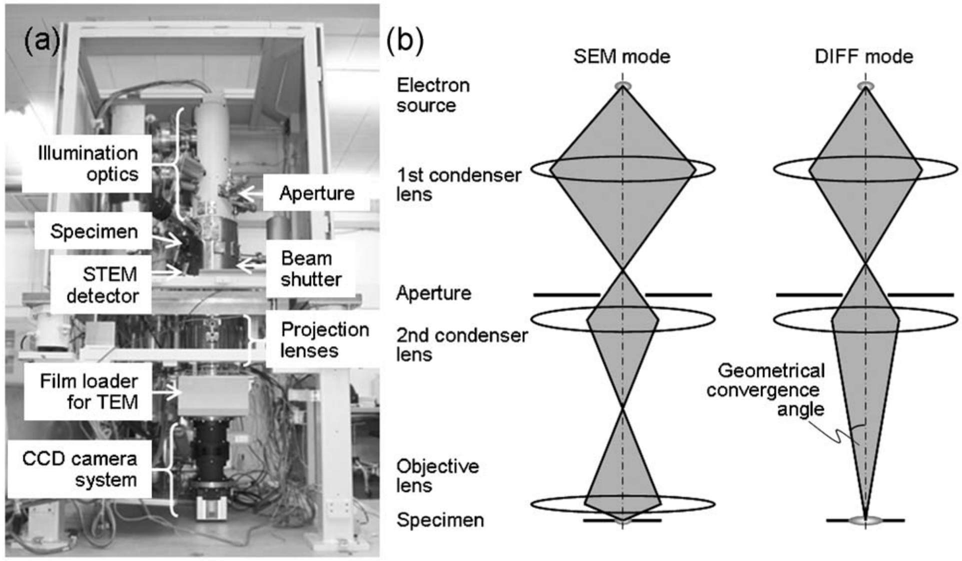

Fig. 1. (a) Electron-diffraction microscope based on in-lens-type conventional SEM. The optical column is installed inside the cabinet. To show construction inside the cabinet, the side panel has been removed. (b) Schematic of rays in SEM and DIFF modes (not to scale).

side-entry specimen holder and accommodates the specimen mesh for a transmission electron microscope.

Schematic ray diagrams of the illumination optics are illustrated in Fig. 1(b). The illumination optics for obtaining the SEM image and for recording the diffraction pattern is interchangeable. An in-lens-type objective lens is used in the SEM mode to focus the illumination beam onto the specimen. As a result, imaging resolution of the SEM observation is 0.4 nm at 30 kV, which makes it possible to observe the specimen and select the position for detailed analysis with high accuracy. In the diffraction pattern observation (DIFF mode), the objective lens was not applied, and the illumination beam was focused on the specimen with the second condenser lens. The convergence angle of the illumination beam was controlled by the aperture. Selecting the appropriate size of the aperture made it possible to obtain a geometrical convergence angle from 0.015 to 0.3 mrad.

To record the diffraction pattern on the imaging plate (IP), a film-loader system for TEM is installed in the new microscope. And a beam shutter to control the exposure time is installed below the specimen. With these arrangements, the diffraction pattern could be recorded in the far-field with a camera length of 570 ($\pm$10) mm. Fig. 2 shows an example of almost the full area (3760 $\times$ 3000 pixels) of a diffraction pattern of a multi-wall carbon nanotube (MWCNT) recorded on the IP (Fujifilm FDL-UR-V) at 30 kV. The exposure time was 30 s. A diffraction semi-angle of around 60 mrad (structural detail finer than 0.12 nm at 30 kV) was recorded. To control the recorded size of the diffraction pattern on the IP, two projection lenses are installed as an additional function of this microscope. To demagnify the size of diffraction pattern, the projection lens slightly converges the diffraction beam. In this case, the image of the specimen is projected on the plane far below the detector. If the image of the specimen is projected on the plane just below the projection lens, an enlarged diffraction pattern is recorded on the IP. In both cases, recorded diffraction pattern is not a pattern that formed on the back focal plane of the lens. Because the projection lenses cause aberration (mainly distortion), a suitable excitation current for the projection lens should be selected taking into consideration an acceleration voltage that would not damage the specimen and would obtain the required resolution for the reconstructed object image. A CCD camera is also installed below the film loader system to monitor the diffraction pattern.

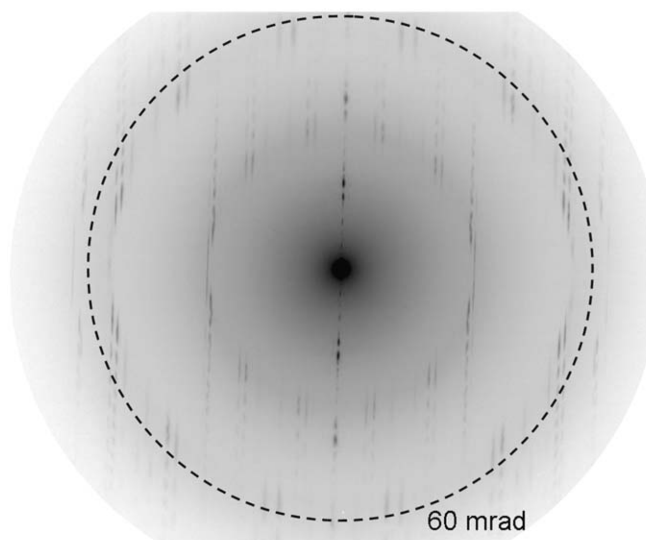

Fig. 2. Diffraction pattern of MWCNT at 30 kV obtained in the far-field.

3. Results and discussion

To demonstrate the lower-voltage diffractive imaging that is possible with this microscope, we reconstructed the image of an MWCNT. In this experiment, we used the MWCNT grown by arc discharge. An individual CNT was selected in SEM mode, and to record the diffraction pattern, the optics of the illumination beam was then changed. Fig. 3(a) shows a SEM image of the MWCNT observed at 30 kV. Fig. 3(b) shows the recorded diffraction pattern of the MWCNT (with 2048 $\times$ 2048 pixels) obtained by using the projection lens (with a camera length of 453 ($\pm$10) mm) at an acceleration voltage of 10 kV. The exposure time was 30 s, and the geometrical convergence angle of the illumination beam was 0.15 mrad. A calculation of the aberration of the condenser lenses

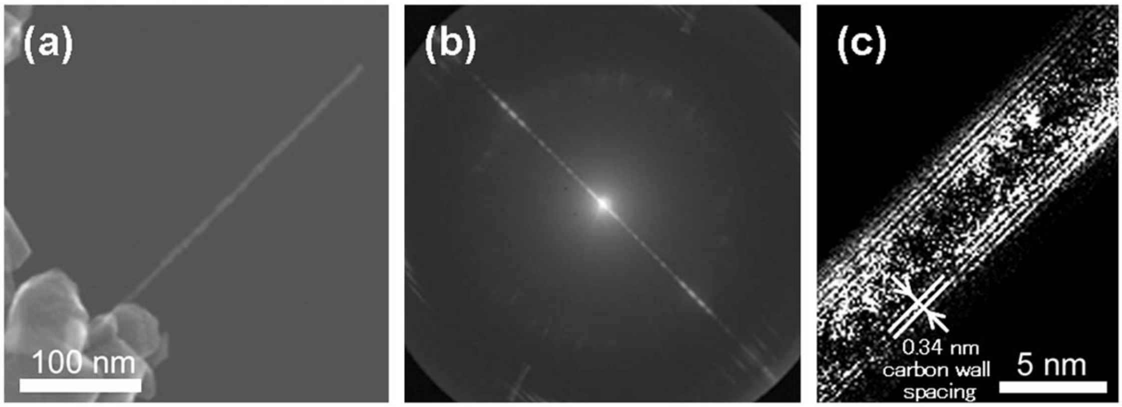

Fig. 3. (a) SEM image of MWCNT at 30 kV. (b) Diffraction pattern of multi-wall carbon nanotube at 10 kV. (c) Reconstructed pattern (amplitude map) from 10-kV diffraction pattern (b).

by Munro's Electron Beam Software Ltd. (MEBS) program [15] showed that at this convergence angle, diffraction aberration is dominant over beam size on the specimen. In this case, the beam size was estimated to be about 100 nm. To record the diffraction pattern at 10 kV, we used a BAS-TR IP (Fujifilm) for a tritium measurement, because of a sudden decrease in the sensitivity, which occurs in a conventional IP (Fujifilm FDL-UR-V) for an electron microscope with an acceleration voltage below 20 kV. We intend to report an evaluation of the sensitivity of the IP for low-voltage electron beams in another paper.

The iteration procedure for reconstruction of the specimen structure was carried out using the diffraction pattern shown in Fig. 3(b). The central 52×51-pixel area of this diffraction pattern was not used in the iteration procedure owing to the intense saturation of the central beam [12]. To compensate for this omitted information, the amplitude calculated by the iteration procedure was used. A combination of 500 repetitions of the hybrid input–output (HIO) algorithm (β=0.9) and 500 repetitions of the error reduction (ER) algorithm were applied in the iteration procedure [5]. The rectangular shape of the 2048×59-pixel area was used as a real-space constraint (i.e., support). To set the support size, CNT width was estimated from the SEM image. Fig. 3(c) shows the result of iterative phase retrieval using an area of 170×130 pixels, which has a pixel size of 0.11 nm. The characteristic features of an MWCNT, as we have previously reported [12], with inner and outer diameters of 2.5 ($\pm$0.1) and 4.5 ($\pm$0.1) nm were reconstructed. The finest feature corresponding to 0.34-nm carbon wall spacing [16] can be clearly distinguished. In consideration of an electron-beam wavelength λ of 0.0122 nm at this acceleration voltage of 10 kV, it is noteworthy that a resolution less than 30λ is comparable with the values obtained by using state-of-the-art electron-beam diffractive imaging [14] or aberration correctors [17–19].

The reconstructed pattern (Fig. 3(c)) contains some noise. This might be caused by the background noise in the diffraction pattern. We also executed the iteration procedures using 20 different initial conditions. Although the obtained images were slightly different from each other, the characteristic structures such as inner and outer diameters of MWCNT were clearly observed. We prepare another paper related to the noise and the ambiguity of images obtained by different runs.

Lateral coherence length of the illumination beam was estimated to be about 41 nm from the convergence angle [20]. Since the diameter of the MWCNT was much less than this coherence length, the inner and outer diameters of the MWCNT, as well as the 0.34-nm carbon-wall spacing, could be reconstructed. However, the MWCNT is longer than this value; therefore, the reconstructed pattern along the tube axis might indicate an averaged structure along that axis, which was almost uniform in this direction (since an arc discharged MWCNT was used).

Although the observation of radiation-sensitive materials at relatively low acceleration voltage decreases knock-on damage, the damage accompanied by the inelastic scattering becomes significant at lower acceleration voltage. Moreover, there are some issues concerning low-acceleration–voltage observation, namely, decreasing brightness and sensitivity of the electron source and detector, respectively. However, in addition to the suppression of the knock-on damage, longer coherence length (due to longer wavelength at the same convergence angle) than that at higher acceleration voltage is an advantage with regard to analysis of nanoparticles [12]. Even in the low-voltage range, an appropriate acceleration voltage must be selected according to the material in question.

The microscope newly developed has a preset function to adjust the difference between the field of view of the SEM and DIFF modes. In addition to this function, to accomplish seamless connection between SEM observation and diffractive imaging, a linked focus adjustment between two modes will be developed further.

4. Conclusions

The possibility of diffractive imaging at lower voltage by using our new electron-diffraction microscope based on a conventional SEM was verified. The microscope was used to observe specimens at suitable resolution in the relatively low-acceleration–voltage region and to record diffraction pattern. It attained 10-kV diffractive imaging with the finest feature corresponding to 0.34-nm carbon wall spacing. This 10-kV imaging indicates the possibilities of atomic-scale analysis at lower voltage, which is sufficiently below the carbon threshold, namely, about 27 kV, which is much lower than that of crystalline graphite, i.e., 54 kV [1]. This diffractive-imaging method will be a key to damage-free analysis of non-crystalline carbon nanomaterials.

This study demonstrates the possibility of seamless connection between SEM images and high-resolution images reconstructed by diffractive imaging. Moreover, our SEM-based electron diffraction microscope is compact and inexpensive, so it is suitable for application in various fields of the research and development.

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