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Low voltage electron diffractive imaging of atomic structure in single-wall carbon nanotubes

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The demand for atomic-scale analysis without serious damage to the specimen has been increasing due to the spread of applications with light-element three-dimensional (3D) materials. Low voltage electron diffractive imaging has the potential possibility to clarify the atomic-scale structure of 3D materials without causing serious damage to specimens. We demonstrate low-voltage (30 kV) electron diffractive imaging of single-wall carbon nanotube at a resolution of 0.12 nm. In the reconstructed pattern, the intensity difference between single carbon atom and two overlapping atoms can be clearly distinguished. The present method can generally be applied to other materials including biologically important ones. © 2011 American Institute of Physics.

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Application of light element materials is rapidly increasing due to the growing demand for energy devices (e.g., lithium ion batteries and fuel cells) and postsilicon electronics (made of, for instance, carbon nanotubes, and graphenes). The importance of atomic-scale observation using low-voltage electron beams for imaging the radiation-sensitive materials has also been increasing because the physical properties of the materials are closely linked to their atomic structures. Although, electron microscopes with spherical aberration correctors are widely used in the atomic scale analysis,^{1,2} to apply them at low-voltage, especially below few tens of kilovolts, it is required to correct some additional aberrations such as chromatic and higher-order aberrations.^{3,4} Moreover, even if an aberration corrector is used, the increasing of numerical aperture of imaging (or probe forming) lens decreases the depth of focus, which makes three-dimensional (3D) structure observation difficult. Electron-diffractive imaging⁵⁻¹² with iterative phase retrieval (iteration procedures)¹³⁻¹⁵ has reconstructed atomic-level specimen structures and has a capability of imaging 3D structures. However, most of these reconstructions have been executed with high-voltage beams which cause serious knock-on damage.^{16,17}

To date, a suitable method for imaging 3D materials composed of light elements with atomic-level resolution and without causing serious damage to the specimen is not yet available. Here, we report low-voltage (at 30 kV) electron diffractive imaging by using a scanning electron microscope (SEM) based dedicated microscope,¹¹ and concomitant developed iteration procedures^{18,19} for determining the atomic structure without seriously damaging the specimen. A single-wall carbon nanotube (SWCNT),²⁰ which is a well-known radiation-sensitive material, has been selected as a represen-

tative specimen with 3D structure consisting of light elements.

Low voltage diffractive imaging was executed by using the dedicated microscope¹¹ based on a conventional SEM (S-5500, Hitachi High-Technologies Corp.) with a cold field emission gun. As with previous phase retrieval works on inline holography,^{17,21-24} high coherence of the source (namely, small size of the electron source) is essential in this method. As a specimen, SWCNTs synthesized by chemical vapor deposition (CVD) on the gold grid (#400) of a transmission electron microscope (TEM) were used. The diffraction pattern (with a convergence angle of 0.15 mrad) was recorded without using a post-specimen lens on an imaging

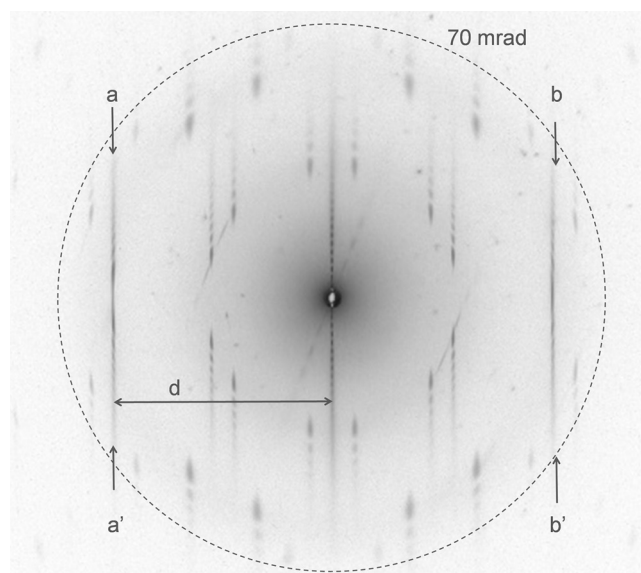


FIG. 1. Diffraction pattern of SWCNT at 30 kV. Exposure time is 30 s. Recorded diffraction angle is more than 70 mrad (semiangle), which corresponds to about 0.1 nm distance in real space. Derived chirality is (30,16).

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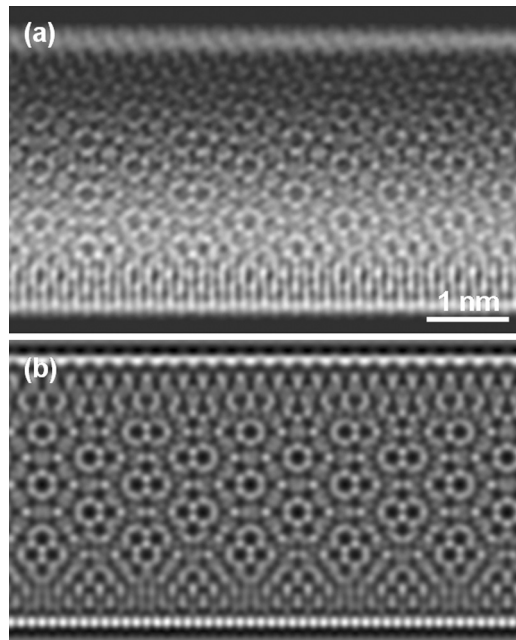


FIG. 2. Reconstructed image and calculated structure of SWCNT. (a) Reconstructed image of SWCNT from diffraction pattern. (b) Exit wave amplitude calculated at 30 kV by using the chirality obtained from diffraction pattern.

plate (IP: Fujifilm FDL-UR-V) mounted 446 mm below the specimen. The diffraction patterns at an acceleration voltage of 30 kV, shown in Fig. 1, clarify some significant features. The chirality is derived immediately as (30,16), in which the

diameter is 3.2 nm and the chiral angle is 20° .^{25,26} Inclination of the specimen against the incident beam is indicated from connected {11} layer lines as pointed by arrows, and the elongated distance of {11} layer line from the equatorial line (indicated as “d” in Fig. 1) represents $8 (\pm 2)$ degrees inclination from normal incidence. The intensities of aa' and bb' in Fig. 1 are asymmetric due to the inclination of the specimen and the curvature of the Ewald sphere.^{27,28}

Before the iteration procedure, the following image-processing steps were performed on the diffraction pattern: (1) noise reduction (subtraction of basal noise⁹ and deletion of scattering from another CNT), (2) background subtraction of axial-symmetric intensity distribution around the direct beam (fitted with a Gaussian function), and (3) recovery of saturated intensity by double reading of the IP. In addition to the image-processing steps, the diffraction pattern is symmetrized^{29,30} (on the basis of information in the right half of Fig. 1) to avoid the asymmetry of the diffraction pattern.

After the image-processing steps were performed on the diffraction pattern, the iterative algorithm was executed as follows. In each iteration procedure, a combination algorithm with 100 repetitions of hybrid-input-output and 1000 repetitions of error-reduction¹⁴ is executed ten times. As a constraint in real space, a real-positive condition is applied to the iteration because the atomic potential that interacts with incident electrons should be real and positive.⁶ Two developed procedures^{18,19} are used in the iterative algorithm. During the iteration, deconvolution algorithm¹⁸ is applied to correct the effect of the convergence angle of the illumination beam

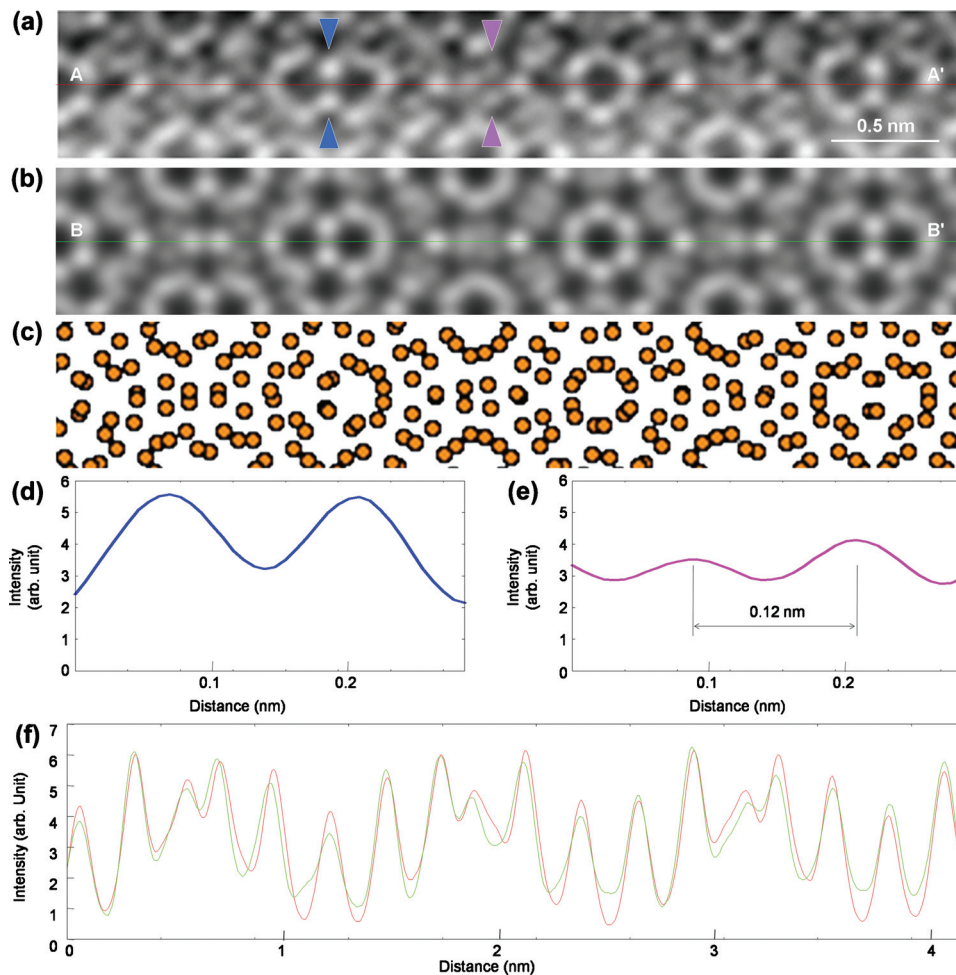


FIG. 3. (Color) Intensity analysis of the reconstructed image. (a) Magnification of central parts of Fig. 2(a). (b) Magnification of central parts of Fig. 2(b). (c) Atomic model of the same area. (d) Line profiles from overlapping atoms [indicated by blue arrowheads in (a)]. (e) Line profiles from isolated atoms [indicated by magenta arrowheads in (a)]. (f) Measured line profiles along red [AA' in (a)] and green [BB' in (b)] lines.

(i.e., improve coherence). The uniqueness problem (i.e., independence of the reconstruction from initial conditions), which is one of the most important issues, is solved by applying the averaging method¹⁹ based on the analysis of a solution set obtained by the iteration procedures. 100 Fourier amplitudes are obtained and averaged after 100 iteration runs under different initial conditions. The averaged Fourier amplitude replaces the observed diffraction intensity, and then the iteration procedure is repeated to recover the diffraction phase, and finally a reconstructed image is obtained. Reconstructed images with size of 1024-by-1024 pixels are processed by an image filtering to smooth out intensity steps between pixels.

The reconstructed image is shown in Fig. 2(a). As a reference, exit-wave amplitude, which represents the image without lens aberrations, at 30 kV is calculated (using MACTEMPASX software). In the exit-wave calculation, chirality and specimen inclination are considered. The calculated amplitude is shown in Fig. 2(b). The exit-wave calculations show that the CNT pattern is sensitive to the CNT inclination angle at both edges and insensitive at the central part. Since the error in estimation of inclination angle is about 2°, it is concluded that the exit-wave amplitude fits the reconstructed pattern well.

A comparison of the reconstructed image with the atomic model shows that the intensities of the bright dots reflect the number of contributing atoms. Figure 3 shows an example of the measured intensity. Figures 3(a) and 3(b) show the trimmed images of the central parts of Figs. 2(a) and 2(b), respectively, and the corresponding atomic model of the same area is shown in Fig. 3(c). The intensities of a single isolated atom (indicated by magenta arrowheads) and two atoms (overlapping layers; indicated by blue arrowheads) are clearly distinguishable. Figures 3(d) and 3(e) represent profiles of the overlapping atoms and the isolated atom, respectively. The difference between the peak heights in Figs. 3(d) and 3(e) is sufficient to distinguish the isolated atom from the overlapping ones. As indicated in Fig. 3(e), the single atoms can be fully resolved one by one at a resolution of 0.12 nm. The line profiles from both patterns along lines AA' and BB' are shown in Fig. 3(f). The profiles from the reconstructed image show a similar behavior to the exit-wave amplitude. It is noted that not only the difference between isolated and overlapping atoms but also intermediate intensities, which reflect the distance between the nearest-neighbor atoms, are represented in the line-profile.

In conclusion, at 30 kV, the atomic structure of a SWCNT is obtained at a resolution of 0.12 nm, which is only 18 times the wavelength of the electron beam. The intensity differences between a single carbon atom and two overlapping atoms can be clearly distinguished, which demonstrates the present method's potential for use in chemical identification.⁴ These results show that the low-voltage diffractive imaging has the capability to directly observe the electrostatic potential of materials at atomic resolution. This SEM-based diffractive imaging, which also has peculiar function of SEM (e.g., ultralow-voltage function of charge or

voltage contrast) and TEM (atomic-resolution imaging), will open a way to analyze nanomaterials used in postsilicon electronics and biomaterials.

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- ³⁰The reconstructed image from the diffraction pattern without symmetrization represents the same atomic structure as shown in Fig. 2(a). The intensity of the reconstructed image is, however, not accurate enough for distinguishing atomic numbers. This result indicates that, under the real-positive constraint, the asymmetry of the diffraction pattern somewhat deteriorates the accuracy of the reconstructed intensity.