Low-energy Electron Diffractive Imaging for Three-dimensional Light-element Materials

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OVERVIEW: Hitachi has been developing a diffractive imaging technique capable of high-resolution imaging without causing serious damage to the specimen in collaboration with Hokkaido University. The technique has growing applications in the fields of environmental engineering, sustainable energy, and life science. Using a low-energy (30-keV) electron beam, images of the atomic structure of SWCNTs with a resolution of 0.12 nm were successfully reconstructed by digitally processing diffraction patterns recorded with a new dedicated electron diffraction microscope (a scanning electron microscope with a diffraction recording function). Using this technique, the microscope can obtain high-resolution images of light-element materials with complex three-dimensional structures without specimen damage. The technique is suitable for use in material and device development in various fields.

INTRODUCTION

USE of electron microscopes for the development of materials and devices has occurred most commonly in the field of semiconductors, where they have frequently been used to identify the structure of dislocations in metals. Recently, demand for electron microscopy has also been increasing in the fields of environment engineering, sustainable energy, and life science. Light-element materials such as the carbon electrodes of lithium-ion batteries are important in these fields.

The need to make observations of different materials can be a driver of innovation in analysis technology. While observations with atomic-scale resolution are usually performed using transmission electron microscopes (TEMs) with high-energy electron beams, light-element materials tend to be

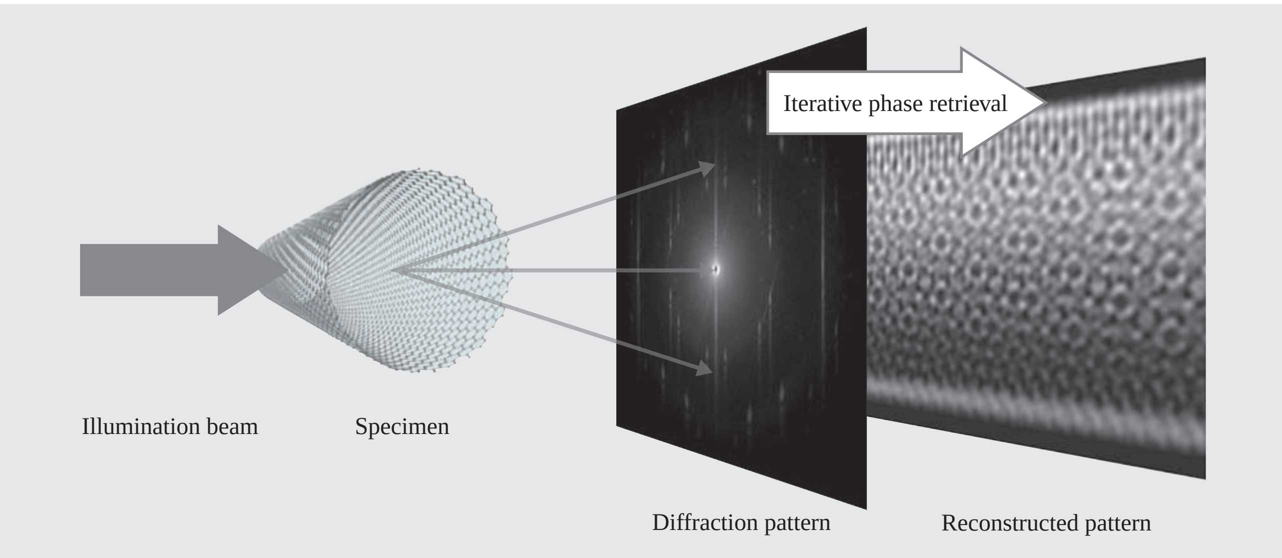


Fig. 1—Schematic Diagram of Diffractive Imaging.
The microscope illuminates the specimen with a parallel electron beam and records the resulting diffraction pattern. The structure of the specimen (reconstructed pattern) is then obtained by using iterative phase retrieval to retrieve the phase information lost when the diffraction pattern was recorded. The diffraction pattern and reconstructed pattern shown here are actual patterns obtained from observation of a single-wall carbon nanotube.

sensitive to radiation damage. The level of knock-on radiation damage caused by incident high-energy electrons pushing atoms in the specimen out of place is sufficiently severe that it is necessary to limit the observation time when using a conventional 200-keV TEM. Using an electron beam with lower energy is one solution to this problem of short observation time, but lens aberrations make it difficult to obtain atomic-scale resolution when using low-energy electron microscopy. Accordingly, the growing demand for analysis of light-element materials has created a need for an imaging technique capable of atomic-scale resolution that does not damage the specimen.

A new technique called diffractive imaging has been attracting interest as a potential solution to this problem. Diffractive imaging reconstructs an image of the specimen structure from its diffraction pattern. Unlike conventional electron microscopy, in which the resolution is restricted by lens aberrations, the resolution of diffractive imaging depends on the size of the diffraction pattern that can be acquired (the wider the diffraction angle, the higher the resolution). This means it is possible to obtain high-resolution images without being limited by lens aberrations. In addition, whereas conventional analysis of crystal structures assumes a periodic structure, this technique can also be used for imaging materials with a non-periodic structure. Hitachi has developed an analysis technique that combines a low-energy electron beam with diffractive imaging, and has tested its performance when used for imaging with atomic-scale resolution.

This article describes this diffractive imaging technique and how it can be used to make observations of light-element materials with complex structures, with a low level of damage to the specimen.

DIFFRACTIVE IMAGING

Fig. 1 shows a schematic diagram of diffractive imaging. The microscope illuminates the specimen with a parallel beam and captures the resulting diffraction pattern by locating a detector sufficiently far from the specimen. Digital processing is used to apply an iterative phase retrieval algorithm to the diffraction pattern to retrieve the phase information lost when the diffraction pattern was recorded. An image of the specimen's structure (reconstructed pattern) is obtained by combining the recorded diffraction pattern amplitudes with the calculated phase information.

Although this method was first suggested by D. Sayre in 1952(1), it was not successfully implemented in practice until 1999 (using X-rays)(2). This was made possible by advances in computer technology and the high intensity of third-generation synchrotron radiation. Since then, numerous examples of diffractive imaging using X-rays have been published, including the three-dimensional structures of nanoparticles(3),

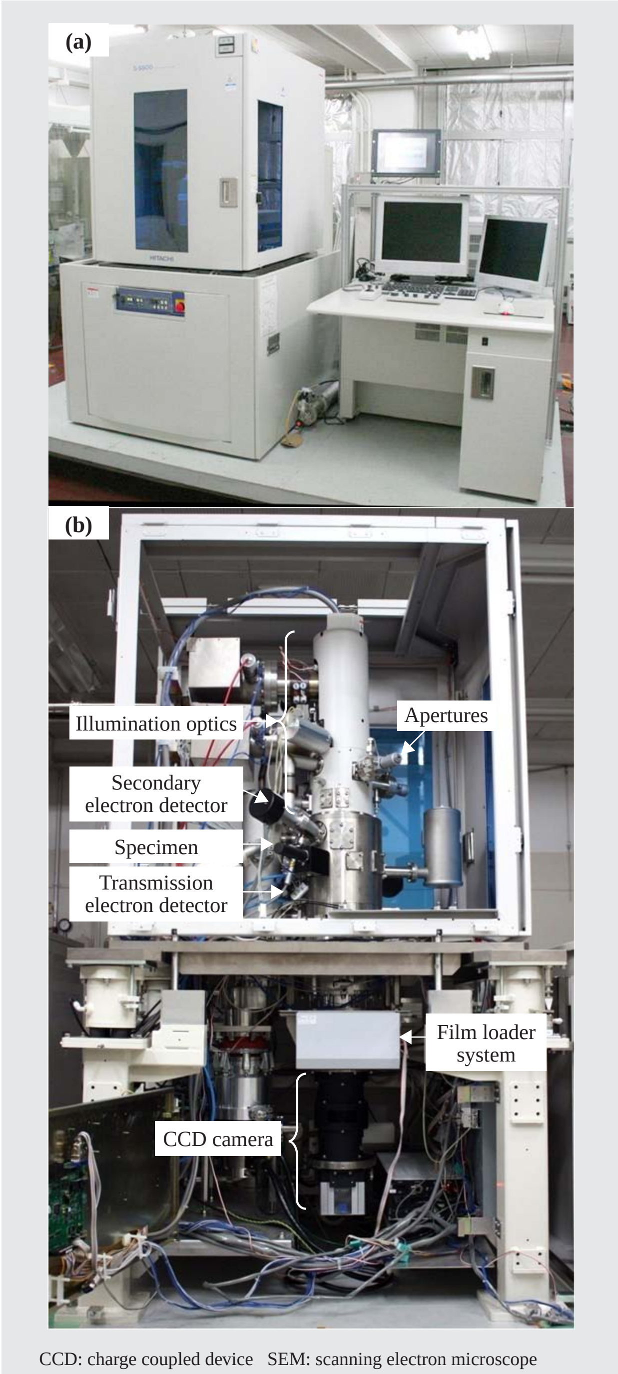
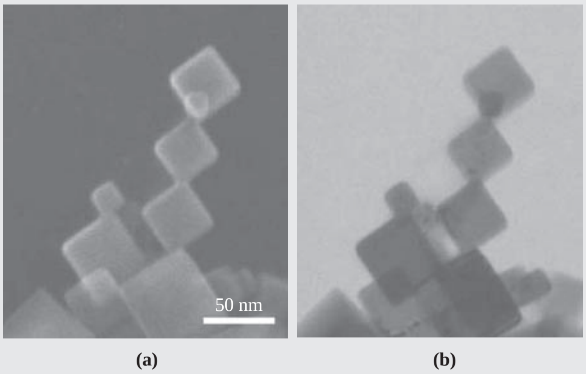


Fig. 2—Dedicated Electron Diffraction Microscope.
The photographs show the exterior (a) and interior (b) of the electron diffraction microscope. A conventional SEM was modified to record diffraction patterns by the addition of a film loader system under the SEM column (illumination optics).



STEM: scanning transmission electron microscope
BF-STEM: bright field scanning transmission electron microscope
MgO: magnesium oxide

Fig. 3—SEM Image (a) and BF-STEM Image (b) of MgO Nanoparticles.
Information about the surface morphology and inner structure of cubic nanoparticles was obtained from an SEM image and STEM image respectively.

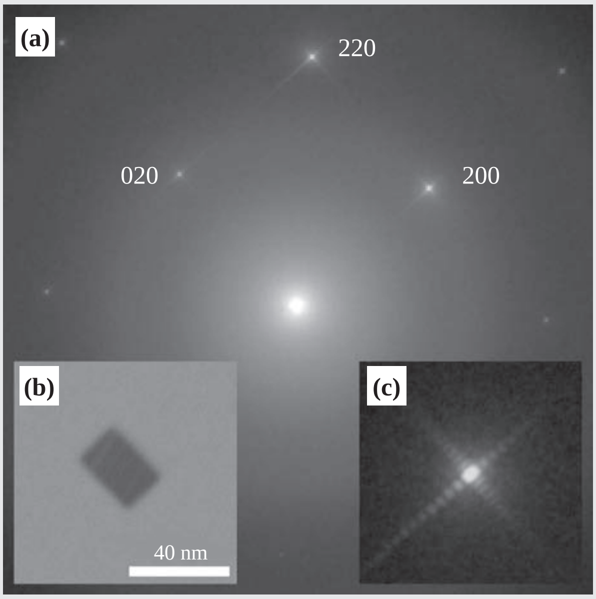


Fig. 4—Diffraction Pattern (a) and BF-STEM Image (b) of Isolated MgO Nanoparticle, and Magnified Image of 200 Diffraction Spots (c).
Fringes, which carry information about the specimen shape, can be observed around the diffraction spots.

viruses(4), chromosomes(5), and cells(6). The first successful demonstration of diffractive imaging using electrons was reported in 2002(7), and several groups have reported examples of its use since then. However, most of these have involved the analysis of material structures using high-energy 200-keV electron beams. With the aim of obtaining atomic-resolution images without causing serious damage to the specimen, Hitachi has been undertaking development work with Hokkaido University to demonstrate the use of diffractive imaging with low-energy electron beams(8).

ELECTRON DIFFRACTION MICROSCOPE

The initial proof of principle for low-energy electron diffractive imaging was conducted using a prototype microscope(8) built by modifying an instrument designed for reflection electron diffraction. Subsequently, to overcome problems with this prototype (including low resolution when used for outline observation and the fact that loading film and operating the shutter had to be performed manually), and to make the technique more practical, a dedicated low-energy electron diffraction microscope was developed(9) based on a scanning electron microscope (SEM) (see Fig. 2). The microscope uses a film loader system located under the conventional SEM column to record the diffraction pattern. It also has a charge-coupled device camera to monitor the diffraction pattern. In addition to conventional secondary electron (SE) detectors, a bright-field scanning transmission electron microscope (BF-STEM) detector is attached below the specimen (retractable). Fig. 3 shows example SE and BF-STEM images of an array of cubic magnesium oxide (MgO) nanoparticles. The SEM image shows the surface morphology and the BF-STEM image shows the inner structure of the particles. Fig. 4 shows the diffraction pattern for a single isolated MgO nanoparticle. The BF-STEM image in Fig. 4 (b) indicates that the size of the nanoparticle is about 30 nm. The diffraction pattern shown in Fig. 4 (a) includes diffraction spots for a 0.21-nm lattice spacing, while the diffraction fringes visible around each diffraction spot, shown in Fig. 4 (c), contain information about the shape of the nanoparticle. These results demonstrate that the dedicated microscope can be used to observe the outline and inner structure of a specimen as well as to perform a crystallization analysis from the diffraction pattern.

VERIFICATION OF LOW-ENERGY ATOMIC-RESOLUTION IMAGING

Single-wall carbon nanotubes (SWCNTs) were used as specimens to verify the performance of atomic resolution imaging(10). The energy of the electron beam was set at 30 keV, which is below the knock-on voltages for SWCNTs (about 60 keV)(11) and carbon atoms at the graphene edge (about 40 keV)(11).

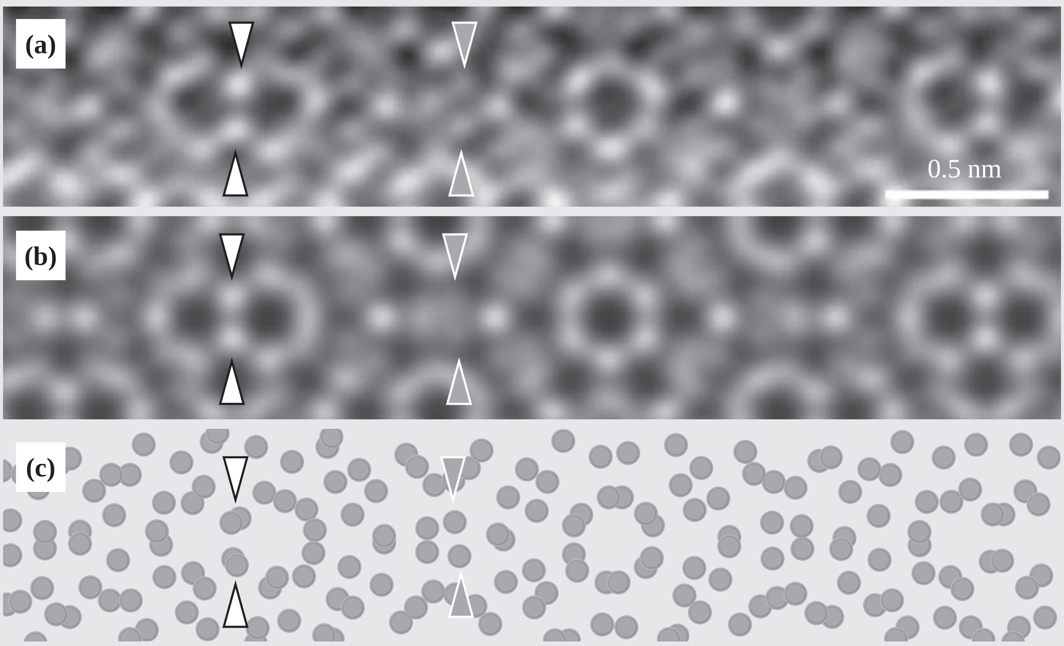
Fig. 1 shows the recorded diffraction pattern and reconstructed image for a SWCNT. Fig. 5 (a) shows a magnified image of the reconstructed pattern, Fig. 5 (b) shows the simulated pattern, and Fig. 5 (c) shows the atomic structure model. SWCNT is a rolled graphene sheet (a hexagonal lattice of carbon atoms). The hexagonal lattice orientations in the upper and lower layers are different, and when the arrangements of atoms in the two layers are combined, it results in the complex pattern shown in Fig. 5 (c). A comparison of these images indicates that the image reconstructed from the diffraction pattern contains information about the atomic structure of the SWCNT with a resolution of 0.12 nm. Based on the diffraction pattern, the diameter of the SWCNT was estimated to be 3.2 nm. A feature of this technique is that it was able to achieve this resolution when imaging two layers separated by more than 3 nm. This is possible because it uses a parallel beam and produces an image without use of a magnifying lens (see Fig. 1).

This work has demonstrated the ability of diffractive imaging to produce images of three-dimensional materials such as SWCNTs with atomic-scale resolution. Moreover, the bright regions indicated by the gray and white arrowheads in the reconstructed image in Fig. 5 (a) correspond respectively to single isolated carbon atoms and to overlapping atoms in the upper and lower layers, as indicated in the atomic model in Fig. 5 (c). Thus, the reconstructed image contains quantitative information sufficient to divide between a single carbon atom and two overlapping atoms. The quantitative accuracy of the image intensity has become increasingly important in recent times, with applications such as using the image intensity to identify differences in atomic number[12]. The results of this work show that diffractive imaging can be used for quantitative analysis.

CONCLUSIONS

This article has described the use of a diffractive imaging technique that can make observations of light-element materials with complex structures with only a low level of damage to the specimen.

The work has demonstrated that diffractive imaging can obtain images of radiation-sensitive materials with complex three-dimensional structures, such as carbon nanotubes, with atomic-scale resolution using a low-energy electron beam that causes little damage to the specimen. In the future, Hitachi intends to utilize this technology and the dedicated microscope in the



SWCNT: single-wall carbon nanotube

Fig. 5—Reconstructed Pattern of SWCNT Obtained Using 30-keV Electron Beam (a), Simulated Pattern (b), and Model of SWCNT Atomic Arrangement (c).
The resolution of the reconstructed pattern (a) is sufficient to resolve two atoms with a spacing of 0.12 nm (indicated by the gray arrowheads). In the figures (a)–(c), the white arrowheads indicate two overlapping carbon atoms and the gray arrowheads indicate single isolated carbon atoms.

development of new materials and devices that use light-element materials.

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