Application of an Imaging Plate to Electron Crystallography at Atomic Resolution

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An imaging plate was used to measure quantitatively the electron diffraction intensities of graphite and polyethylene single crystals. It is shown that the high sensitivity, the wide dynamic range, the good linear response and the digital output data of the imaging plate are useful for structure analysis by using electron diffraction. For polyethylene, hydrogen atoms were resolved, in addition to carbon atoms, owing to the higher scattering power of hydrogen for electron beam than X-ray.

Keywords: Structure Analysis/ Electron Diffraction/ Potential Map

Imaging plate (IP) was developed at first as a high sensitive two-dimensional detector in X-ray radiography in place of conventional X-ray films and soon applied to the field of X-ray crystallography. Recently, from the reason for its suitability in electron detection, it was also applied to the field of electron microscopy [1]. IP has more than three orders higher sensitivity in these accelerating voltages than that of conventional electron microscopic films. It exhibits also wide dynamic range of about four orders and very good linear response of the output signals for the logarithm of incident electron dosage in this range. In diffraction observation, the wide dynamic range of four orders may be appropriate to cover over from strong to weak scattering, and the good linear response and the digital data make it easy to collect the intensity data as the output signals of IP.

In the determination of structures of very small crystallites or thin layer (for example, polymer single crystals or pseudomorphic epitaxial layers), electron diffraction might be a better technique to analyze their structures rather than X-ray or neutron diffraction. Although it has been commonly thought that the electron diffraction is unfavorable in quantitative data collection so far, Dorset has shown that electron diffraction technique is useful for crystal structure analysis using the so-called direct phasing procedure [2] as employed in X-ray crystallography. Accordingly, quantitative data collection with a good recording medium may expected to realize reliable structure determination by electron diffraction.

We prepared thin flaky graphite as a specimen having a simple and well known structure and single crystals of polyethylene as an example of irradiation sensitive polymer crystal, which was grown from dilute xylene solution. Electron diffraction patterns were recorded on IP using transmission electron microscopes. After the data were transformed to electron beam intensities using the calibration line, integral intensities were measured for each diffraction spot. Then absolute intensities and a mean temperature factor were determined using Wilson

STATES AND STRUCTURES —Electron Microscopy and Crystal Chemistry—

Scope of research

Structures of materials and their structural transition associated with chemical reactions are studied through the direct observation of atomic or molecular imaging by high resolution microscopy. It aims to explore new methods for imaging with high resolution and for obtaining more detailed chemical information. The following subjects are studied: direct structure analysis of ultrafine crystallites and ultrathin films, crystal growth and adsorption states of organic materials, and development in high resolution electron spectromicroscopy.

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plot, and the signs of structure factors were assigned so that the electrostatic potential map was synthesized.

Electron diffraction pattern of graphite was recorded on IP (hk0-reflections). The integral intensities of 130 diffraction spots were measured over the intensity range of about four orders with only one sheet of IP. Finally, 19 symmetrically independent diffraction intensities were obtained. The signs of structure factors are assigned plus for all reflections due to the crystal structure of graphite. Then the electrostatic potential map was synthesized from the structure factors, where potential peaks corresponding to the carbon atom positions in the unit cell are clearly seen. The peak at (0, 0) is about two times higher than those at (1/3, 2/3) (2/3, 1/3), which means two carbon atoms exist at (0, 0) in the unit cell, and one atom locates at (1/3, 2/3) and (2/3, 1/3) as expected. Applying a least squares fit, the R-factor of 0.228 was obtained. This result demonstrates the good applicability of IP for quantitative detection of electron beam intensity of diffraction.

The single crystal of PE is lamellar crystal, whose normal is almost parallel to the c-axis. Therefore, electron diffraction shows the c-axis incident pattern. Integral intensities of 164 spots (48 symmetrically independent spots) with the intensity magnitude over more than four orders could be measured. Since the two dimensional space group of polyethylene crystal projected onto the ab-plane is pgg, the structure factor is a real number. The direct phasing method was used to assign the signs of the observed structure factors [3]. In this space group, signs of two reflections with the indices of (hk)≠(gg), where g is an even integer, could be assigned arbitrarily in order to define the origin of the unit cell. From these signs, the signs of the other reflections were determined using the Σ2-relationship, $S(h)S(h') S(h+h')=1$ (S(h) was the sign of reflection h), for the sets of these reflections h, h′ and h+h′ with large values of the multiples of their normalized structure factors.

Using these signs and observed structure factors, potential map is synthesized as in Figure 1. In addition to four clear peaks corresponding to carbon atoms, weak peaks corresponding to hydrogen atoms, which is not easy to be detected by X-ray experiment, can be seen due to the higher ratio of the scattering amplitude of a hydrogen atom to a carbon atom for electron beam compared to X-ray. This point is one of the merits of analyzing

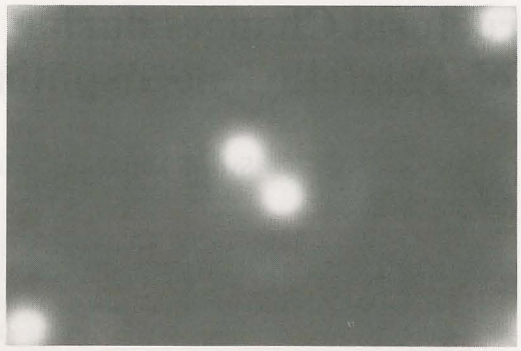

Figure 1. Electrostatic potential map for polyethylene calculated from observed structure factor magnitudes and signs assigned by direct method. There can be seen clearly four peaks corresponding to carbon atoms and weak peaks corresponding to hydrogen atoms.

structures of organic crystals by electron diffraction. Refinement of atomic positions by a least squares fit was carried out using the different temperature factors for carbon and hydrogen atoms. The result showed that the setting angle, i.e. the angle between the plane of zig-zag chain and the b-axis was 46°. It coincides with the results of X-ray experiments of 44–48°. R-factor was 0.198 with the temperature factors of 0.063 nm^2 for C and 0.093 nm^2 for H.

In the present cases, the potential maps show the good availability of IP to the structure analysis of crystals by electron diffraction [4]. In comparison with conventional electron microscopic films, we can record a large number of diffraction peaks on a sheet of IP. Because of the high sensitivity, it has great advantage, in particular, for the experiment of organic crystals which are damaged easily by electron irradiation.

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