High-precision quantitative atomic-site-analysis of functional dopants in crystalline materials by electron-channelling-enhanced microanalysis

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ARTICLE INFO

ABSTRACT

Knowledge of the location and concentration of impurity atoms doped into a synthesized material is of great interest to investigate the effect of doping. This would usually be investigated using X-ray or neutron diffraction methods in combination with Rietveld analysis. However, this technique requires a large-scale facility such as a synchrotron radiation source and nuclear reactor, and can sometimes fail to produce the desired results, depending on the constituent elements and the crystallographic conditions that are being analysed. Thus, it would be preferable to use an element-selective spectroscopy technique that is applicable to any combination of elements. We have established a quantitative method to deduce the occupation sites and their occupancies, as well as the site-dependent chemical states of the doped elements, using a combination of transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) spectroscopy, and electron energy-loss spectroscopy (EELS). The method is based on electron channelling phenomena where the symmetries of the Bloch waves excited in a crystal are dependent on the diffraction condition or incident beam direction with respect to the crystal axes. By rocking the incident electron beam with a fixed pivot point on the sample surface, a set of EDX/EELS spectra are obtained as a function of the beam direction. This is followed by a statistical treatment to extract the atom-site-dependent spectra, thereby quantitatively enabling the estimation of the site occupancies and chemical states of the dopants. This is an extension of the 'ALCHEMI' (Atom Location by Channelling Enhanced Microanalysis) method or 'HARECXS/HARECES' (High Angular Resolution Channelled X-ray/Electron Spectroscopy), and we further extended the method to be applicable to cases where the crystal of interest contains multiple inequivalent atomic sites for a particular element, applying the precise spectral predictions based on electron elastic/inelastic dynamical scattering theory. After introduction of conceptual aspects of the method, we describe the extension of the method together with the development of the theoretical calculation method. We then demonstrate several useful applications of the method, including luminescent, ferrite, and battery materials. We discuss the advantages and drawbacks of the present method, compared with those of the recently developed atomic column-by-column analysis using aberration-corrected scanning TEM and high-efficiency X-ray detectors.

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1. Introduction

Current technological developments are partly due to progress in understanding how the variation of the physical properties of materials is revealed from the microscopic point of view, particularly in terms of atomic-scale spatial/electronic structural analysis of the materials of interest. Humankind has exploited the useful physical and chemical properties of naturally occurring materials and elements, and created novel or enhanced material properties by combinations of those, such as alloying of metals, and doping of semiconductors and insulators. Novel properties have often been discovered unexpectedly by those experienced in synthesizing materials by trial and error. However, the recent developments in advanced measurement techniques and first-principles theoretical calculations based on the density functional theory [1] have enabled us to propose new materials having novel or better properties without repeated trial-and-error experiments. This is performed by first understanding the origin or mechanism of the known properties based on precise measurements comparable with the theoretical simulations. Then, one or a part of the host atoms are replaced by other elements that could conceivably improve the target property to determine if such replacement would work either experimentally or theoretically. One of the most important pieces of

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experimental information for this is detailed knowledge of where each constituent resides in the atomic structure of the materials.

The development of high flux X-ray sources such as synchrotron radiation facilities, and modern neutron sources, as well as a sophisticated structural optimization by Rietveld analysis, has led to X-ray and/or neutron diffraction methods becoming widely used techniques [2,3]. These techniques, however, inevitably require samples with uniform structure, because the incident probe (X-ray and neutron) must illuminate a macroscopic area. In addition, the diffraction techniques rely on the Rietveld fit between the experimental and theoretical sets of diffracted peak intensities using structure factors, and can have difficulty distinguishing between different elements if their structure factors happen to be very close to each other, such as occurs in X-ray diffraction of neighbouring elements in the periodic table.

In a semiconductor chip, the compositions, precipitates, grain size, and impurities in the materials should be controlled and optimized to maximize the desired functions at sub-micrometre or even nanometre scales. This means that those materials require characterization at the nanometre scale to confirm if they are correctly synthesized as designed. In this context, microanalysis methods based on transmission electron microscopy (TEM) are important.

Recent progress in aberration-correction technology [4] and high-sensitivity detectors enables the clarification of local atomic structures and atomic column-by-column elemental distributions and chemical information [5]. These include energy-dispersive X-ray (EDX) and electron energy-loss spectroscopy (EELS) in scanning TEM (STEM) using an electron probe focused down to sub-nm size. Although the STEM spectral-imaging technique is powerful enough to visualize the elemental distributions at atomic resolutions, the fact that an electron behaves as a wave in a solid must be considered when quantifying the column-by-column elemental map. Thus, the incident electron is gradually spread over the neighbouring atomic columns when propagating in a solid to thicker regions (>15−20 nm) even though the electron probe is focused on the sub-nanometre scale [6]. This effect is more significant when the incident direction of the electron is parallel to a low-order zone axis, which is known as the electron channelling effect. This also suggests that the atomic column-by-column analysis would be highly dependent on the sample quality issues such as sample thickness and the presence of surface damage layers, as well as instrumental alignment issues such as the accuracy of sample orientation, correction of lens astigmatism, and sample drift.

Electron channelling in a crystalline material occurs when an incident electron beam propagates along particular atomic planes or columns, and the channelling effect depends on the direction of the beam with respect to the crystal axes. One of the alternative ways to probe atomically localized electronic states using analytical STEM is to utilize amplitude modulations of electron wavefunctions propagating in a crystal; this does not necessitate focusing the electron beam onto the sample because in crystalline materials, high energy electrons behave as Bloch waves, the symmetries and amplitudes of which can be controlled by selecting an appropriate set of Bragg reflections and the excitation error of each reflection in a TEM [7]. The site-specific energy-dispersive X-ray (EDX) analysis technique that takes advantage of electron channelling effects is known as the atom location by channelled electron microanalysis (ALCHEMI) method [8,9], and is used to evaluate the fraction of host atomic sites occupied by impurities. This method has been extended in a more sophisticated and quantitatively reliable manner, such that the fluorescent X-ray intensities from the constituent elements can be measured as a function of the electron incidence direction, with the particular systematic reflection row excited. This high-angular-resolution electron-channelling X-ray spectroscopy (HARECXS) enables us to derive the impurity/dopant occupancies. More generally, it can also clarify the degree of cation mixing

(anti-sites) of the host atoms, by comparing the experimental beam-rocking curves with theoretical simulations [10−13]. An extension of this technique, high-angular-resolution electron-channelling electron spectroscopy (HARECES), records the EELS instead of EDX [14,15], thereby elucidating the local chemical states of a given element in different nearest-neighbour atomic environments. In these studies, a multivariate curve resolution (MCR) technique is crucial for separating the overlapping site-specific electron-energy-loss near-edge structures (ELNES) in the angle-dependent spectral data set [16]. Our research group has demonstrated such site-specific EELS measurements in several crystalline materials [17−19].

In the present article, we review microanalysis based on electron channelling phenomena, followed by recent developments in this field associated with current instrumental progress. Then, we introduce several representative examples, particularly focusing on the method combining incident electron beam-rocking and EDX spectroscopy, where the occupation sites and their occupancies of dopant elements are quantitatively determined in functional materials. Finally, we review the future prospects and directions of this technique.

2. Methods

2.1. Fundamentals of electron channelling phenomena

Suppose the simplest case where a monochromatic electron beam is incident to a crystalline solid with only a single Bragg reflection, such that $\mathbf{g}$ is strongly excited. The electron wave function, $\psi(\mathbf{r})$, propagating in the crystal is described as the steady-state solution of Schrodinger's wave equation:

$$\nabla^2 \psi(\mathbf{r}) + \left(\frac{8\pi^2 me}{\hbar^2}\right)[E + V(\mathbf{r})]\psi(\mathbf{r}) = 0 \tag{1}$$

where ∇^2 is the Laplacian operator, m and e are the mass and electric charge of an electron, respectively, E is the incident electron energy, and $V(\mathbf{r})$ is the crystal potential. In the present two-beam case, the total wave function is expressed by a sum of Bloch waves, $b^{(j)}(\mathbf{k}^{(j)}, \mathbf{r})$ $(j = 1, 2)$ [7]:

$$\psi(\mathbf{r}) = \sum_{j=1}^{2} \varphi^{(j)} b^{(j)}\left(\mathbf{k}^{(j)}, \mathbf{r}\right), \tag{2}$$

and

$$b^{(j)} = \sum_g C_g^{(j)}\left(\mathbf{k}^{(j)}\right) \exp\left(i\left(\mathbf{k}^{(j)} + \mathbf{g}\right) \cdot \mathbf{r}\right). \tag{3}$$

Here, $C_g^{(j)}$ and $\mathbf{k}^{(j)}$ are the solutions of Eq. (1), which reduce to the following two equations under the two-beam approximation:

$$(K^2 - k^2)C_0(\mathbf{k}) + U_{-g}C_g(\mathbf{k}) = 0, \tag{4}$$

and

$$U_g C_0(\mathbf{k}) + \left(K^2 - (\mathbf{k} + \mathbf{g})\right)^2 C_g(\mathbf{k}) = 0 \tag{5}$$

where

$$K^2 = \frac{2meE}{\hbar^2} + U_0 \tag{6}$$

and

$$U_g = \frac{2me}{\hbar^2} \sum_g V(\mathbf{r}) \exp(-i\mathbf{g} \cdot \mathbf{r}). \tag{7}$$

The ratio of the wave amplitudes $C_g^{(j)}/C_0^{(j)}$ are readily calculated at the exact Bragg reflection position and we have

$$b^{(1)} = -i\sqrt{2} \sin\left(\frac{1}{2}\mathbf{g} \cdot \mathbf{r}\right) \exp\left(i\left(\mathbf{k}^{(1)} + \frac{1}{2}\mathbf{g}\right) \cdot \mathbf{r}\right) \tag{8}$$