Discrete Tomography of Ga and InGa Particles from HREM Image Simulation and Exit Wave Reconstruction.

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Abstract

Low-resolution tomography requires recording images every few degrees. As a consequence, the sample is often degraded after such a procedure. However the required input can be reduced drastically by using knowledge about the position and the number of atoms in each atomic column. This concept has been tested in the present investigation where HREM image simulation (MacTempas) together with exit wave reconstruction (FEI Trueimage) have been performed. A cubeoctahedral nanoparticle is used for the simulation with different compositions i.e., pure solid Ga and In-Ga particles. Six different zone axes ([111], [1\overline{1}1], [001], [110], [1\overline{1}0], [011]) have been used and the parameters of an aberration corrected microscope (200kV, Cs = 0 mm, resolution = 0.5Å). The discrete grid data were determined by constructing a channeling map from the reconstructed exit wave images. In this special case only three projections [001], [110], [1\overline{1}0] were sufficient to find a unique volumetric reconstruction, illustrating the potential of the method. The other projections were used for checking the solution. The comparison between the projected potentials (simulated input) and the final result shows that discrete tomography reconstructs the exact position of all 309 atoms and the three-dimensional shape of the nanocrystal.

Introduction

Determination of structure and composition has been the objective of many characterization techniques including electron microscopy (EM). However the spatial resolution offered by EM gives the additional advantage to determine local variations. The spatial resolution of modern electron microscopes is around 0.15 nm but it can be increased by using several techniques. Incoherent scanning transmission electron microscopy (STEM) has a resolution limit of 0.078 nm [1], high voltage electron microscopy can reach 0.089 nm [2], field emission gun transmission electron microscopy (FEG-TEM) coupled to image reconstruction has shown a maximum resolution of 0.085 nm [3]. Resolution can also be improved by using a spherical aberration corrected microscope [4]. All of these values are rather close to the instrumental limit (∼0.05 nm) determined by the width of the atom potential [5]. Nevertheless achieving such a spatial resolution represents only part of the solution. Determination of chemical composition at such a scale with atomic sensitivity as well as tomography are doubtless a much needed goal. Z contrast can produce microanalysis and imaging but the signal to noise ratio is very close to unity for elements below an atomic number of 40 [6]. Thus it becomes important to explore other techniques. HREM and determination of exit waves for reconstruction produce amplitude and
phase images that can be used to determine the position of atomic columns and in principle also their chemical composition. Although determination of chemical composition still has to be developed in order to consider correctly the effect of thickness and the deconvolution of chemical information. On the other hand, tomography usually requires the use of a large number of images taken every 1 – 2 degrees and tilting an angle as large as possible. This produces sample degradation owing to the normally long exposure times. Experimentally the techniques are normally high angle annular dark field STEM [7] and more recently annular dark field TEM [8] with a spatial resolution around 1 nm. In this report, the possibility to perform tomography from images taken from few high symmetry zone axes is explored. HREM is used as the starting experimental technique since its resolution limit has been extended to subAngstrom values with the use of field emission guns (FEG). Additionally, its signal to noise ratio is higher than one for elements with \( Z \geq 10 \) [6]. This is important for materials containing light elements such as oxides, sulphides, etc. owing to the increased number of elements that can be detected and characterized.

**Procedure**

A particle with a cube octahedron morphology has been selected as sample [9]. Atoms of Ga and In have been positioned into such a supercell by means of Crystalkit\textsuperscript{TM}. The total number of atoms in this four shell nanocrystalline particle is 309. Particles consist either entirely of Ga or with the central row filled with In atoms (row parallel to [110]). The particle morphology as well as the atomic arrangement are shown in Fig. 1.

![Fig. 1. (a) Cube octahedron (b) distribution of atoms (Ga and In) in cube octahedral particle.](image)

Six different zone axes have been selected to perform HREM image simulation as a function of defocus. They are high symmetry crystallographic directions in the nanoparticle and correspond to [111], [1 1 1], [001], [1 1 0], [ 1 1 0], [011]. The current procedure starts by simulating a through focus series of 20 lattice images (size 10 nm by 10 nm) for each zone axis. Calculation of lattice images has been performed around Lichte defocus (focus at least delocalization [10]) for all 6 zone axis orientations and by using the multi-slice algorithm in the MacTempas\textsuperscript{TM} program package. As for microscope parameters, data from two microscopes are used as input. First, an aberration-corrected microscope (200 kV, \( C_s = 0 \) mm, resolution = 0.5 Å, sampling rate = 0.1
Å/pixel) [TEAM project] is chosen. In this case, the Lichte defocus is $\Delta f = -18.9$ nm and the focus series is calculated between $\Delta f = -19$ nm and $\Delta F = -3.8$ nm with a focus step of 0.8 nm between subsequent images. The second microscope is a common FEG-TEM (150 kV, $C_S = 0.62$ mm, resolution = 1.5 Å, sampling rate = 0.2 Å/pixel) similar to a CM200 FEI microscope. Lichte defocus is around –375 nm and the focus step in use is 1.9 nm. A subslicing of the crystal structure of the nanocrystal was used to create one projected potential per atomic layer in order to improve the accuracy of the multi-slice calculations (e.g. 9 projected potentials in <001> and 17 projected potentials in <110>, respectively). All these images are used to determine complex exit wave functions by a subsequent exit-wave reconstruction (EWR) using the FEI program package “TrueImage™” (FEI®). These wave functions are used to construct a channeling map and produce a discrete grid data containing the position of the atomic columns and the number of atoms in each column. Finally, these computed projection data from image simulation represent the input for a discrete tomography procedure. Lately several efficient algorithms have been used for tomographic reconstruction but they require a large number of measured projections (typically more than 100). Most of such algorithms do not take the specific characteristics of the sample into account for example, that the atoms are arranged in a crystalline structure or regular grid and that only a few different atomic species constitute the sample. Thus general algorithms cannot be used here, since the number of available projections is so small [11]. Additional details of the algorithm and its stability with respect to noise are given in [11]. The procedure to determine a channeling map and more details regarding the tomographic algorithm are given elsewhere [12, 13].

**Results and Discussion**

Figure 2 shows simulated images for the two microscopes under consideration. In both cases Lichte defocus is used for simulation and the images represent the first step of the corresponding focus series. The images show expected differences owing to the different values of $C_S$ and microscope resolution. The TEAM microscope image shows clear similitude with the expected

![Image](image.png)

**Figure 2.** Image simulation of Cube octahedral Ga particles with parameters from (a) TEAM microscope (zone axis = [001]) and (b) FEG-TEM microscope (zone axis = 110]. Lichte defocus is used in both cases. The corresponding projection of the sample is given in the insets.
projection of the particle (see inset), but in general more intensity maxima than atomic columns are imaged as a result of beam interference as expected in single HREM images away from Scherzer focus. On the other hand, the FEG-TEM image has contributions (secondary intensity maxima and general background) that make it difficult to recognize the sample shape (see inset) and complicate considerably an interpretation. Such a direct interpretation of the image is normally difficult to expect in a normal FEG TEM microscope due to aberrations and delocalization but in this case the use of Lichte defocus complicates it even further.

Figure 3 shows an example of a reconstructed phase image for the [001] zone axis orientation. In this case a Ga-In particle is used. Fig. 3b shows the expected projection with the In atoms having a larger size. As expected, correction of delocalization and spherical aberration makes possible the direct interpretation of this type of images. Particle shape and column positions are recovered in the reconstructed phase image. However, a phase image also contains information regarding the chemical composition of the atomic columns as can be seen by measuring the intensity maxima. Such a measurement is shown in Figure 4 for two different directions in the phase image (Fig. 4a) as indicated by the superimposed rectangles. The corresponding intensity measurements are given in Figs. 4b and 4c for the horizontal and diagonal rectangles, respectively. Clearly in this particular case, the number of atoms and its nature are well known (see Fig. 3b) and therefore the intensity differences can be easily traced back to the chemical composition of the particular atomic column in the phase image. The arrows in Figs. 4b-c point out the intensity peaks (and the corresponding atomic columns) where the contribution of an In atom disrupts the tendency set by an increasing or decreasing number of Ga atoms in the atomic column. For example in Fig. 4b, the central five columns contain each five atoms but the center column contains four atoms of Ga and one atom of In. This differentiation of intensity contributions from single atoms in a column is already shown on a gold sample by high-angle annular dark field scanning transmission electron microscopy [6] and by phase contrast microscopy (e.g. exit wave reconstruction) [12]. In general the number of atoms in each column can be determined by applying the channeling theory [5] for each projection as shown in a separate publication [12]. The same procedure is used here i.e., a channeling map from the
reconstructed EW images is used in order to create the discrete grid data i.e., the position of the atomic columns and the corresponding number of atoms in each column (details in [12], [13]).

![Figure 4](image_url)

**Figure 4.** Phase image of an In-Ga nanoparticle for the zone axis orientation [001] and the intensity measurement in two directions (b) along a horizontal and (c) a diagonal direction as indicated by the superimposed rectangles and the arrows.

Figure 5 shows the results of the tomographic reconstruction from the described wave functions and grid data. A future publication will describe the details of the algorithm. However a hybrid approach is employed for computing the three-dimensional reconstruction. First, the [001] projection is used to determine an outer boundary for each atomic layer in the <001> zone axis, within which all atoms must lie. Subsequently, a two-dimensional method is applied to reconstruct each of the atomic layers independently. The problem of reconstructing the two-dimensional layers from two projections ([110] and [110] in our case) is one of the standard problems in discrete tomography. In the present investigation, only three projections ([001], [110], [110]) have been required in order to find a unique solution and recover the nanoparticle volume. The remaining three projections have been used to check the solution.

![Figure 5](image_url)

**Figure 5a** shows three of the total nine slices obtained by the tomographic reconstruction algorithm. In this figure an X represents a position filled by an atom while dots represent vacant sites. Fig. 5b shows the calculated projected potentials from the image simulation procedure, they are shown for comparison with the results in Fig. 5a. As can be seen, the final tomographic reconstruction shows that the exact position of all 309 atoms in the original nanocrystalline particle can be determined by this discrete method.

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Figure 5. (a) Three of the final nine slices obtained from the reconstructed nanocrystal using a discrete tomography algorithm, filled positions representing atoms are marked by “X”. (b) Three of the nine projected potentials (atomic layers) of the cube-octahedron nanocrystal in a <001> zone axis, for comparison purposes.

References.

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