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# Refinement of chemically sensitive structure factors using parallel and convergent beam electron nanodiffraction

K Müller<sup>1</sup>, M Schowalter<sup>1</sup>, A Rosenauer<sup>1</sup>, J Jansen<sup>2</sup>, K Tsuda<sup>3</sup>, J Titantah<sup>4</sup>, D Lamoen<sup>4</sup>

<sup>1</sup> Institut für Festkörperphysik – Bereich Elektronenmikroskopie, Universität Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany

<sup>2</sup> National Centre for HREM, Kavli Institute of Nanoscience, Delft University of Technology, 2628 Delft, The Netherlands

<sup>3</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 980-8577 Sendai, Japan

<sup>4</sup> EMAT, Universiteit Antwerpen, 2020 Antwerpen, Belgium

Email of K. Müller: mueller@ifp.uni-bremen.de

**Abstract.** We introduce a new method to measure structure factors from parallel beam electron diffraction (PBED) patterns. Bloch wave refinement routines were developed which can minimise the difference between simulated and experimental Bragg intensities via variation of structure factors, Debye parameters, specimen thickness and  $\omega$ -orientation. Due to plane wave illumination, the PBED refinement is highly efficient not only in computational respect, but also concerning the experimental effort since energy filtering is shown to have no significant effect on the refinement results. The PBED method was applied to simulated GaAs diffraction patterns to derive systematic errors and rules for the identification of plausible refinement results. The evaluation of experimental GaAs PBED patterns yields a 200 X-ray structure factor of  $-6.33 \pm 0.14$ . Additionally, we obtained  $-6.35 \pm 0.13$  from two-dimensional convergent beam electron diffraction refinements. Both results confirm density functional theory calculations published by Rosenauer et al. and indicate the inaccuracy of isolated atom scattering data, which is crucial e.g. for the composition evaluation by lattice fringe analysis.

## 1. Introduction

Development of efficient theoretical models during the past decade offers impressive insights into solid state properties for today's electron microscopists. In the field of transmission electron microscopy (TEM), the exact modeling of electron scattering properties, such as temperature and atomic scattering factors, has gained new interest. One should, however, bear in mind that the experimental verification should keep pace with new theoretical data. For example, DFT calculations of modified atomic scattering amplitudes (MASA [1]) have been published for the chemically sensitive 200 structure factor (SF) of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  alloys. The MASA model accounts for the redistribution of electrons due to chemical bonding, leading to a significant improvement of accuracy for the composition evaluation by lattice fringe analysis (CELFA [2]) in the case of  $\text{In}_x\text{Ga}_{1-x}\text{As}$ .

The intention of this article is threefold: First, the PBED method is introduced. An analysis of systematic errors of the refinement of SF and thickness will be given. The motivation to develop PBED techniques stems from the high computational efficiency due to plane wave illumination, as it

has been demonstrated for structure refinements by Jansen et al [3]. Second, we report on measurements of the 200 SF for GaAs using our PBED method and two-dimensional convergent beam electron diffraction (CBED) refinements [4,5]. Third, PBED results for InAs will be given. Conclusions as to the precision of both methods and the difference between the MASA concept and isolated atom scattering data [6,7] will be drawn.

## 2. Introduction and test of the PBED method

### 2.1. Methodical basics

Plane wave illumination of a crystal leads to a diffraction pattern containing intense Bragg spots and thermal diffuse (TD) background. The Bragg intensities can easily be calculated using atomic scattering amplitudes and absorptive form factors e.g. from [6,7]. To profit from the plane wave illumination, the integrated spot intensities less the TD background are to be extracted accurately. The extracted intensities are then compared with those obtained from a single Bloch wave simulation per iteration in the refinement, making the PBED method much faster than e.g. two dimensional CBED. However, bending and thickness gradients in real specimens require the illuminated area to be only a few nanometers in diameter. For this purpose, we fabricated C2 apertures with diameters of less than 10 $\mu$ m which consequently lead to Bessel-like probe profiles.

The main steps of the PBED method are

1. Acquisition of PBED patterns from nanometre-sized areas,
2. Extraction of Bragg intensities and background subtraction,
3. Derivation of initial guesses for the refinement (thickness, orientation) and
4. Minimisation of the  $R$ -value defined by [3]

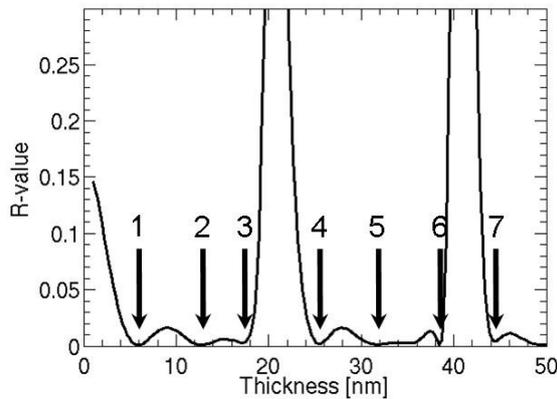
$$R = \sum_m \frac{(I_m^E - s \cdot I_m^S)^2}{\sum_m (I_m^E)^2} \quad (1)$$

in a nonlinear least-squares refinement procedure. In equation (1),  $R$  is the normalised summed difference between experimental and simulated Bragg intensities  $I_m^E$  and  $I_m^S$ , respectively. Our Bloch wave routines are written in MATLAB and the program can refine the specimen thickness, its orientation, Debye parameters, SF and the scaling factor  $s$ , which is used to scale the simulated intensities with respect to experimentally recorded counts. Different data sets may be used simultaneously for a constraint refinement of SF and Debye parameters. Except for the SF refinement the method is very similar to the multi slice least-squares program (MSLS [3]) written by Jansen et al.

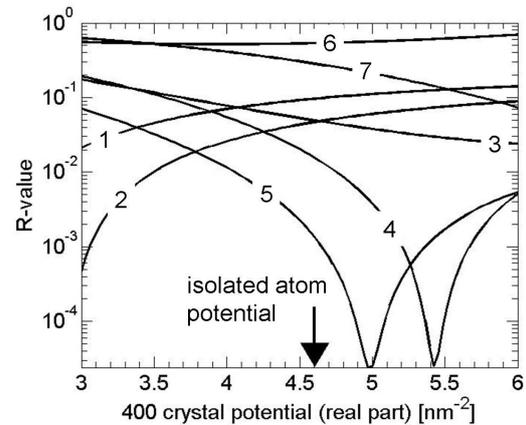
### 2.2. Evaluation of simulated PBED patterns

Steps 2-4 listed in the last subsection have been applied to three simulated GaAs diffraction patterns in zone axis [053] containing TD background [8]. Parameters were chosen similar to the experimental situation in a Titan 80/300 used for the real measurements (sections 3, 4). A spherical aberration of 2mm was chosen for the condenser and a small beam convergence of 0.5mrad was applied to simulate a slight misalignment of the condenser. The probe diameter was 10nm and an acceleration voltage of 300kV was used. Specimen thicknesses were chosen to be 13.19nm, 23.08nm and 32.96nm.

After the background subtraction, the estimation of initial parameters is a serious problem. Whereas a guess of orientation can be derived from the intersection of Kikuchi bands, a guess of thickness might be ambiguous as shown in figure 1, where the  $R$ -value is plotted versus the thickness. Each minimum corresponds to one possible initial thickness and, if not measured separately, rules must be derived to identify the most plausible one. As we expect bonding effects to modify only low order SF, isolated atom potentials should be true for higher momentum transfers. We therefore performed potential scans for the real part  $\text{Re}(U_{400})$  of the 400 Fourier component of the crystal potential as depicted in figure 2. Here,  $\text{Re}(U_{400})$  was varied around the isolated atom value [6] (indicated by the arrow) for each of the seven thickness guesses in figure 1.



**Figure 1.** *R*-value as a function of thickness for the simulated diffraction pattern with a true thickness of 32.96nm. The arrows indicate possible initial thickness guesses.



**Figure 2.** *R*-value as a function of the 400 potential (real part). Each curve corresponds to one thickness in figure 1, indicated by the numbers.

Obviously we trust that thickness most for which the 400 potential for isolated atoms is reproduced best, as it is the case for curve 5, corresponding to a thickness of 31.78nm. However, the isolated atom potential is not reproduced perfectly since we replaced the 200 SF by a 30% smaller value in all simulations of figures 1 and 2 to approach the real situation where the 200 SF is not known exactly.

Finally we refined  $\text{Re}(U_{200})$ , the thickness and the orientation for each of the three simulated PBED patterns to see how accurate our refinement result reproduces the true values. It turned out that the deviations of the 200 potential and the thickness from the input values were less than  $0.03\text{nm}^{-2}$  and  $0.16\text{nm}$ , respectively. Concerning the verification of the MASA model, this error is small enough, since  $\text{Re}(U_{200})$  from [1] is  $0.1\text{nm}^{-2}$  larger than that from [6,7]. Furthermore, *R*-values well below 0.2% indicate that the integrated spot intensities of diffraction patterns acquired with aberration-manipulated, slightly convergent probes can be well approximated by plane wave illumination.

### 3. PBED and CBED measurements of the 200 structure factor for GaAs

#### 3.1. PBED measurements

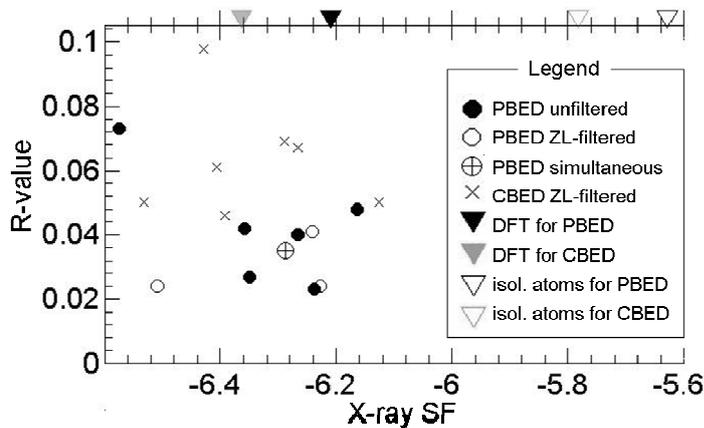
Three zero-loss energy filtered and six unfiltered GaAs PBED patterns have been recorded on a Titan 80/300 facility near the zone axis [053] at 300kV. All nine PBED patterns have been evaluated as described in section 2. The evaluation of experimental patterns turned out to be strictly analogous to that of the simulated ones, especially concerning the initial thickness guesses. The stability of each refinement has been checked by the inclusion of more beams, the reproduction of known properties (such as  $\text{Re}(U_{400})$ ) and by assuring that the final thickness and the final orientation are close to the initial guesses.

The refinement results for the 200 SF (converted to X-ray SF) are shown in figure 3 as filled and empty black circles for unfiltered and zero-loss filtered measurements, respectively. Debye parameters of  $B_{\text{Ga}}=0.68\text{\AA}^2$  and  $B_{\text{As}}=0.59\text{\AA}^2$  were taken from [9]. From all PBED measurements, a mean 200 X-ray SF of  $-6.33\pm 0.14$  can be derived, whereas no significant influence of energy filtering can be observed in the investigated thickness range up to 25nm. Furthermore, we refined the Debye parameters for Ga and As, as well as the 200 SF constraint for all nine sets, allowing each set to have its individual thickness and orientation, which were also included in the refinement. The result for the 200 SF is shown as an encircled plus, which nearly falls together with the average over individual refinements.

#### 3.2. CBED measurements

To compare our PBED results and the precision of our method with a traditional approach, the program MBFIT [4,5] was used to refine the 200 SF from seven zero-loss filtered CBED diffraction

patterns. The results for the 200 SF (converted to X-ray SF) are depicted as crosses in figure 3. From these measurements, a 200 X-ray SF of  $-6.35 \pm 0.13$  results, which agrees perfectly with the PBED value. However, the Debye parameters have been refined to  $B_{\text{Ga}} = 0.76 \text{ \AA}^2$  and  $B_{\text{As}} = 0.62 \text{ \AA}^2$ , being larger than in the PBED case and yielding different theoretical values (grey triangles in figure 3).



**Figure 3.** Refinement results for the PBED (circles) and the CBED (crosses) measurements of the GaAs 200 SF together with theoretical data for isolated atoms [6] (light triangles) and SF expected from the MASA concept [1] (filled triangles). Theoretical values for PBED and CBED differ slightly due to the different Debye parameters. The electron SF were converted to X-ray SF using the Mott-Bethe formula.

#### 4. PBED measurements of the 200 structure factor for InAs

Analogous to section 3.1, seven unfiltered InAs PBED patterns have been recorded near the zone axis [053]. The study of bonding effects on the 200 SF for InAs is more difficult than in the case of GaAs since, in terms of X-ray SF, the DFT value of 53.68 is very close to the isolated atom X-ray 200 SF being 53.85. Thus the expected difference falls into the range of the precision observed in sections 3.1 and 3.2. However, the statistical evaluation of the seven refinement results yields an X-ray 200 SF of  $53.69 \pm 0.11$  with Debye parameters of  $B_{\text{In}} = 1.0 \text{ \AA}^2$  and  $B_{\text{As}} = 0.86 \text{ \AA}^2$  according to [9]. The constraint refinement using all seven sets simultaneously yields 53.71 for the X-ray 200 SF.

#### 5. Conclusions

A method was developed and tested to measure structure factor amplitudes from PBED patterns. It was successfully applied to the chemically sensitive 200 SF of GaAs and InAs. Two-dimensional GaAs CBED patterns have also been refined to compare the precisions of both methods, which turned out to be comparable if derived from statistics. Methodologically, PBED simulations were about 100 times faster than two dimensional CBED simulations, making the method suitable for standard PC. Furthermore, no energy filtering is necessary. However, an advantage of the CBED method is that refinement results and initial guesses can be judged by visual control, whereas additional rules had to be derived for PBED refinements. All measurements for GaAs and InAs are in good agreement with the MASA model, whereas the isolated atom potentials cannot be verified. Using MASA for the quantitative compositional analysis of  $\text{In}_x\text{Ga}_{1-x}\text{As}$  alloys (e.g. with CELFA) is herewith shown to be essential also from the experimental point of view.

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