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Three dimensional analysis of the composition in solid alloys by variable probe in scanning transmission electron microscopy

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ABSTRACT

This paper reports on a novel approach to quantitatively reconstruct the column by column composition and the 3D distribution of guest atoms inside a host matrix by scanning transmission electron microscopy high angle annular dark field technique. We propose a new mathematical framework that allows to jointly analyze the information from a set of experiments with variable beam convergence and/or defocus. Our scheme allows to reconstruct the atomic distribution along the imaged columns from the measured intensity, for any dependence of the probe intensity on the depth. It is therefore well suited to incorporate channeling effects that are usually neglected in other approaches. As a case study, we focus here on the systematic variation of the beam convergence that permits to set the maximum of the channeling oscillations at different depths. We aim here to define the reliability and the limitation of this technique by the application of the method to accurate dynamic simulations in the case of the InGaN alloy.

1. Introduction

In the last decade a lot of efforts have been devoted to develop new electron microscopy techniques able to image single dopant atoms in semiconductors or to calculate, with the highest precision, the composition of an alloy with very high lateral resolution [1–7]. This ability is necessary for studying the next generation semiconductor devices since their sizes reached length scales where even the very local distribution of dopant atoms can cause appreciable changes in the device behavior.

For this kind of problems, STEM-HAADF is a particularly well suited approach that holds the promise of straight forward analyses of chemical sensitive signals with atomic resolution. However, in spite of the progress made in the last years in instrumentation and methodology, the column-by-column quantitative analysis along highly symmetric directions has physical limits, since resonant excitation of one dimensional electronic states bound to the atomic column (channeling) strongly influence the propagation of the probe inside the sample [8,9]. In consequence, the contrast due to a foreign atom in a host matrix strongly depends on its in-depth position [1,10] making quantitative analyses of the average composition in the column unreliable: this phenomenon is often referred to as "top-bottom effect" [2]. This limitation in quantitative analyses can only be overcome if we could gain additional information on the position of the atom along the column.

A common approach to gain three dimensional information on the atomic distribution along the column is by "depth sectioning", i.e. by comparing images taken at different defoci in a trough-focal series [11,12]. Though STEM trough-focal series 3D reconstructions have been successfully applied for single heavy dopant atoms in a light matrix such as *Y* in Al_2O_3 [13], *Au* in Si [14], and *Tm* in GaN [15], its application to more general cases, such as alloys, is hampered by the effects of channeling causing the oscillatory probe current evolution along the projected column. One may overcome these limitations by removing channeling itself through e.g., hollow cone illumination [16]. However, this technique suffers from the serious drawback that part of the beam intensity and also depth resolution is sacrificed. Scanning electron confocal microscopy (SCEM) has been shown to improve the in depth resolution [17–19] but also suffers from channeling effects. Only recently a method to use channeling to retrieve 3D information for the case of a single atom has been introduced [20]. A more general framework that conceptually allows for solving the problem for a higher number of guest atoms in a column and retrieves the 3D information directly without need of simulating all possible positions is still lacking.

In this paper we propose a novel approach that implicitly includes any kind of probe evolution with depth. It allows to determine the average composition of an atomic column in a dilute alloy with single atom accuracy and at the same time,

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provides information on the in-depth atom distribution with an adjustable precision. Our method explicitly accounts for channeling effects and is based on the systematic variation of probe parameters. In detail, we will focus on a rarely explored variable: the convergence angle [21]. Our approach, though more general, has some similarities with the Alchemy [22] method for TEM. However, due to the convergent beam, the contrast in STEM is less sensitive to sample tilt. As a case study for our method, we use the $In_xGa_{1-x}N$ ($x<10\%$) system because in this material the effect of short range order of the *In* atoms is known to critically influence the optical properties of these alloys. Even the most advanced atom probe tomographic techniques [23] cannot characterize such correlations at the atomic scale since they suffer from artifact due to the evaporation efficiency when using laser pulses.

2. Method

2.1. Depth resolved STEM

Our aim is to analyze STEM HAADF experiments taken with a systematic variation of the imaging parameters, such as convergence angle or defocus, and to reconstruct the three-dimensional atomic distribution. The reconstruction is based on the inversion of the correlation matrix between the experimental data and the atomic distribution of guest species in the host. However, the details depend on the accurate parameterization of such atomic distribution and the correct description of the channeling.

The starting point is the kinematic approximation, in it the HAADF intensity at each column, is given as follows:

$$I=\sum_{\substack{z_i=\text{atomic}\\ \text{positions}}} J(z_i,[x])\sigma_{z_i} \tag{1}$$

with i the index of atomic position along the column, z the thickness, $[x]$ the composition, $J(z_i,[x])$ the probe current evolution inside the sample and σ_i the atomic cross section, depending on the atomic species considered, at the given depth z_i. In this work we will assume that $J(z_i,[x])$ is only weakly dependent on the composition $[x]$ or on the distribution of guest atoms along the column. In this case, the function $J(z_i,[x])$ can be approximated as the average current $J(z_i)$ for the given mean composition neglecting the compositional fluctuation among the individual columns. For a detailed discussion on the limits and consequences of this assumption, we refer to [2,24]. Here, we focus on the systematic variation of $J(z_i)$ by altering the probe parameters. For amorphous materials $J(z_i)$ is a slowly and monotonous changing function with depth. Its variation, in dependence of beam parameters and in the absence of channeling, has largely been described in literature [25]. In case of crystalline materials channeling causes a strong oscillation of $J(z_i)$. The oscillation is described as the interference between the 1s Bloch state and all higher excited states. According to Peng [26], the main contribution these higher excited states can be approximated by the sum of plane waves with the main phase velocities along z. Since this main phase velocity is proportional to the convergence angle, the oscillation frequency increases with increasing probe convergence angle and causes a substantial change of $J(z_i)$ along z.

We aim to exploit the change of the probe convergence, in the presence of channeling, as schematically drawn in Fig. 1. Moving the maxima of the channeling oscillation along the column we obtain a convoluted signal that is related to the depth distribution of the atoms in each column. By taking the probe current (density) along the atomic column into account we overcome the ambiguity in the scattered intensity due to the top bottom effect and obtain a reliable 2D map of the host atom distribution.

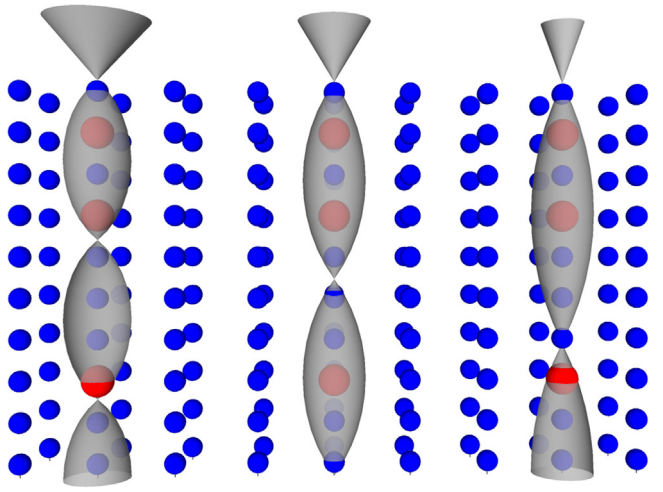

Fig. 1. Scheme of the effect of a variable converge experiment to probe different channeling depth.

Experiments with multiple convergence angles offer the opportunity to recover the atomic distribution along the column. On the other hand, neglecting the complex shape of $J(z_i)$, as generally done in through-focus STEM experiments, does not allow for a direct interpretation of the experimental results.

2.2. Mathematical model for calculating the STEM intensity

As a starting point, it is useful to derive a compact form for the contrast between an InGaN layer and the GaN matrix in terms of the local occupancy of the atomic sites by indium atoms. The HAADF intensity of an InGaN column is given by the following equation:

$$I=I_{\text{GaN}}+\sum_{z_i} J(z_i)D(z_i)\Delta\sigma \tag{2}$$

Here $I_{\text{GaN}}=\sum_{z_i}J(z_i)\sigma_{\text{GaN}}$, $J(z_i)$ is the probe current density evolution along the column, $\Delta\sigma=\sigma_{\text{In}}-\sigma_{\text{Ga}}$ is the difference of the scattering cross section of *In* and *Ga*, and $D(z_i)$ is function that describes the occupation of the lattice either with In or Ga, respectively: it is 1 if the lattice position is occupied by an In atom, elsewise it is 0. The function $D(z_i)$ has to be bound to the normalization $N_{In}=\sum_{z_i}D(z_i)$ where N_{In} is the number of In atom in the specified column.

From here on we substitute $J(z)$ with its normalized version $J(z)/\sum_{z_i}J(z_i)$, so that the image contrast between InGaN and GaN is given by the following equation:

$$C=\frac{I_{\text{InGaN}}}{I_{\text{GaN}}}-1=\sum_{z_i}^{N} J(z_i)D(z_i)\frac{\Delta\sigma}{\sigma_{\text{Ga}}} \tag{3}$$

Through this equation, we obtain the contrast as dependent on the distribution of guest atoms in the columns with $D(z_i)$, governing the top bottom effect. Since the occupation of an atomic position by an *In* or *Ga* atom is unknown, the distribution of In atoms $D(z_i)$ represents an independent variable. Thus, a determination of $D(z_i)$ requires as many independent measurements as atoms are present in the column. In a very thin specimen of 11 nm thickness, we have a discrete distribution of $N_T\approx 20$ atoms, and hence would need $N=20$ independent measurements to retrieve this configuration.

A typical approach would be to produce a through focus series i.e. taking 20 images with different focus values on the same column and afterwards try to reconstruct the atomic distribution from the resulting intensity. In a more general framework one could combine any set of 20 experiments