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Measurement of atomic electric fields and charge densities from average momentum transfers using scanning transmission electron microscopy

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ABSTRACT

This study sheds light on the prerequisites, possibilities, limitations and interpretation of high-resolution differential phase contrast (DPC) imaging in scanning transmission electron microscopy (STEM). We draw particular attention to the well-established DPC technique based on segmented annular detectors and its relation to recent developments based on pixelated detectors. These employ the expectation value of the momentum transfer as a reliable measure of the angular deflection of the STEM beam induced by an electric field in the specimen. The influence of scattering and propagation of electrons within the specimen is initially discussed separately and then treated in terms of a two-state channeling theory.

A detailed simulation study of GaN is presented as a function of specimen thickness and bonding. It is found that bonding effects are rather detectable implicitly, e.g., by characteristics of the momentum flux in areas between the atoms than by directly mapping electric fields and charge densities. For strontium titanate, experimental charge densities are compared with simulations and discussed with respect to experimental artifacts such as scan noise. Finally, we consider practical issues such as figures of merit for spatial and momentum resolution, minimum electron dose, and the mapping of larger-scale, built-in electric fields by virtue of data averaged over a crystal unit cell. We find that the latter is possible for crystals with an inversion center. Concerning the optimal detector design, this study indicates that a sampling of 5 mrad per pixel is sufficient in typical applications, corresponding to approximately 10×10 available pixels.

1. Introduction

The control and measurement of solid state phenomena such as ferroelectricity, magnetism as well as spontaneous or piezoelectric polarisation in crystals is involved in or even paves the way for the engineering of many innovative nanoelectronic devices. Prominent examples are ferroelectric tunnel junctions [1,2], spin light-emitting diodes [3–5] or InGaN-based light-emitting diodes [6–8]. Owing to its high spatial resolution and the strong coupling of electrons to electric and magnetic fields via the Lorentz force, transmission electron microscopy (TEM) is predestined for the characterisation of such fields. The differential phase contrast (DPC) technique [9] has allowed for many impressive measurements in this domain.

As to the investigation of magnetic fields, magnetic domain walls in permalloy have been observed directly [10,11], the vortex structure and domain wall widths of permalloy particles could be resolved [12] and magnetic vortex cores in permalloy could be shifted and pinned by magnetic fields [13].

Recently, DPC has been employed in studies of electrical properties, such as spontaneous polarisation in GaAs nanowires [14], piezoelectric fields in GaN/InGaN/GaN heterostructures [15], atomic-scale mapping of the electric field in $BaTiO_3$ [16] and

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dopant-modulated built-in electric fields in pn junctions [17].

As originally proposed for electron microscopy by Rose [9], DPC evaluates the asymmetry of intensity in the central part of diffraction patterns (the Ronchigram) by means of a split four-quadrant detector [10]. Most DPC measurements of both magnetic and electrical properties have relied on the established intuitive interpretation of the DPC signal being caused by a shift of the Ronchigram as a whole, reflecting the classically expected angular deflection of the electron beam in the specimen caused by the Lorentz force.

Some more recent works adopt a quantum mechanical interpretation of diffracted intensities in terms of probability currents [18,19], ptychographic reconstructions of the object phase [20,21] or the quantum mechanical expectation value for the electron momentum transfer [22]. The authors of this paper recently related this expectation value to the projection of the electric field using Ehrenfest's theorem [23] in simulation and experiment, which allowed the measurement of atomic electric fields in $SrTiO_3$ [22].

While fields of a large extent of some tens of nanometers could successfully be characterized using segmented detectors and the conventional interpretation assuming a shift of the diffraction pattern as a whole, this approach has been shown to be inadequate for the quantification of atomic electric fields using contemporary aberration-corrected STEM at a resolution below 100 pm [22]. In this case the detailed intensity distribution in diffraction patterns has to be considered. On top of that, reliable field strengths are only obtained for very thin specimens. This situation hence demands a comprehensive study investigating the reliability of electric field characterization as a function of the spatial resolution in STEM, the specimen thickness as well as the scale at which electric fields vary, which is the goal of this paper.

In the following, these issues are addressed via detailed simulation studies focused on electric fields in a GaN crystal. In Section 2, we consider the measurement of the angular deflection from electron diffraction patterns in a quantum mechanical approach and point out limitations of DPC when employing segmented detectors. Section 3 treats the relation between angular deflection and electric field distribution in the framework of different models; the equivalence of one model with the phase object approximation is demonstrated. We then investigate the scattering of single atomic columns in Section 4 which has the advantage that electron channeling can be studied apart from Bragg scattering, and interpret results in a simple s-state channeling model. Section 5 deals with the reliability of the electric field determination in GaN crystals as a function of specimen thickness and scattering amplitudes used in the simulation. The mapping of bonding charges is discussed via the comparison of data obtained in isolated atom approximation with density functional theory (DFT) data. Section 6 addresses the influence of inelastic scattering on the diffraction pattern. In Section 7 we suggest a figure of merit for the spatial resolution and discuss requirements towards momentum space sampling and electron dose for given accuracy and precision as a guide for practical setups. Experimental and theoretical charge densities of $SrTiO_3$ are presented in Section 8. We address the mapping of large-scale electric fields from atomic-resolution DPC data in Section 9, followed by a discussion in Section 10.

2. The angular deflection of electrons as a quantum mechanical observable

2.1. Diffraction patterns and the expectation value of the electron momentum transfer

In the Schrödinger picture of quantum mechanics, the wave function ψ is the central entity to describe the state of a quantum mechanical system. The wave function has different equivalent representations, for example $\psi(\mathbf{r})$ and $\psi(\mathbf{p})$ describe the same state in real and momentum space, respectively, with position $\mathbf{r}$ and momentum $\mathbf{p}$. Both representations are related by Fourier transform, i.e. $\psi(\mathbf{p}) \propto \mathcal{F}[\psi(\mathbf{r})]$. Considering image formation in a transmission electron microscope within the framework of Fourier optics, this fact is particularly interesting because the specimen exit plane and the back focal plane of the objective lens are also related by Fourier transform, giving rise to the Fraunhofer diffraction pattern in the back focal plane.

Thus, recording this pattern means recording the two-dimensional intensity distribution $I(\mathbf{p}_\perp) = |\psi(\mathbf{p}_\perp)|^2$ with $\mathbf{p}_\perp$ the vector of the lateral momentum parallel to the detector plane which is typically perpendicular to the optical axis. Furthermore, by the postulates of quantum theory,

$$\langle \mathbf{p}_\perp \rangle = \int d^2 p_\perp \; \mathbf{p}_\perp I(\mathbf{p}_\perp) \tag{1}$$

is the quantum mechanical expectation value of the lateral momentum, which, for a sufficient number of detected electrons, will be identical to the average lateral momentum. Without loss of generality, the initial average momentum can be chosen to be $\langle \mathbf{p}_\perp^0 \rangle = 0$ for the STEM probe incident on the specimen, so that Eq. (1) expresses the average momentum *transfer*. It is related to the scattering angle α by $h \cdot \sin\alpha = p_\perp \lambda$ with the relativistically corrected electron wavelength λ and the Planck constant h.

The previous considerations are well-established facts from quantum theory and Fourier optics. They do, however, reveal explicitly that the determination of the average momentum transfer does neither require the measurement of the phase of the wave function $\psi(\mathbf{p}_\perp)$, nor are any model assumptions to be made as to the interaction of the STEM probe with the specimen. At the same time the integration in Eq. (1) essentially condenses the two-dimensional intensity distribution $I(\mathbf{p}_\perp)$ with all its complexity into one single vector $\langle \mathbf{p}_\perp \rangle$ which nevertheless has a fundamental physical meaning.

2.2. Measurement of the average momentum transfer

It is this intuitive condensation of extensive, possibly complicated diffraction pattern data $I(\mathbf{p}_\perp)$ into one fundamental quantity $\langle \mathbf{p}_\perp \rangle$ that constitutes the appeal of average momentum transfer measurements [22]. However, the integral nature of Eq. (1) has important consequences for the design of the experimental setup because a suitable detector must realise the integration of the diffraction pattern coordinates $\mathbf{p}_\perp$ weighted by the local intensity $I(\mathbf{p}_\perp)$, or allow for it in postprocessing. Actually such a "center of gravity" or "first moment" detector had already been proposed in 1977 [24]. Recently, charge-coupled device (CCD) cameras for electron microscopy [25] reaching kHz frame rates [26,27], delay-line detectors [28] or direct complementary metal-oxide-semiconductor (CMOS) cameras [29,30] have been developed. Thereby the acquisition of four-dimensional data sets (a two-dimensional diffraction pattern for each STEM raster position) in acceptable time becomes feasible, enabling reliable measurements of $\langle \mathbf{p}_\perp \rangle$ at a dense STEM raster.

2.3. Limitations of conventional DPC

In contrast to the considerations of the previous section, DPC STEM has as yet primarily employed segmented ring detectors to investigate, e.g., electric fields, which we refer to as *conventional* DPC in the following. Its applicability for the quantitative measurement of $\langle \mathbf{p}_\perp \rangle$ will be considered next.

We used the STEMsim software package [31] to simulate diffraction patterns of a GaN crystal in $[11\bar{2}0]$ orientation as a

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