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Measuring Atoms in Oxide Heterostructures by Quantitative Aberration-Corrected Transmission Electron Microscopy

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In recent years aberration-corrected transmission electron microscopy has demonstrated that the new research opportunities offered by this technique are meeting the growing demand of materials science for atomic-scale characterization of materials [1,2]. Genuine atomic resolution has become available allowing to measure individual atomic positions and lateral atomic shifts with a precision in the picometer range. On this basis the electron microscope has become a unique high-precision measurement tool allowing the direct correlation of macroscopic physical properties and of the results of *ab-initio* calculations with individual atomic position measurements. However, in order to do so the electron microscopic investigations have to become more quantitative, much beyond the level which appeared to be sufficient in pre-aberration correction times.

The goal is first of all to measure the set of individual atom positions in a sample, $\mathbf{X}=\{\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots\}$. This set denotes universal coordinates in the crystallographic sense, i.e. free of joint rotations or displacements. Of course we are not interested to measure the atom positions in a tilted sample since the respective coordinates are not universal. Although this may sound trivial, it is not so in reality: The precision of the new-generation optical instruments is substantially higher than the mechanical precision of even the best sample goniometers. Therefore, it is in general unavoidable that the results are affected by small residual sample tilts. We note that a (uncontrollable) tilting angle of only 0.5 mrad leads to a geometrical shift in a 10 nm thick specimen of 5 pm. However, this is not all: The atomic contrast maxima are affected by tilt not in a geometrical but in a quantum-mechanical way. The Bloch states appertaining to two different atom species (different nuclear charge number, different scattering potential) in an ordered crystal are reacting differently to tilt. As a result positions and distances measured taking the primary atomic-maxima data cannot be trusted.

An additional goal in modern transmission electron microscopy is to measure atomic-scale concentrations (occupancies). It has been shown that this is possible on a relative scale [3] (see also below). This requires the measurement of atomic intensity maxima. However, the values of these intensities are affected by sample thickness, by sample tilt and by aberrations in the optical part of the imaging process. The former two parameters are not known. The aberrations, including those adjusted on purpose for contrast (spherical and defocus aberration) are not known sufficiently accurately either. Detailed measurements have shown that in picometer microscopy one of the critical issues is the drift of the optical parameters [4]. The values measured by the Zemlin tableau technique hours or even minutes before image acquisition may be unreliable. This is clearly an entirely different scenario compared to that defining the (today inadequate) standards of the pre-aberration-correction era. Trustable picometer precision results can only be obtained by a quantitative complete and self-consistent inversion of the imaging process by quantum-mechanical and optical image calculations. While in the past qualitative simulation results were considered sufficient and the problem was considered solved when the exit-plane wave function was retrieved from a set of images which then was taken (employing in general without further justifica-

tion the projected potential approximation) as a direct representation of the atomic arrangement, this is no longer adequate.

Recently the ultimate that can be achieved to date in quantitative transmission electron microscopy was investigated studying the atom relaxations and the intermixing at the interface of a $LaAlO_3/SrTiO_3$ hetrostructure [5]. A primary set of data was collected by fitting two-dimensional Gaussians to the intensity distributions in images acquired in a TITAN 80-300 transmission electron microscope at 300 keV. A sub-set of these data describing the (known) atomic lattice away from the interface was taken as a 'template' in order to derive the values for the imaging parameters at the time of image acquisition. For this a first-approximation model of the template structure was taken as input for the Schrödinger equation searching for solutions as a function of specimen thickness and tilt. The image intensity distribution (still in the template area) was used as input for a reconstruction of the electron exit plane wave function taking spherical aberration, defocus aberration, two and threefold astigmatism, and coma as parameters. A quantitative fit of the theoretical to the experimental image intensity distribution was achieved. We note that this has to include the diffuse background intensity between the intensity maxima since this is much more sensitive to parameter changes than the maxima.

A critical issue in such calculations is the problem of the so called Stobbs factor which describes the fact that the measured image contrast (defined as the standard deviation of the intensity from the image mean intensity, normalized to one) is by typically a factor of three too low when compared to the calculated value. It could be shown that the bulk of the Stobbs factor originates from the particular transfer properties of the CCD camera as expressed by the modulation transfer function [6]. However, it was found that a fully quantitative matching on an absolute scale of the experimental contrast requires a convolution of the simulated image intensity with a Gaussian function in addition. The root-mean square (rms) width of this Gaussian is termed effective image spread, s. The value of s represents the radius of a blurring operation that has to be applied to the simulated image in order to establish an optimum absolute contrast match between simulation and experiment. This value was found to be quite small, i.e. 20 pm. It has to be pointed out that comparing a theoretical contrast calculation with a real experimental situation (with finite electrical lens current stabilities, mechanical vibrations, the effect of electron bombardment, radiation damage etc.) a perfect 1:1 match can hardly be expected without such a phenomenological factor.

After the imaging parameters, the actual values of specimen thickness and tilt and all the aberrations prevailing at the time of image acquisition were established, the atomic interdiffusion and picometer-range atom relaxations close to the interface could be measured with optimum precision. This is the first case where absolute-scale contrast matching was achieved. Furthermore absolute occupation data and picometer precision position data could be measured simultaneously in transmission electron microscopy in the same position of the sample for the first time.

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