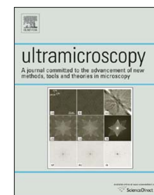
Ultramicroscopy 170 (2016) 35–42

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



When does atomic resolution plan view imaging of surfaces work?

Pratik Koirala [a], Yuyuan Lin [a], Jim Ciston [b], Laurence D. Marks [a,*]

[a] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA
[b] National Center for Electron Microscopy, The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

ARTICLE INFO

Article history:
Received 6 April 2016
Received in revised form
7 July 2016
Accepted 5 August 2016
Available online 6 August 2016

Keywords:
Transmission electron microscopy
Plan view imaging
Surface reconstruction

ABSTRACT

Surface structures that are different from the corresponding bulk, reconstructions, are exceedingly difficult to characterize with most experimental methods. Scanning tunneling microscopy, the workhorse for imaging complex surface structures of metals and semiconductors, is not as effective for oxides and other insulating materials. This paper details the use of transmission electron microscopy plan view imaging in conjunction with image processing for solving complex surface structures. We address the issue of extracting the surface structure from a weak signal with a large bulk contribution. This method requires the sample to be thin enough for kinematical assumptions to be valid. The analysis was performed on two sets of data, c(6 × 2) on the (100) surface and (3 × 3) on the (111) surface of $SrTiO_3$, and was unsuccessful in the latter due to the thickness of the sample and a lack of inversion symmetry. The limits and the functionality of this method are discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The challenge of extracting a signal with low intensity from a projection with other strong signals has always been pertinent to the field of signal processing. A similar challenge exists in the surface science community to extract the surface structure from one with a large bulk component. Several techniques have been developed both from the theoretical and experimental fronts to address this issue. For conducting materials and simple unit cells, low-energy electron diffraction (LEED) is a very powerful approach [1–6], particularly when complemented by atomic resolution scanning probe methods [4,7–23]. Transmission electron diffraction (TED) [24,25] in unison with direct methods [26–29], X-ray scattering studies [29–31], reflection high energy electron diffraction (RHEED) [20,32,33] and recently high resolution secondary electron microscopy (HRSEM) [34] have also been effectively used to study surface structures. In many cases, these methods are complementary.

With more complex reconstructions and also insulators, many of these techniques have very severe limitations. This is particularly relevant for oxide materials which have an abundance of surface reconstructions; even the prototypical perovskite material $SrTiO_3$ has highly complex surface structures [1,2,4,6,9,12–14,16,17,19,21–25,27,29,34–37]. The surfaces of these oxides are of prime importance as many phenomena occur at the surface. For instance, the 2D electron gas [38,39] at the $LaAlO_3/SrTiO_3$ interface is a direct consequence of the interfacial structures of the two oxides. This paper presents plan view high resolution transmission electron microscopy as a viable approach for imaging complex surface structures and the complexities therein.

Transmission electron microscopy (TEM) is a powerful technique for studying complex surfaces due to its high signal to noise ratio. TEM is used in two different modes, plan view [40–50] and profile view [48,49,51–71], with respect to the orientation of the sample surface. Imaging of nanoparticle surfaces is more suited to profile view imaging as has been demonstrated for gold and silver particles [51–63] and more recently for oxide nanoparticles [72,73]. It can give out of plane relaxations but includes little to no information along the beam direction. On the other hand, plan view imaging provides two-dimensional information in the plane of the surface, although no information normal to the surface, and has been previously used to solve two highly complex surface reconstruction [34,41].

In plan view one has surface structures on both top and bottom surfaces, and must extract the single surface information to move forward. The approach used to date is to assume a kinematical model and linear imaging theory, and consider the image after bulk removal to be a simple addition of the top and bottom surface [41] as:

$$\Psi(\mathbf{r})=1+\boldsymbol{\sigma}[V(\mathbf{r})+V(\mathbf{d}-\mathbf{r})]$$

* Corresponding author.
E-mail address: l-marks@northwestern.edu (L.D. Marks).

http://dx.doi.org/10.1016/j.ultramic.2016.08.001
0304-3991/© 2016 Elsevier B.V. All rights reserved.

$$I(\mathbf{r})=1+\int \boldsymbol{\sigma} T(u)\left\{V(u)+V^{*}(\mathbf{u})\exp(2\pi i\mathbf{d}.\,\mathbf{u})\right\}\times\exp(-2\pi i\mathbf{u}.\,\mathbf{r})du+\eta(\mathbf{r})$$

where, V($\mathbf{r}$) and V($\mathbf{d}-\mathbf{r}$) are the potentials of the top and bottom surfaces respectively, d is the in plane translation vector between the top and bottom surfaces, $\boldsymbol{\sigma}$ is the relativistic interaction constant, T($\mathbf{u}$) accounts for the microscope parameters and $\eta(\mathbf{r})$ is the noise in the image. For completeness, we note that without the bulk component this is not a true "image" of the surface, rather a surface sensitive difference closer to a difference map in a conventional crystallographic sense. One deals with the same type of signal when using direct methods for surfaces, and the loss of the bulk component in general has not proved to be an issue in interpreting the maps [26–29,74].

While this method can work [34,41], it ignores dynamical diffraction coupling with the bulk (e.g. [44,47,50,75–77]) and the limitations and functionality of this method have not been analyzed in detail to date. In this paper, we discuss this in more detail, showing that the method is only robust when the surface contains inversion symmetry.

2. Methods

2.1. Sample preparation

Self-supported single crystal samples were prepared from bulk (100) and (111) $SrTiO_3$ substrates purchased from MTI Corporation (Richmond, CA). They were cut into 3 mm discs using an ultrasonic cutter, mechanically thinned to a thickness of ~100 μm using silicon carbide sandpaper, then dimpled with a Gatan 656 Dimple Grinder and 0.5 μm diamond slurry until the thickness at the center was ~30 μm. The samples were then washed with de-ionized water, soaked in acetone overnight and finally cleaned with methanol. The samples were then Ar^{+} ion milled to electron transparency using a Gatan Precision Ion Polishing System (PIPS) starting at an energy of 5 keV and milling angle of 10°. The ion energy and milling angle were gradually brought down to 3 keV and 6° respectively for final polishing and surface cleaning.

The samples were then annealed in flowing dry oxygen at 1050 – 1200 °C for 10 h in a quartz tube furnace. Both samples were baked in air at 300–500 °C for 1–4 h directly before the imaging experiments.

2.2. Imaging experiments

High Resolution TEM (HRTEM) experiments were performed on the TEAM 0.5 instrument (FEI Titan-class) at the National Center for Electron Microscopy (NCEM). The (100) sample with c(6 × 2) surface reconstruction was imaged at an accelerating voltage of 80 kV with an energy spread of 0.1 eV, 0.2 mrad convergence angle, 1.4 nm defocus spread and the aberration corrector tuned to balance C_3 against the uncorrected residual C_5 ($C_3=-16$ μm, $C_5=6$ mm). A focal series of 41 images was acquired at defocus steps of −1.05 nm. The focal series was used for determining the appropriate defocus to maximally enhance bulk subtraction.

The (111) sample with the (3 × 3) surface reconstruction was imaged at an accelerating voltage of 300 kV with an energy spread of 0.1 eV, 0.15 mrad convergence angle, 0.7 nm focal spread and the aberration corrector tuned to balance C_3 against the uncorrected residual C_5 ($C_3=-15$ μm, $C_5=6$ mm). A focal series of 41 images was acquired at defocus steps of −1.72 nm. No significant beam damage was observed in either of the two samples.

2.3. Simulations and post processing

High resolution TEM simulations were performed using MacTempasX Code [78] with experimental parameters and the post processing of both experimental and simulated images (see Supplemental information for the Crystallographic Information File c (6 × 2).cif), bulk removal and correction for top and bottom surface translation, was done using the in house open source code Electron Direct Methods (EDM) [79].

3. Results

High resolution plan view images acquired on two sets of reconstructions on the (001) and (111) surfaces from the same material, $SrTiO_3$, were subject to image analysis outlined in the methods section. Two model cases, one demonstrating a successful use of the aforementioned method and one a failure, are discussed to present the functionality of the analysis pertaining to two important parameters:

1. Sample thickness, discussed with c(6 × 2) on $SrTiO_3$ (001) and the (3 × 3) on SrTiO3 (111) as a model cases
2. Symmetry, discussed with (3 × 3) on $SrTiO_3$ (111) as a model case

3.1. c(6 × 2) surface reconstruction on $SrTiO_3$ (001) surface

High resolution plan view images in a focal series of 41 images were processed using the method outlined in the previous section. The consistency of experimental parameters and defocus were cross checked with simulations from MacTempas. Removal of bulk was done by taking a fast Fourier transform of an image and removing all linear combination of the bulk reciprocal lattice vectors. An unavoidable consequence of this is that the overlapping surface and bulk spots are removed so this is strictly a difference map as mentioned earlier. This was followed by the separation of the top and bottom surface. The resulting image from one of the experimental images acquired at a defocus of 6 Å is given in Fig. 1 along with the corresponding DFT relaxed structure.

In the limits of linear imaging theory, the resulting image can be directly correlated to the intensity of different atomic sites at the surface. The corresponding structure of the c(6 × 2) surface reconstruction (see Fig. 1) is consistent with atomic resolution secondary electron images [34] as well as x-ray and scanning tunneling microscopy [4] data. The details of the actual structure and surface chemistry are discussed elsewhere [34].

It is evident from Fig. 1 that the method used for the extraction of surface structure is effective. The correlation between the actual structure in Fig. 1b and the relative intensities in the experimental image is strong. The position of Sr atoms appear relatively brighter on the experimental image, consistent with Sr being heavier than Ti and O. Separation performed on all 41 images in the focal series show strong intensity at the Sr position with small modulations in the rest of the image.

Simulations were performed using MacTempas with the structure in Fig. 1(b) (Supplementary information c(6x2).cif) for varying bulk thicknesses. The results of the analysis performed at four different thicknesses and hence different bulk contributions and dynamical scattering are given in Fig. 2. Since this method relies on linear imaging theory, there is a critical thickness beyond which the approximations are no longer valid.

Surface signal is highly sensitive to the thickness of the sample. Images simulated at 4.15 nm and 5.32 nm thickness show a strong surface signal evident after bulk subtraction. However, the images simulated at 6.49 nm and 7.66 nm thickness show weak surface

Download English Version:

https://daneshyari.com/en/article/1677341

Download Persian Version:

https://daneshyari.com/article/1677341

Daneshyari.com