

## Atomic resolution transmission electron microscopy of surfaces

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A brief overview of transmission electron microscopy as it applies specifically to obtaining surface crystallographic information is presented. This review will encompass many of the practical aspects of obtaining surface crystal information from a transmission electron microscope, including equipment requirements, experimental techniques, sample preparation methods, data extraction and image processing, and complimentary techniques.

### I. INTRODUCTION

The atomic scale structures of crystalline surfaces play an important role in the overall properties of materials systems, especially those relating to heterogeneous catalysis, thin film growth, and the increasingly miniaturized world of micro electrical mechanical systems (MEMS). Nanoscale engineering of materials has become commonplace, and as technologies begin to emerge on smaller and smaller length scales, surface properties become increasingly more important relative to those of the bulk.

The loss of coordination at the surface and the so-called “dangling bonds” that result increase the surface free energy and provide a driving force for the reconstruction of surfaces whose structure cannot be predicted from bulk thermodynamic arguments. This inability to predict the structure of surfaces a priori has necessitated a field of study devoted entirely to experimentally determining the surface atomic structure of materials. Only through the complete knowledge of the surface structure of materials can one truly understand the nature of the processes that play out on them.

Since even in high-vacuum conditions surfaces are contaminated in seconds,<sup>1</sup> to study the atomic structure of surfaces in a truly meaningful way ultrahigh vacuum (UHV) techniques are required. Although some surface reconstructions are stable in air (oxides, noble metals), hydrocarbons, moisture, and other atmospheric contaminants adsorb onto these surfaces and must be avoided. Finally, some reconstructions (those of semiconductors, for example) are stable only in UHV environments, so if

one wishes to study these often interesting systems, in situ UHV techniques are required.

The most common UHV techniques for studying the atomic scale crystal structure of surfaces in real space include scanning tunneling microscopy (STM), transmission electron microscopy (TEM) including high-resolution electron microscopy (HREM), and scanning transmission electron microscopy (STEM). Several common reciprocal space techniques include low-energy electron diffraction (LEED), grazing incidence x-ray diffraction (GIXD), transmission electron diffraction (TED), and reflection high-energy electron diffraction (RHEED). Comparative reviews of the above techniques<sup>2,3</sup> and their application to surface crystallography can be found in Refs. 4 and 5.

Of the above mentioned methods, high-voltage transmission electron microscopy methods (TEM, TED, HREM) have proven indispensable to the surface crystallographer as they allow for the capture of both real and reciprocal space crystallographic information from a single area of the specimen at subatomic scale resolution. Parallel data capture can lead to real-time investigation of surface phenomena, and recently, these techniques have been used to extract not only surface atomic positions but also the surface charge density.<sup>6</sup> No other technique proves as versatile. With the recent advent of so-called environmental cell<sup>7,8</sup> and aberration corrected TEMs,<sup>9</sup> this technique has proven even more so.

In this review, we will discuss aspects of extracting surface information from transmission electron microscopy experiments. We will cover practical aspects such as the equipment and hardware required, experimental techniques used, and sample preparation methods. We will also consider post-experimental computational aspects such as image processing, simulation, and direct methods (see Sec. VI for an overview of this technique).

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Finally, we will highlight some complimentary techniques used to supplement the information gained from the in situ microscopy.

## II. INSTRUMENTATION

An excellent review of the historical development of UHV-TEM hardware has recently been written by Poppa.<sup>10</sup> We will not attempt to duplicate this thorough effort here but instead will discuss the practical hardware requirements and current state of the art equipment used in investigating surface crystallography.

Generally, in situ TEM requires design and integration of an experimental laboratory inside of the microscope column. For example, high-temperature processes require a heating stage, deformation processes require a tensile (or compression) stage, nanocrystal and thin film growth studies require integration of gas handling equipment into the microscope column,<sup>11,12</sup> and chemical reaction studies often require full-blown environmental cell microscopes. When performing in situ TEM of surfaces, however, the critical factor is to have in situ transfer between the UHV sample preparation chamber and the UHV microscope, since it is not (yet) feasible to have integrated surface sample preparation equipment inside of the microscope column.

The required sample preparation equipment consists of at least some kind of ion sputtering gun for both cleaning samples thinned ex situ and for thinning samples to be prepared in situ, and a heating mechanism for annealing out the damage from ion milling, equilibrating the surface, and forming a surface reconstruction. Of course these are rather minimal requirements, and the specifics of the systems investigated may require additional hardware, such as an evaporation source for depositing adatoms in adatom-induced reconstructions or a chamber for chemical cleaning ( $O_2$  annealing of oxides). Researchers at Northwestern University (Evanston, IL) have solved the problem of safe and reliable UHV sample transfer, which makes sample preparation an in situ technique, by making samples from self-supporting single crystal specimen held inside of a rigid 3-mm ring made of Mo, BeCu, or even  $Al_2O_3$ . In this configuration, the samples can remain clean and intact throughout the investigation.

In addition to the atomic structure information provided by the UHV-TEM, many researchers wish to learn about the chemical aspects of the surfaces under investigation to build up a more complete picture. In fact, current state-of-the-art UHV-TEMs are often interfaced via UHV to a complement of peripheral surface science and sample treatment chambers for true in situ analysis. These elaborate setups provide for UHV sample transfer to prevent contamination and allow for the complete chemical characterization of specimen under investigation.

Techniques such as scanning tunneling microscopy (STM), which is itself a surface sensitive technique and very powerful in its own right, can be used in tandem with microscopic techniques to investigate surface atomic structure as they can provide surface information in real space at atomic resolution. X-ray photoelectron (XPS) and Auger electron (AES) spectroscopies are other inherently surface sensitive techniques, which can complement results obtained in the microscope. They can tell the surface crystallographer the type of the species on the surface of the specimen and may even hint at the oxidation state, which is useful when investigating phenomena such as heterogeneous catalysis at the atomic scale.

At Northwestern University, a Hitachi UHV-H9000 based system<sup>13</sup> called SPEAR (Sample Preparation Evaluation Analysis and Reaction) has successfully integrated a full specimen preparation facility (ion milling, sample heating and cooling) and UHV-HREM in addition to XPS, AES, and scanning electron microscopy (SEM) (Fig. 1). The entire system is also integrated to two thin film deposition chambers, capable of direct current (dc) magnetron sputtering and ion beam deposition. Additionally, a gas treatment cell (McAllister Technical Services, Coeur d'Alene, ID) has recently been added which is capable of treating samples in nearly any gaseous atmosphere at temperatures up to 1200 °C and pressures ranging from UHV to atmospheric (Fig. 2).

A very versatile UHV-HREM based system (JEOL JEM-2000VF) is the UTSICS (UHV-TEM-STM-Integrated Characterization System) at the National Institute for Materials Science in Tsukuba, Japan. This

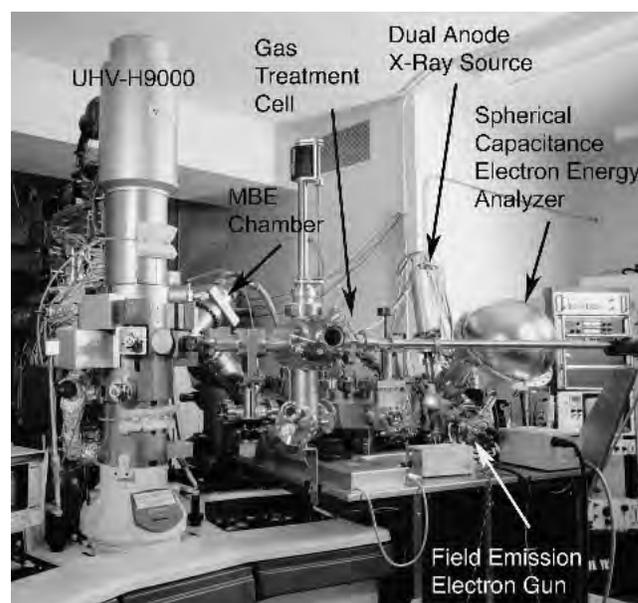


FIG. 1. Hitachi-UHV-H9000 based SPEAR system at Northwestern University showing components attached to roundhouse UHV sample transfer chamber.

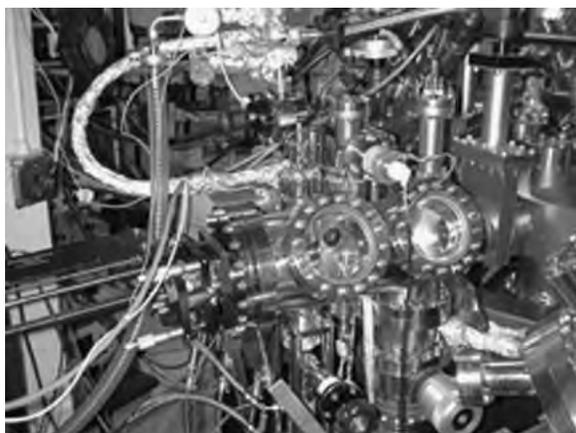


FIG. 2. Close-up view of the gas treatment cell used to anneal and treat TEM samples for in situ study. The cell has provision for annealing in gasses at pressures ranging from UHV to atmospheric and temperatures up to 1200 °C.

system, in addition to a host of surface characterization equipment similar in nature to SPEAR, has the microscope specimen chamber designed for in situ metal deposition capable of  $5 \times 10^{-8}$  Pa background pressure.<sup>10</sup> In addition, this system incorporates STM capability for real-space atomic resolution surface imaging.

### III. EXTRACTING SURFACE INFORMATION FROM THE TEM

When one thinks about experimental techniques for investigating surfaces, TEM is not often the first thing that comes to mind. In fact, for many years, many traditional surface scientists did not even consider TEM a viable technique because by far the majority of all this work had been (and continues to be) performed to investigate bulk materials properties. The fact is, TEM is inherently surface sensitive and both experimental<sup>14</sup> and computational<sup>15,16</sup> methods have been developed that have proven quite robust for extracting useful information from the typically weak surface signal. Historically, the first true application of UHV TEM to surface studies was the investigation of the anomalous superstructure on (111)Au and Pd nucleus formation on (111)Ag surfaces by Yagi et al.<sup>17</sup> In a well known work, TEM (TED) was used by Takayanagi et al. to solve the Si(111)- $7 \times 7$  dimer adatom stacking fault (DAS) surface structure and end the long dispute which existed among surface scientists.<sup>18,19</sup> Since the first efforts at determining surface structure via TEM methods, many systems have been investigated including semiconductors,<sup>20</sup> metals on semiconductors,<sup>21,22</sup> and oxides.<sup>6,23</sup>

In situ TEM of surfaces is a general term encompassing a wide variety of techniques from which a host of properties can be explored. Surface morphology, surface unit cell dimension, surface atomic positions, and finally

surface charge density can all be obtained from a transmission electron microscope experiment.

Determination of surface morphology is a relatively simple experiment. In fact, this type of experiment was the first in situ investigation of surfaces via TEM when Cherns looked at atomic-level steps on the (111) surface of gold.<sup>24</sup> The standard low-resolution TEM diffraction contrast imaging modes [bright field (BF)/dark field (DF)] in plan-view can be used with great success, revealing surface step bunching, terrace formation, and faceting (Fig. 3). Indeed, these modes can also reveal the condition and quality of the surface being investigated, as one can easily distinguish defects such as dislocations, voids (Fig. 4), and bending in the sample foil.

If higher resolution is needed, weak-beam darkfield and phase contrast (HREM) techniques can be used to effectively image surface topography. In the weak beam method, images are formed using a first order reflection while the bright Kikuchi line lies outside of the third order reflection<sup>25</sup> and have higher resolution than conventional DF imaging. Lehmpfuhl and Warble<sup>26</sup> used this technique to image atomic surface steps on the surface of MgO platelets with great success. Focus-dependent phase contrast (HREM) imaging is also useful for imaging surface morphology, where atomic level steps can be readily distinguished. Surface contrast can be enhanced by tilting the sample off-zone, as first demonstrated experimentally by Zhang on the (111) surface of gold<sup>27</sup> and further corroborated with experiment and simulation of the (111) surface of Si.<sup>28</sup>

Like LEED, transmission electron diffraction can easily be used to determine the surface unit cell dimensions. Again, this is a relatively simple experiment in which a reasonably thin specimen is examined using either standard selected-area diffraction (SAD) or even focused

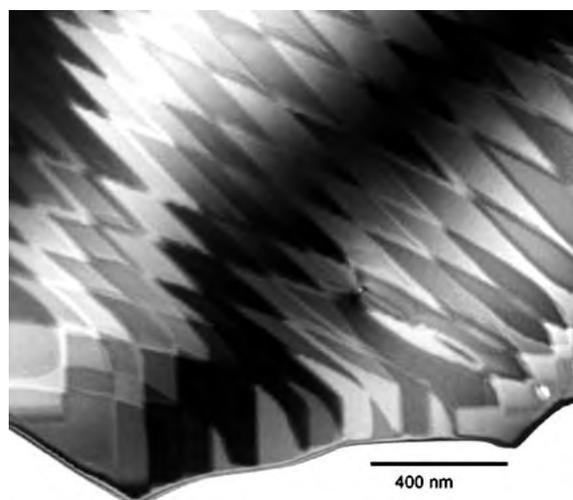


FIG. 3. Bright-field TEM image of the MgO (001) surface after annealing in oxygen for 3 h. This image of a nicely equilibrated surface shows surface step bunching, terrace formation, and faceting.

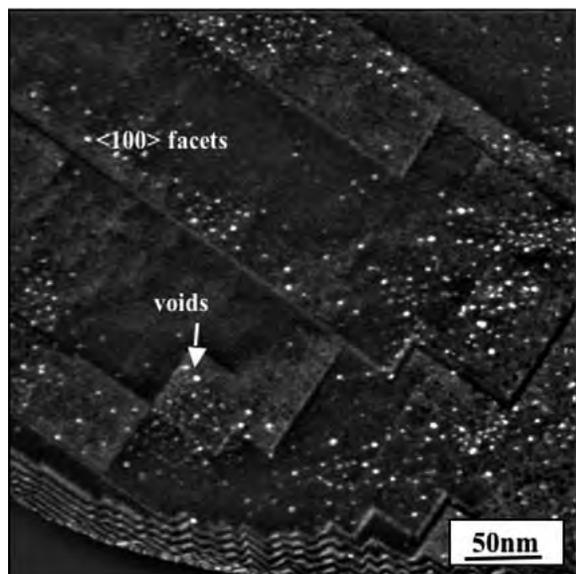


FIG. 4. Dark-field TEM image of the  $\text{SrTiO}_3(001)\text{-}c(6 \times 2)$  surface reconstruction showing voids in the sample foil, which are an artifact of ion milling. Thickness fringes near the hole (lower left corner), as well as surface terraces and step bunching can also be seen.

probe diffraction. Due to dynamic effects when the specimen is aligned along a crystallographic zone axis, often to record the relatively weak surface spots, the specimen must be tilted far off the zone axis (Fig. 5) to a more kinematical diffraction condition, as Takayanagi did to resolve the  $\text{Si}(111)\text{-}7 \times 7$  spots. This benefits the extraction of surface crystallographic information in two ways. First, due to the truncation of bulk rel-rods in reciprocal

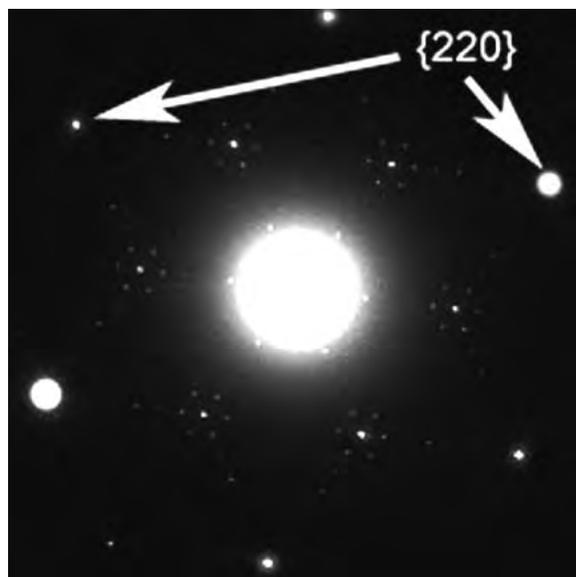


FIG. 5. Experimental TEM diffraction pattern of the  $\text{Si}(111)\text{-}7 \times 7$  structure prepared in situ inside of the SPEAR system at Northwestern. By tilting off the zone axis, the surface spots can be resolved readily, and in addition, minimal dynamical effects contribute to the diffraction pattern.

space,<sup>29</sup> tilting off zone results in an increase in the intensity of the surface signal relative to that of the bulk. When it is considered that surface signals are typically on the order of  $10^4$  weaker<sup>30</sup> than bulk signals, any enhancement is beneficial. Second, tilting off the zone axis reduces dynamic effects, which can complicate the quantitative analysis of diffraction patterns for phase recovery via direct methods, which work best in the kinematical approximation.<sup>31</sup>

Knowledge of the surface unit cell dimension is the first step in determining the surface atom positions. This is accomplished with a combination of TED and direct methods, which are often augmented by HREM, DF imaging, and associated spectroscopic techniques such as Auger electron spectroscopy and XPS. A more thorough review of this process can be found in the review by Subramanian and Marks.<sup>5</sup>

Very recently, the TEM has proven itself yet again as a novel surface technique when Subramanian et al.<sup>6</sup> were able to experimentally refine valence charge density from TED data to extract the surface charge density of the  $\text{MgO}(111)\text{-}\sqrt{3} \times \sqrt{3}\text{-}R30^\circ$  reconstruction (Fig. 6). This represents the first time that valence charge density has been determined experimentally from TED data, and the results agree well with empirical bond-valence estimations.

#### IV. FIVE SURFACE IMAGING MODES

Most reviews on the subject classify imaging into one of two modes based on the orientation of the sample relative to the electron beam. In the interest of consistency, we will do the same here. An excellent review of surface imaging by Cowley can be found in Ref. 3.

##### A. Plan-view imaging

Plan-view imaging is the name of the technique when samples are viewed parallel to the surface normal

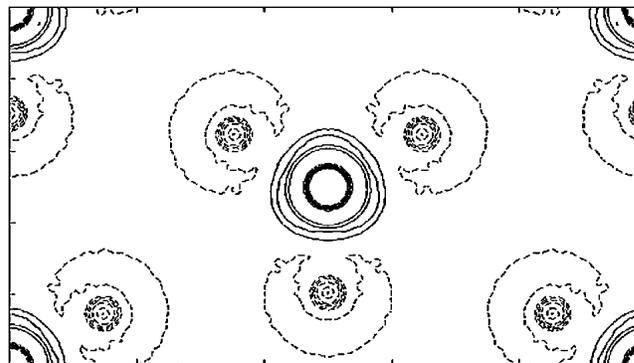


FIG. 6. Experimental deformation charge density map (surface-bulk) projected onto the (111) plane of  $\text{MgO}$ . The contour interval is  $1.5 \times 10^{-4} e^-/\text{\AA}^2$  with the continuous and dashed lines representing positive and negative contours, respectively. The centered unit cell is shown in the figure with the atop Mg atom at the center surrounded by three second-layer O atoms. The surface Mg atom has excess  $e^-$  density compared to bulk Mg atom in  $\text{MgO}$ . For more details see Ref. 6.

direction, the transmitted beam having interacted with the entirety of the sample. Surface information is relatively easy to obtain (and interpret) in this configuration, and all standard imaging modes including BF, DF, and HREM can be used. When viewing surfaces in conventional HREM mode, whether on or tilted off zone, the bulk lattice constant dominates the contrast, top-bottom effects occur, and image processing is required. However, after careful processing, surface structure can be often resolved with great detail. In fact, the dimers in the third layer of the Si(111)- $7 \times 7$  DAS structure (Fig. 7) have been resolved using conventional HREM in plan-view mode.<sup>32</sup>

High-resolution DF mode, in which an image is formed by putting a small objective aperture around a set of bulk-forbidden diffracted beams, is useful for obtaining information about surface domain and terrace structure.

## B. Profile view imaging

Profile imaging is the name given to the technique of viewing atomic columns parallel to the surface of interest, or side-on. First used to study the Au(110)- $2 \times 1$  surface<sup>33</sup> and small particles,<sup>34</sup> this technique has been successfully extended to semiconductors<sup>35,36</sup> and superconductors.<sup>37</sup> Imaging in this mode must be done carefully, as the surfaces under observation may not be thermodynamically equilibrated or representative of extended two-dimensional structures. In addition, Fresnel effects can complicate interpretation and the proper conditions of defocus are required.<sup>38</sup> If these drawbacks

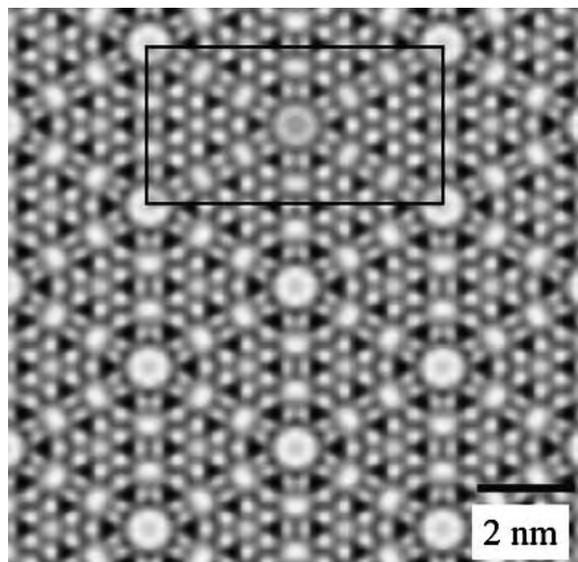


FIG. 7. Experimental and simulated (inset) HREM image of the Si(111)- $7 \times 7$  structure. The experimental image has been rotationally and translationally averaged<sup>32</sup> and clearly shows all of the components of the DAS structure including the buried dimers in the third layer which cannot be resolved in an STM image of this surface.

are understood, however, this mode is extremely useful as it is a way to obtain three-dimensional information (relaxations along the surface normal) from a TEM experiment.

## V. SAMPLE PREPARATION

To perform in situ TEM of surfaces, there are stringent cleanliness requirements that do not apply to investigations of bulk materials. Not only do adsorbent molecules in ambient atmosphere provide a source of contamination, often the sample preparation process itself is a significant source. Contamination can have one of two effects on a sample prepared for surface analysis: first, it can change chemically and crystallographically the very surface being investigated, and second it can interfere with image acquisition as in the case of carbonaceous deposits in HREM and contribute to diffuse scattering in a diffraction experiment. In the case of semiconductor materials (Si, Ge, for example) and any material with a high sticking probability, where samples inevitably have to be prepared under in situ conditions, this is not such a problem. When prepared in situ, samples undergo a cleaning (ion bombardment) and annealing step, which is done in UHV with little chance of adsorbent contamination (providing the vacuum is good and the specimen chamber is clean, of course) after introduction of the pre-thinned foil. For samples which are air stable and/or prepared ex situ, such as some oxide and noble metal reconstructions, contamination can come from nearly anything in which the sample comes in contact. We have found that sample contamination from the annealing boat, furnace tube, polishing media, and ion bombardment equipment can all have a deleterious effect on surface cleanliness. To alleviate these problems, we have found it useful to thoroughly clean annealing boats, gas handling equipment, and furnace tubes in aqua regia solution (followed by a de-ionized water rinse) before annealing. To lessen contamination associated with mechanical thinning compounds, we use only water soluble media (when appropriate), and ultrasonically clean all samples after polishing. Avoiding contamination from ion-bombardment thinning and cleaning has proven to follow directly from having well aligned and well maintained equipment. For example, when cleaning samples in situ, care must be taken to avoid cross-contamination from accidentally milling the sample holder ring. In the SPEAR system, we have found that the best way to avoid this contamination is to mill very small regions while simultaneously imaging the area being milled (Fig. 8) using a secondary electron detector.

To remove damage from ion bombardment (which includes residual stress, non-stoichiometry, and roughness) samples must be subject to an equilibrating anneal, whether they are prepared in or ex situ. In oxides, we

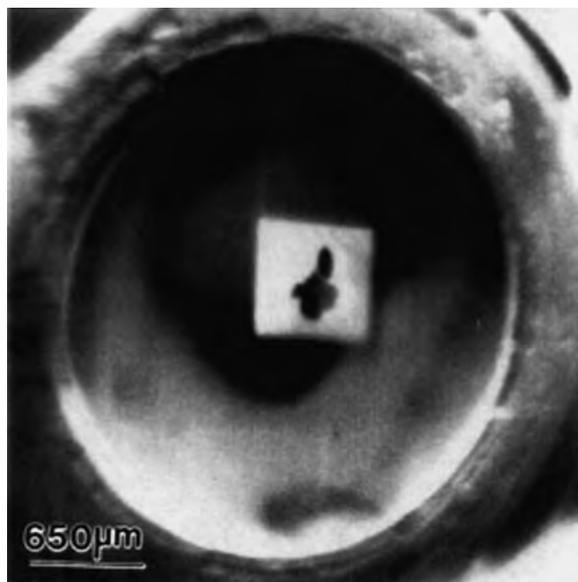


FIG. 8. Secondary electron image from an ion-milled TEM sample prepared in the SPEAR system. The electron transparent region near the irregularly shaped hole in the specimen foil (center) has been milled. The milled region appears lighter in contrast and is shaped as a square, which is a result of the rastering of the ion beam. Milling of the specimen ring, which is a significant source of contamination for in situ TEM studies, has clearly been avoided.

have found that annealing near temperatures which activate surface diffusion ( $0.3\text{--}0.5 T_m$ ) in the proper gaseous environments serve to equilibrate, order, restore stoichiometry, and anneal out nearly all defects associated with ion milling (voids in the near-hole region are often an artifact that cannot be annealed out). In the case of samples prepared in situ, however, it is sometimes difficult if not impossible to remove damage associated with ion beam cleaning. In these cases, there is a trade-off between annealing out defects and coarsening of the sample, which has been seen on noble metal surfaces cleaned using Xe ions.<sup>39,40</sup>

## VI. EXTRACTING SURFACE INFORMATION

All of the above experimental methods for imaging and recording surface information in a transmission electron microscope require some degree of post-experimental processing to effectively extract the surface contribution. Even in the case of off-zone phase contrast imaging, where the bulk contribution is diminished and contrast from the surface layer is enhanced,<sup>29</sup> filtering is still required to remove (shot) noise and the top-bottom effect and produce a high-quality image.

We have found that to avoid the dangers of selective Fourier space filtering, Wiener-filter methods (in particular random-phase parametric versions) are the most robust for removing noise from HREM images.<sup>41</sup> These

type of filters exploit the premise that the phase of the noise is random and can enhance the signal-to-noise ratio by up to a factor of 10. In addition to the Wiener filter, HREM images often need to be translationally and/or rotationally averaged (numerical inversion) to deconvolute the image contribution from the top and bottom surfaces of the foil. These methods have been applied quite successfully in a number of cases including the Si(111)- $7 \times 7$ ,<sup>32</sup> Si(111)- $5 \times 2$  Au,<sup>21</sup> and SrTiO<sub>3</sub> (001)- $2 \times 1$ .<sup>23</sup> More details of this method can be found in the original papers (above) as well as Ref. 42. To date, only average information has been attainable due to the relatively low signal-to-noise level with conventional electron sources, but there is no reason why local atomic-scale information cannot be achieved with some of the more modern electron microscopes with lower aberrations and brighter electron sources.

In the case of transmission electron diffraction, a more reliable and robust method of obtaining the surface structure information is found in a set of techniques for phase recovery called direct methods (DM). In a diffraction experiment, the phases of the diffracted beams are lost since only the intensity, or  $|F|^2$ , can be measured. This is well-known as the “phase problem” in crystallography, and is a fundamental tenet of diffraction. If the both the phases and amplitude (or the square root of the measured intensity) of diffracted beams were known, then the structure factor would be completely described and a simple Fourier inversion of the data would yield a scattering potential map. It is only with the combination of both phase and amplitude information that the data can be inverted and a scattering map obtained. A full explanation of electron DM techniques for surfaces are beyond the scope of this paper, but several thorough treatments can be found in Refs. 15, 16, and 43, while more cursory treatments can be found in Refs. 5 and 44. Starting out with a TED pattern, the intensities of the surface diffraction spots can be measured easily and consistently.<sup>14</sup> DM serves to approximate the missing phases by exploiting a priori probability relationships, which must exist when scattering comes from atom-like features. Together with the measured amplitude, these approximated (recovered) phases can be used to create maps (Fig. 9) of the scattering potential (charge density for x-rays and electrostatic potential for electrons). The a priori relationships make no assumption of the scattering potential but only insist in various ways that it must come from atom-like features, must be positive, and finally must be localized to the near-surface region. These methods have proven extremely powerful and the list of surface structures solved using DM is quite extensive and includes semiconductors and, recently, oxides, as mentioned above.

In the case of both HREM and diffraction experiments, image simulation is crucial to verifying the observed results (Fig. 7, inset). The Multislice algorithm is the

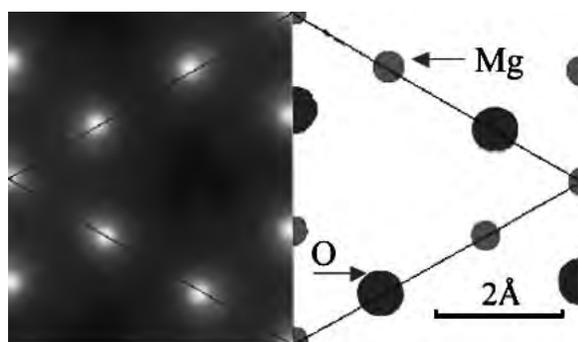


FIG. 9. Structure solution for the  $\text{MgO}(111)\text{-}\sqrt{3} \times \sqrt{3} \text{ R}30^\circ$  surface reconstruction: (a) Output from direct methods and (b) schematic diagram of the same surface after replacing charge density with atoms. Large dark circles correspond to O atoms and small light circles correspond to Mg atoms.

common technique used to simulate HREM images of bulk as well as surface structures to verify that the observed contrast has indeed come from the proposed surface layer. In the case of structure solution from TED and DM, a full (kinematical) simulation of the proposed structure will confirm that it matches the experimental diffraction data to the appropriate  $\chi^2$  or R-factor criterion.<sup>16</sup>

In addition to transmission electron-microscopy techniques for the in situ investigation of surfaces, a host of related surface science techniques can be used to provide complimentary information that is often needed to supplement, enhance, and corroborate the microscopy

data. These techniques include but are not limited to XPS, AES, STM, and computational density functional (DFT) methods. These experimental methods (XPS, AES, and STM) are often available to the in situ microscopist by the attachment to the microscope of clean UHV surface science chambers (see Sec. II above for a more thorough treatment of these systems and their capabilities related to in situ TEM of surfaces).

Recently, DFT methods have proven to be a useful addition to the solution of surface structures via TEM, where they have been shown to be helpful in further optimizing the atomic positions of the  $\text{SrTiO}_3(001)\text{-}2 \times 1$  and  $c(4 \times 2)$  surface reconstructions solved by a combination of DM and HREM.<sup>23,45</sup> In these cases, plane-wave pseudo-potential calculations were able to not only confirm the  $x,y$  positions of the surface atoms from the DM analysis but also relax and refine the structure in the  $z$ -direction to obtain a full three dimensional solution which cannot be gained from a TEM experiment alone. In addition, near-minimal basis linear combinations of atomic orbitals (LCAO) DTF calculations were able to provide chemical information in the form of partial charges. In the case of the  $c(4 \times 2)$  structure, the DFT geometry optimization codes were also able to resolve the ambiguity that existed as to how the surface reconstruction was registered to the bulk lattice (Fig. 10). Obviously, DFT methods are proving themselves to be instrumental to the complete understanding of how surfaces behave as chemical entities and are becoming indispensable to the surface crystallographer.

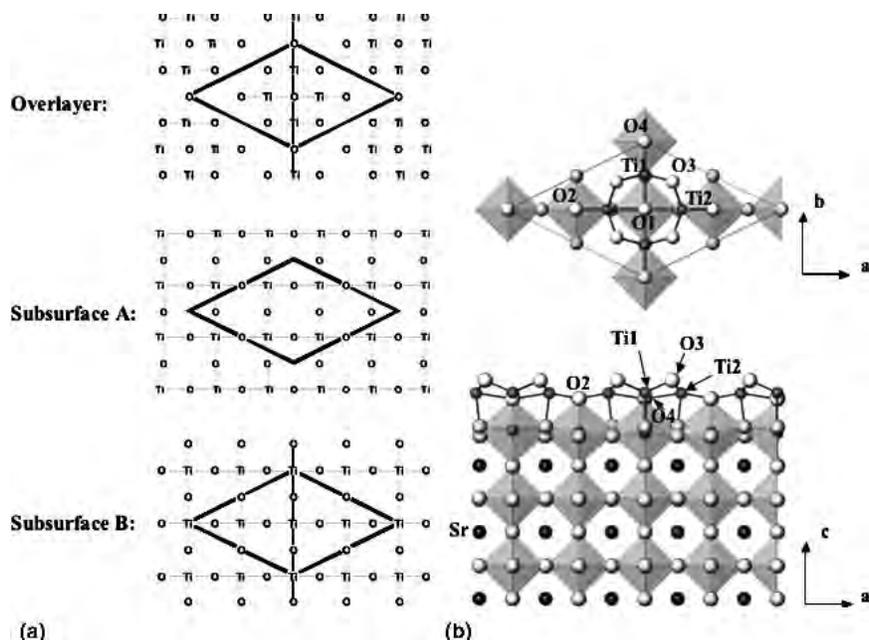


FIG. 10. Atomic structure models of the  $\text{SrTiO}_3(001)\text{-}c(4 \times 2)$  unit cell. (a) Schematic diagram showing the  $c(4 \times 2)$  reconstruction and the two possible registries on the bulk and (b) three-dimensional (from plane-wave pseudopotential calculations) model of the low energy configuration in plan and side view. DFT calculations<sup>45</sup> were able to differentiate between the two and show that subsurface B is lower in energy by  $0.53 \text{ J/m}^2$ .

## VII. CONCLUSION

High-voltage transmission electron microscopy is a viable tool for the in situ study of surfaces via UHV-pumped side chambers for sample preparation, reaction, and characterization. To date, metal, semiconductor, and oxide materials have been investigated with great success. When compared to scanning probe techniques, TEM has several distinct advantages. The first is that TEM probes the entire thickness of the sample, where electrons interact with the bulk of the crystal as well as the surface. This means a TEM image and diffraction pattern inherently contains information from the surface as well as the bulk. An AFM or STM image of a surface, in contrast, is representative of only the outermost layer. If a reconstruction extends down several layers [such as the Si(111)- $7 \times 7$ ], STM will see only the outermost of these and therefore is not providing the complete picture. Also, while HREM probes actual atomic positions (columns of atoms projected parallel to the electron beam), STM probes electron orbitals, where atomic structure information must be deconvoluted from electronic structure information.

There are some limitations to TEM techniques of surfaces, however, and these are by far dominated by sample issues. Because electrons interact very strongly with matter, samples for TEM must be thin and are therefore difficult to prepare and often very delicate. In addition, some samples (maximal-valent oxides in particular) suffer from electron beam irradiation damage, where the samples are damaged (or destroyed) during the course of study. Such damage processes can limit imaging, but are much less important for diffraction experiments where the electron flux (and damage rate) can be several orders of magnitude smaller.

TEM is its most powerful when combined with supplementary techniques such as AFM, STM, XPS, AES, and DFT. When using a combination of the above techniques, surfaces can be characterized nearly completely. This has great ramification for fields in which surfaces play an integral role such as thin film growth and heterogeneous catalysis.

## ACKNOWLEDGMENT

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