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Surface crystallography via electron microscopy

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Dedicated to Professor Fang-hua Li on the occasion of her 70th birthday

Abstract

The study of atomic structure of surfaces is fundamental to the understanding of electronic, chemical and mechanical properties of surfaces and numerous techniques have been developed to this end. Transmission Electron Microscopy techniques, namely transmission electron imaging (TEM) and diffraction (TED), due to their ability to provide structural information at very high resolutions, have emerged as powerful tools for the study of surface structure. In this article we review the experimental method alongside the various post-processing routines that are necessary to extract vital structural information from experimental data.

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1. Introduction

Atomic scale processes at surfaces dictate the macroscopic properties of solid surfaces and have been the subject of numerous theoretical and experimental studies. Many processes like thin film growth or catalysis are non-equilibrium kinetic processes and knowledge about the surface structure can provide valuable insight into their nature. The abrupt truncation of the bulk lattice at a surface results in dangling bonds that increase the surface free energy. In most cases these atoms can relax and/ or organize themselves into structures that have translational periodicities larger than those of bulk. This is more evident on low index surfaces since they have higher dangling bond densities. These reconstructions generally involve a few atomic layers and are accompanied by strain fields that decay exponentially into the bulk [1,2]. Reconstructions can be broadly divided into two classes: native and adatom induced, depending on the presence or absence of foreign species on the surface. Surface structures are classified by one of the 17 crystallographic plane groups since they possess only

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two-dimensional periodicity. The 2-D surface mesh generated by bulk truncation is the most natural co-ordinate system to describe the structure, and the reconstruction is described by its size and orientation relative to the primitive 1×1 lattice [3].

The biggest limitation to the study of surfaces is the requirement of stringent ultra-high vacuum (UHV) conditions. For a meaningful study of surface structure it is imperative that the specimen be prepared and observed in a controlled environment. Most semiconductor surface reconstructions are unstable except in UHV and even there they have a limited lifetime depending on the residual gases. The notable exceptions to the above rule are the reconstructions on noble metal surfaces [4] and oxides [5–7] that are stable at air. The only viable method is to design the original instrument to attain UHV conditions [8].

In this paper we discuss the various electron microscopy tools employed to study surfaces. The various experimental techniques commonly employed to study surfaces are discussed in Section 2. Section 3 deals with the image processing techniques for noise filtering and deconvolution of surface images, and the phase problem in surface crystallography and the various viable methods to tackle it are reviewed in Section 4.

2. Experimental techniques

Studies of surface structure date back to 1960's and since then a myriad of techniques have been employed to probe the nature of surfaces. These can be broadly divided into two categories: electron probe and photon probe techniques. Electron probe techniques such as transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), reflection electron microscopy (REM), low energy electron microscopy (LEEM) provide real space information at various resolutions while diffraction techniques like grazing incidence X-ray diffraction (GIXRD), transmission electron diffraction (TED), low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED) provide Fourier space information. In addition to the techniques listed above, various spectroscopic techniques are available to detect the chemical composition and electronic structure of the surface such as X-ray photoelectron spectroscopy (XPS), reflection electron energy loss spectroscopy and auger electron spectroscopy (AES). These techniques differ in geometry, resolution, sensitivity and the nature of the information derived. Among the electron probe techniques, the resolution obtainable in REM and LEEM is insufficient at present to resolve the atomic structure of the surfaces. RHEED is very sensitive to displacements normal to the surface and is primarily used as a tool to detect the surface topography in modern molecular beam epitaxy (MBE) systems. LEED is the most common technique for determining surface structures, but is complicated multiple scattering effects that require detailed calculation. In addition, there does not exist (at present) any method similar to direct methods (see later) for obtaining an initial approximate structure solution, so success is limited by the ability to guess something close to the correct structure. The weak nature of the interaction of X-rays with matter coupled with the low signal levels from surface makes conventional XRD a non-feasible technique for surface structure analysis. The advent of bright synchrotron sources and the use of grazing incidence have revived GIXRD as a viable surface characterization tool. The various scanning probe techniques like scanning tunneling microscopy (STM) and atomic force microscopy (AFM) probe only the outermost layer and hence do not provide the complete picture. In addition, STM studies are limited to conducting samples since the electrons have to tunnel between the tip and the sample. A brief comparison of the various techniques is presented in Table 1 and the interested reader may find more information from review articles on XRD [9,10], STM [11,12], REM/RHEED [13,14], and LEEM/LEED [15,16] and references therein.

2.1. Transmission electron microscopy

In this paper we focus on the TEM/TED techniques and the analysis of the data obtained through them. There are two main methods that

Table 1
Comparison between various surface science techniques

Technique	Surface sensitivity	Bulk sensitivity	Data collection mode	Nature of information	Lateral resolution
STM/STS	Good	Poor	Serial	Real space atomic and electronic structure	~1 Å
GIXRD	Good	Poor	Serial	Fourier space atomic structure	<0.1 Å
LEEM	Good	Good	Parallel	Real space structure	50–80 Å
LEED	Good	Good	Parallel	Fourier space structure	<0.1 Å
RHEED/REM	Good	Poor	Parallel	Fourier/real space structure	5–10 Å
TEM	Good	Good	Parallel	Real space structure	1–2 Å
TED	Good	Good	Parallel	Fourier space structure	<0.1 Å
XPS/AES	Good	Poor	Serial	Surface electronic structure	200 Å

can be used, namely profile imaging and plan-view imaging.

In profile imaging mode, atomic columns are imaged parallel to surface and information about the size of reconstruction perpendicular to the surface can be obtained. This technique exploits the full resolution of the microscope and was first employed to study the Au (1 1 0)-2×1 surface [4]. Since then it has been used to study silicon [17], germanium [18], compound semiconductors [19,20] and various other surfaces [21–23]. Quantitative studies of atomic displacements/relaxation from profile images should be done through careful simulations since the images are very prone to artifacts from Fresnel effects [24,25]. The drawback of this technique is that the structure in the observed surface region may not be the equilibrium structure and it may not be representative of an extended two-dimensional surface. Also, the structure of the reconstructed surface should project well along the beam direction for the image to be informative. Profile imaging is presently a popular tool to carry out in situ studies of various reactions that occur on surfaces.

In plan-view imaging the surface is imaged along the surface normal. The transmission geometry has relatively low signal levels (10% for very strong reflections) since the signal essentially originates from a few atomic layers. Radiation damage due to high incident beam energies is sometimes a cause of concern and has been observed in the Au–Si(1 1 1)-5×2 surface [26], although others are not sensitive.

Perhaps the simplest and in many cases most powerful approach is diffraction. Surface structures with periodicities different from the bulk give rise to weak superstructure spots which can readily be measured. When the beam is along zone axis the intensities of these spots are complicated by the plasmon scattering around strong bulk spots, as well as dynamical diffraction by the bulk material. However tilting to an off-zone condition attenuates the bulk spots more than the surface spots thereby improving the signal to noise ratio [27]. This is due to the fact that the superstructure spots are 'relrods' along the surface normal in reciprocal space. With care, the intensities of these spots can be treated within the kinematical approximation [28,29] and structural solution can be attempted. However, for surfaces, there is the additional complication of incomplete data sets since surface reflections periodically overlap with the bulk reflections and hence cannot be measured. Traditional crystallographic methods are model dependent, i.e. for successful inversion they require a starting model close to the true structure. Patterson function analysis which has proved quite useful in solving the Si(1 1 1)-7×7 structure can be ineffective when the number of atoms involved is large.

Various imaging modes exist, ranging from conventional bright-field and dark field to high resolution (HREM). In conventional HREM images, i.e. with the sample on-zone, the bulk lattice contrast tends to dominate so image processing (see below) is required. An alternative is to tilt off the zone axis. However, to date this still gives images with too much noise for the surface details to show, so again processing is required.

3. Processing of experimental surface HREM images

Image processing is an indispensable tool in extracting useful information from high-resolution plan-view images of surfaces. For on-zone images the contribution of bulk scattering can be digitally removed by masking the bulk spots in the diffractogram. However, the images (both filtered on-zone as well as unfiltered off-zone images) still contain too much noise to be useful. The approach we have used is a weiner filter [30]. This operates on the premise that the noise is essentially random and can be simply estimated and can improve the signal/noise ratio by a factor of 3–7. This is because the statistical noise scales with the square root of the number of pixels whereas the signal scales with the number of pixels.

In some cases wiener filtering alone is enough, for instance for the Au-Si (1 1 1)-5×2 [26] Often the surface reconstruction may be on both the top and bottom surface, so the two must be deconvoluted. Since the reconstruction on the two surfaces should have the same structure, and can only differ by a unit-cell translation (and possibly a known rotation) there are only a limited number of possible kernels for the deconvolution. As an illustration, Fig. 1 shows an unprocessed on-zone HREM image of Si (1 1 1)-7×7 surface with the diffractogram. Although a periodic motif is observable, information at hand is not sufficient to draw conclusions about atomic scale structure. Fig. 2 shows the image after the application of a weiner filter a numerical soft aperture to remove the bulk (2 2 0) beams and deconvolution of the top and bottom surface. The filtered image shows more detail and the diffractogram is noticeably better. Fig. 3 shows the rotationally (three-fold) and translationally averaged single surface image with a multislice image simulation inset. This image clearly displays all the features of the reconstruction including the buried dimers and the sub-surface stacking fault [31]. The same methodology has been more recently used for the $SrTiO_3$ (1 0 0)-2×1 [32] surface.

4. Direct methods

Despite their ability to provide direct structural information at the atomic scale, imaging techniques are seldom sufficient to solve a surface structure due to limitations in the resolution from the weak signals. In reciprocal space, the intensities of beams diffracted from the surface can be measured with relative ease and precision and this process can even be automated [33,34]. The resolution obtainable in a diffraction experiment is far superior and the process of data collection is parallel and fast, without the complications of radiation damage. Direct Fourier inversion of these intensities is impossible since the phases of the scattered beams are lost in the diffraction experiment. However, the intensities can be used

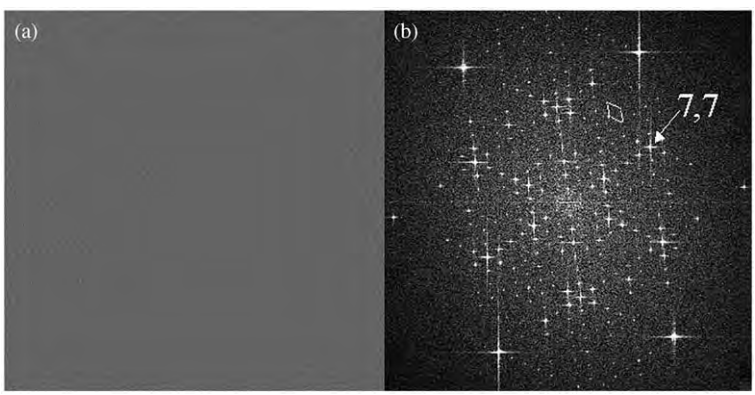

Fig. 1. (a) Unprocessed image of Si surface. (b) Power spectrum.

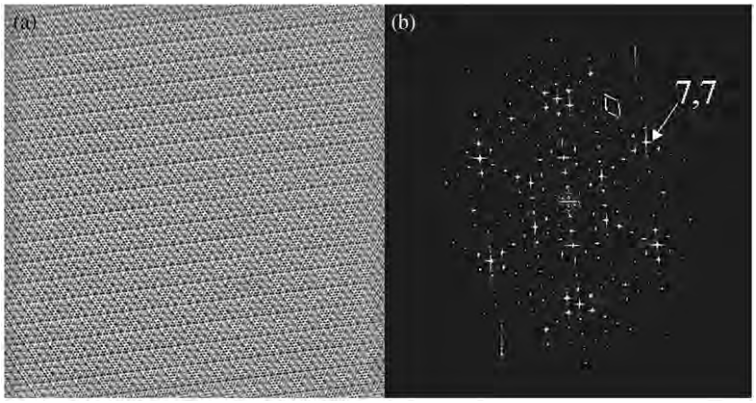

Fig. 2. (a) The image after the application of the noise filter and a numerical soft aperture to the {2 2 0} beams. (b) Power spectrum.

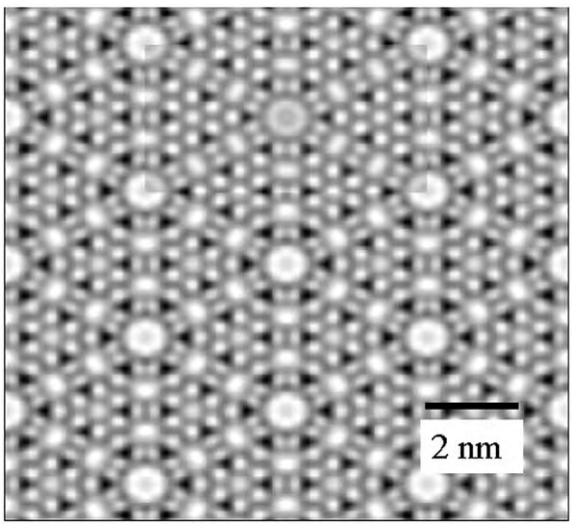

Fig. 3. Rotationally and translationally averaged image. The inset is a multislice image simulation.

with various structure determining techniques, collectively known as direct methods, to yield a reasonable estimate of the true surface structure. Crystallographic direct methods have become popular for surfaces over the last few years and have been successfully used to solve various structures. Here we will present a brief description of the technique involved, which is applicable both to electron and X-ray diffraction, and the interested reader may refer to more recent review articles in this field [35,36]. In simple terms, direct methods exploit a priori information to constrain the phases of measured reflections. The common constraints used are:

1. Atomicity: Scattering originates from atoms and hence the solution should have atomic features i.e. regions of large charge densities separated by charge-free regions.
2. Positivity: Charge density in a real crystal is always positive
3. Localization: The region of space with significant atomic displacements from bulk positions is limited to the near-surface region.

The phases of the measured reflections cannot be totally random—i.e. they have to obey the above constraints and this can be used to gauge the 'figure of merit' (FOM) of a given set of phases. These constraints are iteratively imposed in a Gerchberg–Saxton fashion [37] using the projection onto sets algorithm [38,39] to refine the phases of the measured reflections. Some of the constraints used may not convex, and this results in a scenario where there are multiple solutions. Generally, the more the number of convex constraints, the easier it is to find the true solution. The solution space is spanned by multi-solution search techniques such as the genetic algorithms [40,41] or simulated annealing [42,43]. The various techniques employed in structure analysis differ in the way the constraints are enforced. For example, 'atomicity' can be used in the form of the triplet phase relationship [44] or as the positive quartet

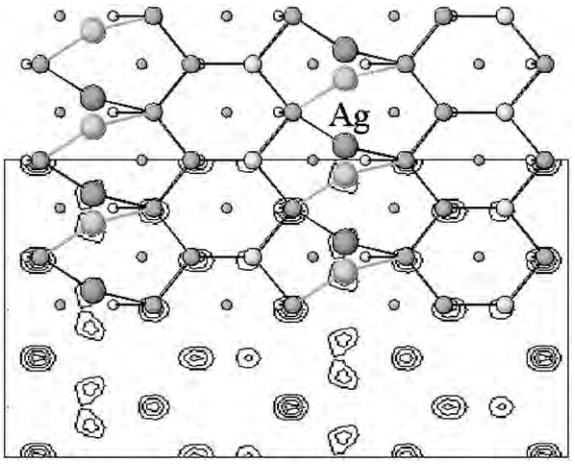

Fig. 4. Honeycomb chain-channel structure of Ag–Si (1 1 1)-3×1, with both the original map and the final refined structure shown. The structure contains Ag atoms (marked) in one of two positions due to twinning, the rest of the surface is silicon.

[45,46]. In most cases, direct methods provide a model that can then be used as the starting point for further refinements. The various techniques employed for structure completion include Fourier-difference methods [47], projection-based methods [47] and heavy atom holography [26,48]. The structure so determined can be further refined by using the conventional *R*-factor or χ^2-type analysis against simulated data. Direct methods have been widely used to solve a variety of surface structures and a classic example is the solution of the Ag–Si (1 1 1)-3×1 surface. None of the proposed "chain models" were consistent with the various experimental observations until the "honeycomb chain-channel" structure was proposed by Collazo-Davila et al. [49] (see Fig. 4), which was subsequently verified through ab initio calculations [50]. This structure, which was unsolved for nearly five years, underscores the fundamental strength of direct methods i.e. making no assumptions about the original structure.

5. Discussion

Electron diffraction intensity analysis was used for the first time to solve the Si (1 1 1)-7×7 surface structure more than fifteen years ago. Over the past ten years a significant number of other surface structures have been solved using a combination of TEM/TED techniques. An aspect meriting a closer look is the kinematical treatment of TED data. To a first approximation one can deal with transmission electron diffraction from a surface structure purely kinematic—this is often good enough to determine the initial map for a subsequent refinement. However, it is not acceptable or even a needed approximation for a full refinement. Dynamical refinements can be easily carried out using the multislice algorithm including the reconstruction (plus subsurface relaxations) on both the top and bottom surfaces. The main shortcoming of TEM/TED techniques is that the information they provide is two-dimensional i.e. that of the structure projected along the direction of the incident beam. From this data, the in-plane atomic co-ordinates can be refined to 0.01 A precision but the structure cannot be optimized along the surface normal. Hence TEM/TED experiments must be carried out in conjunction with other techniques for three-dimensional structural solution. Ab initio calculations represent one possible solution to this problem and have been employed successfully in a recent study of $SrTiO_3$ (0 0 1)-2×1 surface [32]. Such calculations can also provide useful information about the nature of bonding between the various surface atoms thereby providing valuable insight into the driving forces behind the reconstruction.

Acknowledgements

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References

[1] P.N. Keating, Phys. Rev. 145 (1966) 637.
[2] I.K. Robinson, W.K. Waskiewicz, P.H. Fuoss, L.J. Norton, Phys. Rev. B 37 (1988) 4325.
[3] L.D. Marks, E. Bengu, C. Collazo-Davila, D. Grozea, E. Landree, C. Leslie, W. Sinkler, Surf. Rev. Lett. 5 (1998) 1087.
[4] L.D. Marks, Phys. Rev. Lett. 51 (1983) 1000.

[5] M. Gajdardziska-Josifovska, P.A. Crozier, J.M. Cowley, Surf. Sci. Lett. 248 (1991) L259.
[6] C. Noguera, J. Phys.: Condens. Matter 12 (2000) R367.
[7] H-J. Freund, H. Kuhlenbeck, V. Staemmler, Rep. Prog. Phys. 59 (1996) 283.
[8] C. Collazo-Davila, E. Landree, D. Grozea, G. Jayaram, R. Plass, P.C. Stair, L.D. Marks, J. Mic. Soc. Am. 1 (1995) 267.
[9] I.K. Robinson, D.J. Tweet, Rep. Prog. Phys. 55 (1992) 599.
[10] I.K. Robinson, Acta. Cryst. A54 (1998) 772.
[11] C. Girard, C. Joachim, S. Gauthier, Rep. Prog. Phys. 63 (2000) 893.
[12] J.A. Kubby, J.J. Boland, Surf. Sci. Rep. 26 (1996) 61.
[13] Z.L. Wang, Rep. Prog. Phys. 56 (1993) 997.
[14] K. Yagi, Surf. Sci. Rep. 17 (1993) 305.
[15] E. Bauer, Rep. Prog. Phys. 57 (1994) 895.
[16] M.A. VanHove, Surf. Rev. Lett. 4 (1997) 479.
[17] M. Takeguchi, M. Tanaka, H. Yasuda, K. Furuya, Surf. Sci. 493 (2001) 414.
[18] M. Mitome, K. Takayanagi, Surf. Sci. 242 (1991) 69.
[19] T.D. Mishima, N. Naruse, S.P. Cho, T. Kadohira, T. Osaka, Phys. Rev. Lett. 89 (2002) 276105.
[20] P.D. Brown, A. Kirkland, C.J. Humphreys, Inst. Phys. Conf. Ser. 138 (1993) 209.
[21] E.F. Bres, J.L. Hutchinson, J. Biomed. Mater. Res. 63 (2002) 433.
[22] W.Z. Zhou, Y. Xin, D.A. Jefferson, J Solid State Chem. 149 (2000) 327.
[23] W.Z. Zhou, J.M. Thomas, Curr. Opin. Solid State Mat. Sci. 5 (2001) 75.
[24] L.D. Marks, Surf. Sci. 139 (1984) 281.
[25] P. Lu, D.J. Smith, Ultramicroscopy 25 (1988) 265.
[26] L.D. Marks, R. Plass, Phys. Rev. Lett. 75 (1995) 2172.
[27] P. Xu, L.D. Marks, Ultramicroscopy 45 (1992) 155.
[28] J.C.H. Spence, Ultramicroscopy 11 (1983) 117.
[29] L.D. Marks, T.S. Savage, J.P. Zhang, R. Ai, Ultramicroscopy 38 (1991) 343.
[30] L.D. Marks, Ultramicroscopy 62 (1995) 43.
[31] E. Bengu, R. Plass, L.D. Marks, T. Ichihashi, P.M. Ajayan, S. Iijima, Phys. Rev. Lett. 77 (1996) 4226.
[32] N. Erdman, K.R. Poeppelmeier, M. Asta, O. Warschkow, D.E. Ellis, L.D. Marks, Nature 419 (2002) 55.
[33] P. Xu, G. Jayaram, L.D. Marks, Ultramicroscopy 53 (1994) 15.
[34] J.M. Zuo, J.C.H. Spence, Ultramicroscopy 35 (1991) 185.
[35] L.D. Marks, N. Erdman, A. Subramanian, J. Phys.: Condens. Matter 13 (2001) 10677.
[36] L.D. Marks, Phys. Rev. B 60 (1999) 2771.
[37] R.W. Gerchberg, W.O. Saxton, Optik 35 (1972) 237.
[38] D.C. Youla, Image recovery, in: H. Stark (Ed.), Theory and application, Academic Press, Orlando, 1987.
[39] P.L. Combettes, Adv. Imag. Electron Phys. 95 (1996) 155.
[40] D.E. Goldberg, Genetic Algorithms in Search, Optimization and Machine Learning, Addison-Wesley, Reading, 1989.
[41] E. Landree, C. Collazo-Davila, L.D. Marks, Acta Cryst. B 53 (1997) 916.
[42] G.M. Sheldrick, Acta. Cryst. A 46 (1990) 467.
[43] A.T. Brunger, Ann. Rev. Phys. Chem. 42 (1991) 197.
[44] C. Giacovazzo, Direct Phasing in Crystallography, Oxford University Press, New York, 1998.
[45] J. Rius, C. Miravitlles, R. Allmann, Acta. Cryst. A 52 (1996) 634.
[46] X. Torrelles, J. Rius, F. Boscherini, S. Heun, B.H. Mueller, S. Ferrer, J. Alvarez, C. Miravitlles, Phys. Rev. B 57 (1998) R4281.
[47] J.M. Cowley, Diffraction Physics, Elsevier, New York, 1984.
[48] D.L. Dorset, Acta Cryst. A53 (1997) 356.
[49] C. Collazo-Davila, D. Grozea, L.D. Marks, Phys. Rev. Lett. 80 (1998) 1678.
[50] S.C. Erwin, H.H. Weitering, Phys. Rev. Lett. 81 (1998) 2296.