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New methods of imaging surfaces (and buried interfaces)

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Abstract Recent developments have shown that it is possible to obtain information at the atomic level from surfaces, in some cases to one Angstrom or better resolution. This paper reviews these developments, discusses their current limitations, and points out that they can be used as readily for buried interfaces.

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Introduction

Obtaining atomic scale information about surfaces has been an outstanding problem for many years. Despite the advent of scanning probe techniques and in particular scanning tunnelling microscopy (STM), it is only rarely possible to obtain such information—STM images the local density of states at the surface, not atoms. Hence one can seldom differentiate between different types of atoms using STM. In addition, atomic positions below the first atomic layer are rarely resolvable except by inference. While techniques such as low energy electron diffraction (LEED) [1], grazing incidence X-ray diffraction [2,3], and transmission electron diffraction [4–10] are all capable of refining atomic positions to accuracies of 0.001 nm, one has to have an initial approximate set of atomic coordinates for these approaches to work. Recently, there have been developments in what is called photoelectron holography [11,12] as a method of obtaining such initial estimates.

In many respects similar problems exist for buried interfaces, although here only transmission electron microscopy and X-ray techniques have the potential to obtain the information. While cross-sectional analysis of both homophase and heterophase boundaries is now routine, there is always the issue that one only observes a projection of the structure, not a full two-dimensional or three-dimensional image of the interface. Studies in the plan-view geometry (i.e. electron beam perpendicular to the interface) from a number of groups have shown that it is possible to obtain more, for instance the observation of buried reconstructions [13,14], but this has yet to be extended to detailed definition of atomic positions.

Over the last year there have been a number of developments at Northwestern University, in collaboration with a number of other groups around the world. As a consequence, it appears that one can almost routinely obtain atomic scale information from surfaces in a plan view geometry both in images and directly from diffraction patterns. The intention of this paper is to briefly explain this work, pointing out in the process that all the techniques should be directly applicable to buried interfaces with little to no change.

Background to the problem

It is useful to consider the general background of the information that can be obtained from a surface in the plan-view geometry in a transmission electron microscope. While the profile imaging technique [15,16] can sometimes be used, a general problem is that a thin profile edge is not thermodynamically stable, and is hence the exception rather than the rule. There is also the problem that information is only available in projection.

A rough number for the scattering by a single layer of atoms is 1–2% of the transmitted beam amplitude [17]. While small compared to the general level for bulk diffraction, this is readily observable on the phosphor screen of a microscope provided that:

(i) the sample is thin enough that bulk inelastic scattering effects do not give too high a background;
(ii) the surface is well-enough ordered that one has reasonably sharp diffraction spots rather than weak intensity smeared over a larger region by the shape transform; and
(iii) the bulk sample contains a relatively low concentration of point defects due to prior ion-beam thinning.

Of the three, the last is probably the reason why surface diffraction effects are generally not considered to be very important in bulk electron diffraction.

In a diffraction pattern where many of the periodicities of the surface are not buried by bulk spots, this will give intensities ranging from 10^{-4} to 10^{-6}; the latter is a typical lower limit where diffuse, inelastic scattering background is similar or higher than the elastic surface scattering. (To date, no information is available about how much further this could be extended using energy-filtered diffraction patterns.) Under strong diffraction conditions (e.g. a zone-axis orientation) there will be multiple diffraction effects which depend strongly upon whether the surface of interest is on the top or the bottom [18]. For instance, if the bottom surface is of interest, one has to consider the registry of the atoms on the bottom surface with respect to channelling of the Bloch waves through the sample. Tilting the sample off the zone axis reduces these effects somewhat, but only for the stronger beams; one cannot ignore diffraction from a strong surface spot (amplitude 10^{-2}) into a weak one (amplitude 10^{-3}). As a consequence, while surface diffraction in a weakly (bulk) diffraction condition can be approximated as kinematical, it needs to be remembered that this is only an approximation.

Exploiting directly the surface diffraction information is now relatively well developed as a structure refinement technique. First was introduced by Takayanagi *et al.* [4] who employed Patterson functions to solve the structure of the Si (111) 7×7 surface, it has also been used by Twesten and Gibson for kinematical refinements [7] and at Northwestern University for dynamical refinements with the full crystal thickness and tilt information included [5,6,8–10]. (Rather than simply integrating over the intensity it is better to subtract off the background by a polynomial fit [7] or use a cross-correlation measurement [19].) A major problem with more general usage is that Patterson function techniques do not always work—without a better method of generating an initial estimate of the structure it competes with other techniques such as LEED that are often better.

Almost all conventional electron microscope imaging and diffraction techniques can be used for a surface, although some (e.g. microdiffraction with a small coherent probe) have not yet been investigated in any depth. The earliest technique was to image in dark field using the so-called bulk forbidden/surface allowed reflections [20], what are called in a surface notation the 1×1 spots. Following along similar lines, dark-field imaging using spots solely due to surface reflections proved rather successful [21]. However, there is also good contrast from, for instance, surface steps using bulk diffracted beams and one can readily interfere surface and bulk spots to obtain fairly high resolution (0.5–1 nm) dark-field images [8].

While dark-field techniques developed rapidly, high-resolution methods lagged behind. It has been shown [5,8,22–25] that information was present, but it was not generally exploited. A high-resolution image taken from such a surface will contain information from both surfaces, coherently interfering with a total contrast level of 1–5% at best. Noise in such images comes not only from disorder and counting statistics, but also from any strong bulk diffracted beams. Hence while a power-spectrum will show that surface information is present in the image, rarely if ever is the information obvious without image processing. Figure 1 shows the surface information in a power spectrum before and after image processing which will be explained in detail later. It should also be remembered that the two surfaces are at slightly different defoci with respect to the final image, the focal difference being equal to the sample thickness. One useful consequence of the weak contrast is that linear imaging theory can be applied rather accurately to the images, with the possible exception of the largest spacings (since there are many non-linear terms which can add coherently).

Atomic scale information

Excluding issues concerned with sample preparation, the two primary limitations to routinely obtaining atomic scale information about surfaces using transmission electron microscopy are: (i) how to handle the low signal levels in high-resolution images which contain all the required information; and (ii) how to fully exploit the diffraction information, better than a Patterson function approach. While there is still room for substantial improvements, it would be accurate to state that these two problems now appear to be solvable to a level where exploitation (for both surfaces and by inference for buried interfaces) can start.

Extracting overlapping surface information from the noise

The first key to extracting surface image information is how to handle noise in an unbiased fashion. The solution has been known for more than 50 years, but is little used. Provided that one can estimate the noise $\eta(u)$ in an image in the diffraction plane, the best estimate of the signal $S(u)$ in a least-squares sense is given by:

$$S(u) = I(u)\, S_e(u)^2/(S_e(u)^2+\eta(u)^2) \tag{1}$$

where $S_e(u)$ is an estimate of the signal, of form:

$$S_e(u)^2 = I(u)^2-\eta(u)^2 \quad I(u)>\eta(u) \tag{2}$$

$$S_e(u)^2 = 0 \quad I(u)<\eta(u) \tag{3}$$

This filter, called a Wiener-filter [26,27], assumes only that a good estimate can be made of the noise spectrum, which is readily available away from the diffraction spots in a power-spectrum. Therefore, it makes no assumptions about the signal, and so does not introduce artificial spacing like Fourier mask filters. Since statistical noise scales as the square root of the number of pixels while the true signal (for a periodic object) scales as the number

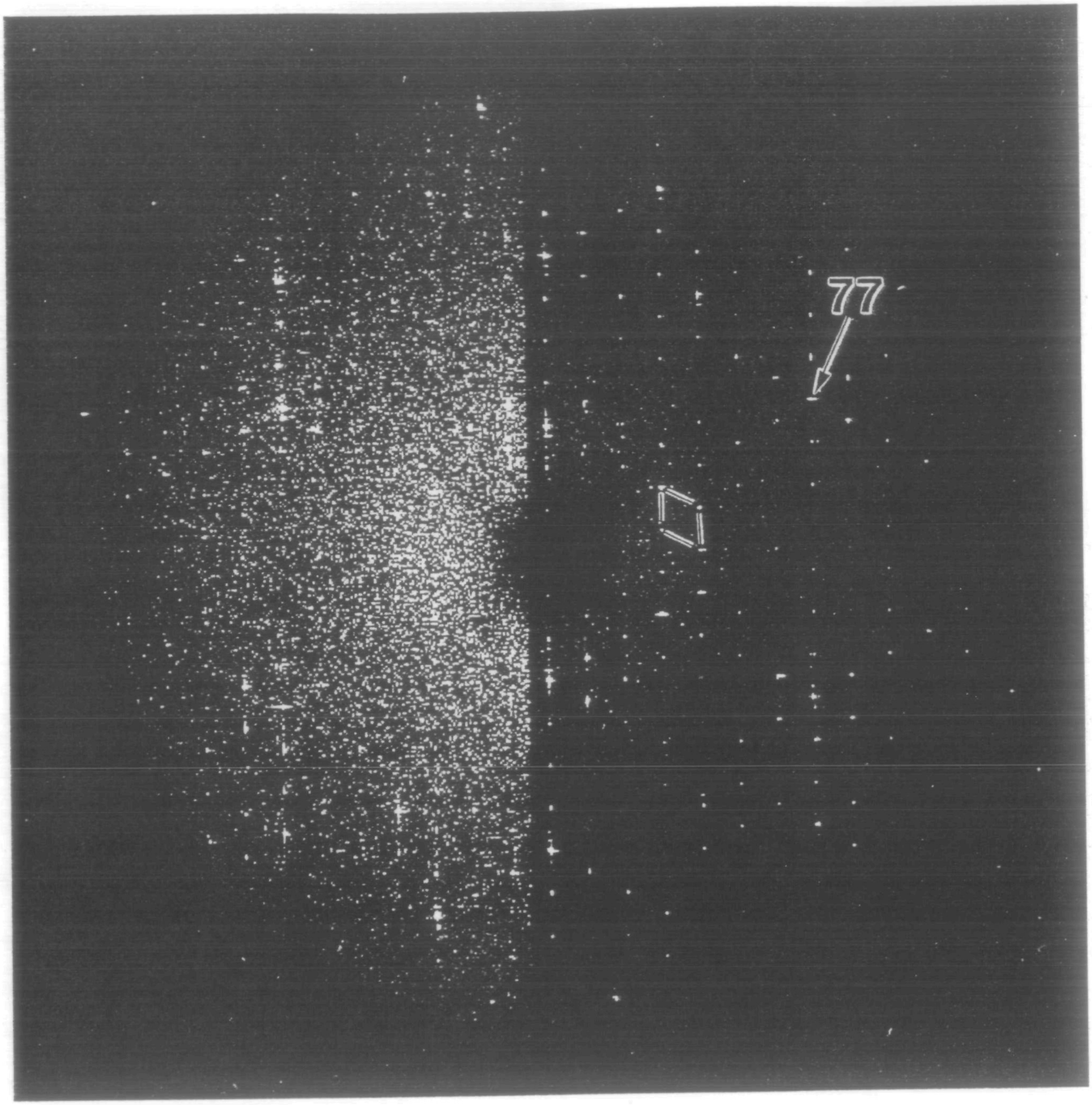

Fig. 1 Power spectra of an Si (111) 7×7 image, showing clearly that a large number of surface spacings are present in the final image: on the left, before filtering and on the right after Wiener filtering. The (7,7) or surface 1×1 spot is marked, as is the unit cell.

of pixels, it is more effective with larger pictures (e.g. for a 1024×1024 image the signal-to-noise ratio is enhanced by approximately a factor of 6). This is more than adequate for surface information, see for instance Figs 1 and 2. In Fig. 1, the raw power spectrum (left) contains substantial shot noise, which is also apparent in Fig. 2 (top), the raw image. After application of the filter both the power spectrum (Fig. 1, right) and the image (Fig. 2, bottom) are markedly better.

The second step is to eliminate the bulk information, and recover a single surface from two overlapping surface images. The first is simple, a digital mask to bring the amplitudes of the fringes at smaller spacings to zero. For the latter, one can also employ a Wiener-filter. For the two surfaces one has a final image of:

$$I(r) = I_{top}(r) + I_{bot}(r+d) \qquad (4)$$

where d is some (unknown) translation, and in general the top ($I_{top}(r)$) and bottom ($I_{bot}(r+d)$) images will be related by some symmetry operation (e.g. inversion). For

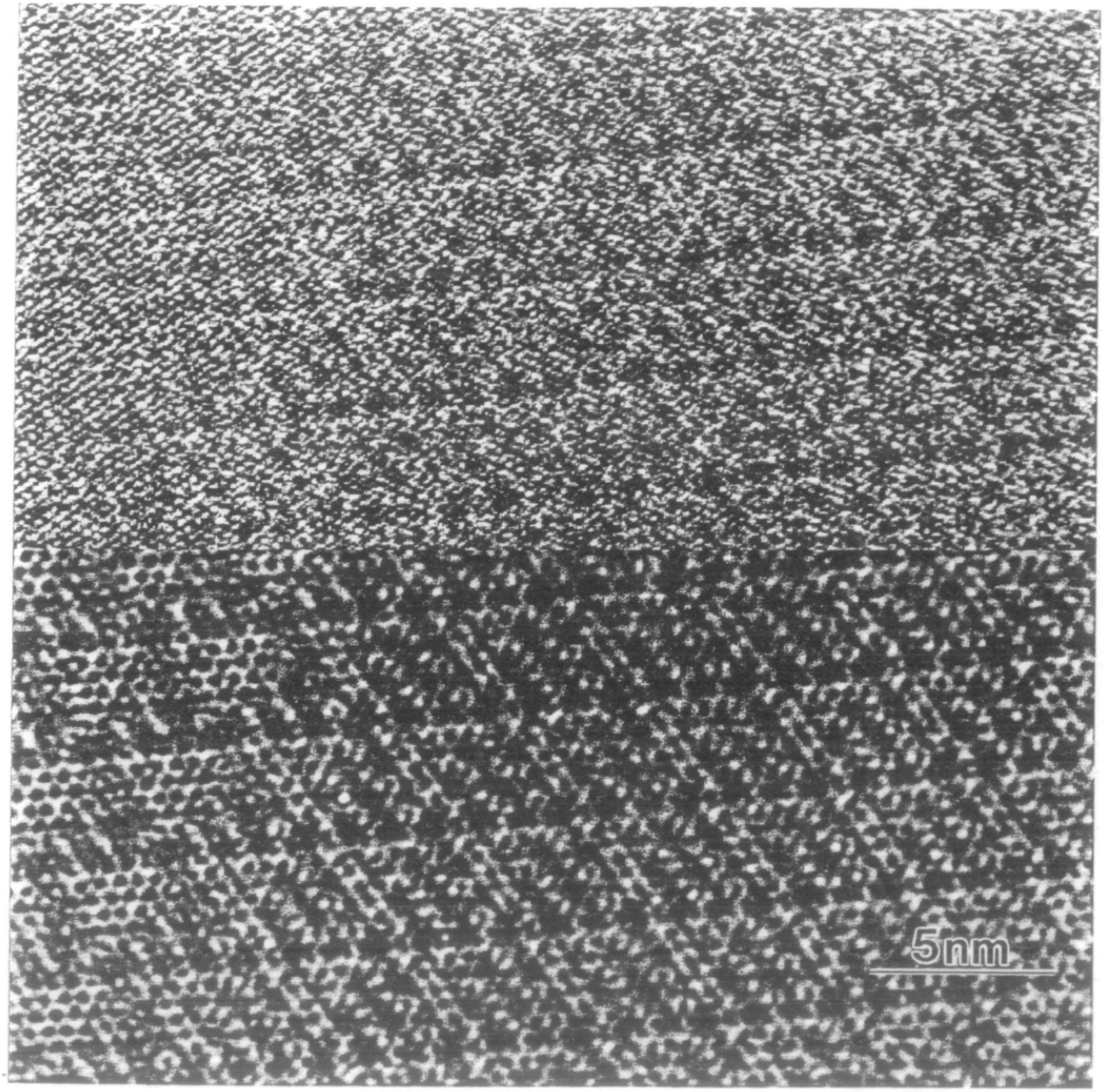

Fig. 2 Images of an Si (111) 7×7 surface before (top) and after (bottom) Wiener filtering and removal of the bulk (220) fringes.

the case when the structure contains an inversion center, the single surface image is given in reciprocal space by:

$$I_s(u) = I(u)T^*(u)S_e(u)^2/(|T(u)S_e(u)|^2+\eta(u)^2) \qquad (5)$$

with

$$T(u) = 1+\exp(2\pi iu.d) \qquad (6)$$

(If a Wiener filter is used first to remove the noise, the $\eta(u)^2$ term on the bottom is replaced by some small number large enough to prevent noise amplification, to give a pseudo-inverse.) Since the surface has some symmetry (e.g. 6-fold rotation for the Si (111) 7×7 surface), the translation d can only take on certain values for commensuration with the bulk lattice. Hence one can find d from the least-squares minimum between symmetry equivalent reflections. As an example, Fig. 3 shows the result for a Si (111) 7×7 surface taken close to Scherzer defocus; all the atoms (black features) including the dimers in the third layer are directly resolvable [28]; the 'blacker' features in the image are the locations of the adatoms, where (in projection) two atoms overlap. (One small artifact exists at the origin of the unit cell

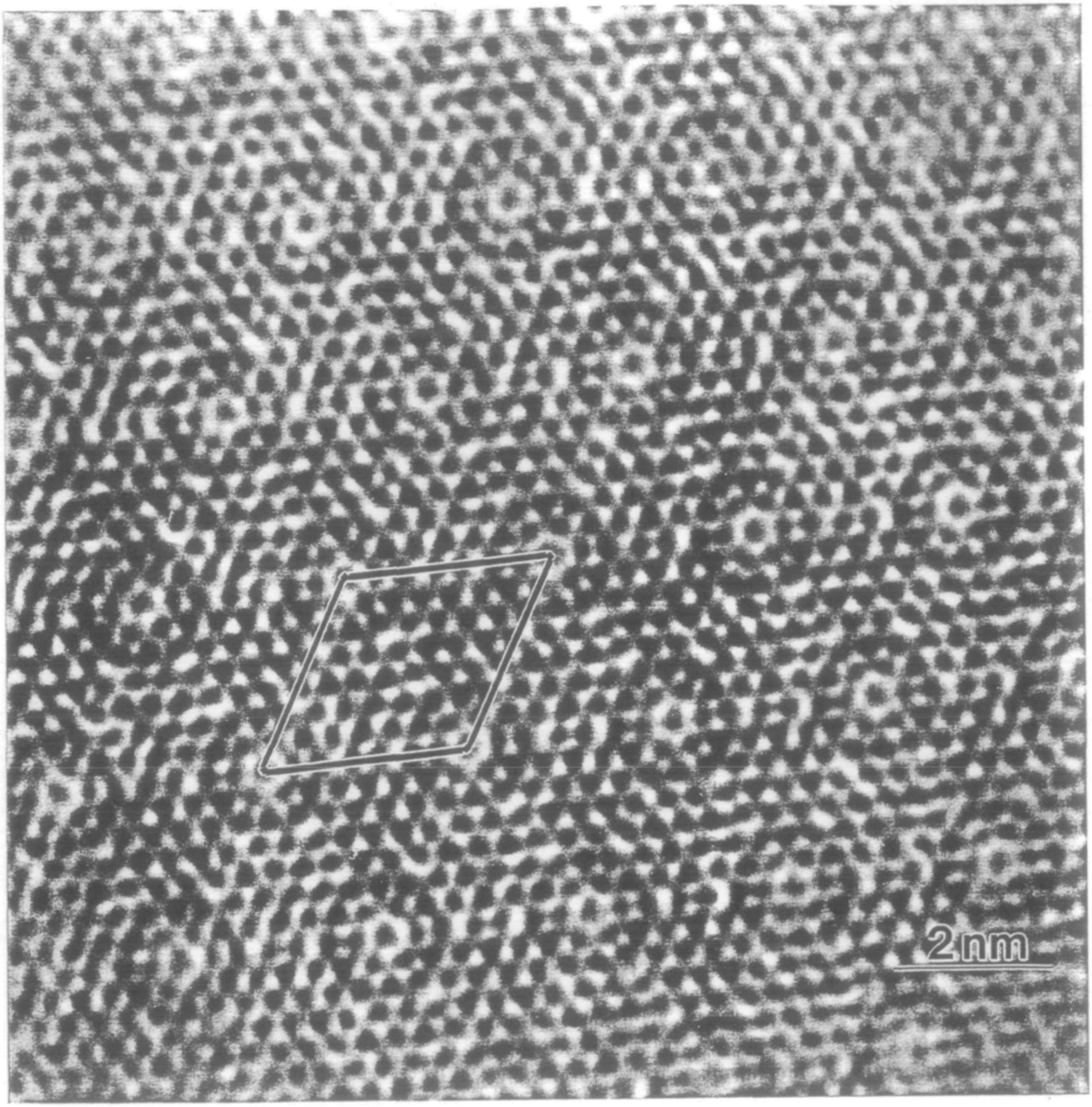

Fig. 3 Image of the Si (111) 7×7 surface after separation, with atoms black.

where an apparent atom appears—this is due to the limited number of beams used not the filter or the numerical seperation process.)

Ab-initio structure determination from direct methods

As mentioned earlier, the problem with transmission electron diffraction (and also X-ray) data from surfaces is that it is easy to refine, but difficult to determine a viable initial estimate of the atomic positions. The corresponding problem for bulk X-ray diffraction, the 'phase problem' can in most cases be solved [29–34]. Highly simplified, since in a kinematical case the Fourier transform of the true amplitudes and phases is real with sharp features at the atomic sites and close to zero between them, one can generate probabilistic relationships governing the phases of different beams. The most common one used is called the Σ_2 relationship, and is similar to double-diffraction. If $\phi(g)$, $\phi(h)$ and $\phi(g+h)$ are the phases of three strong beams,

$$\phi(g+h) \approx \phi(g) + \phi(h) \qquad (7)$$

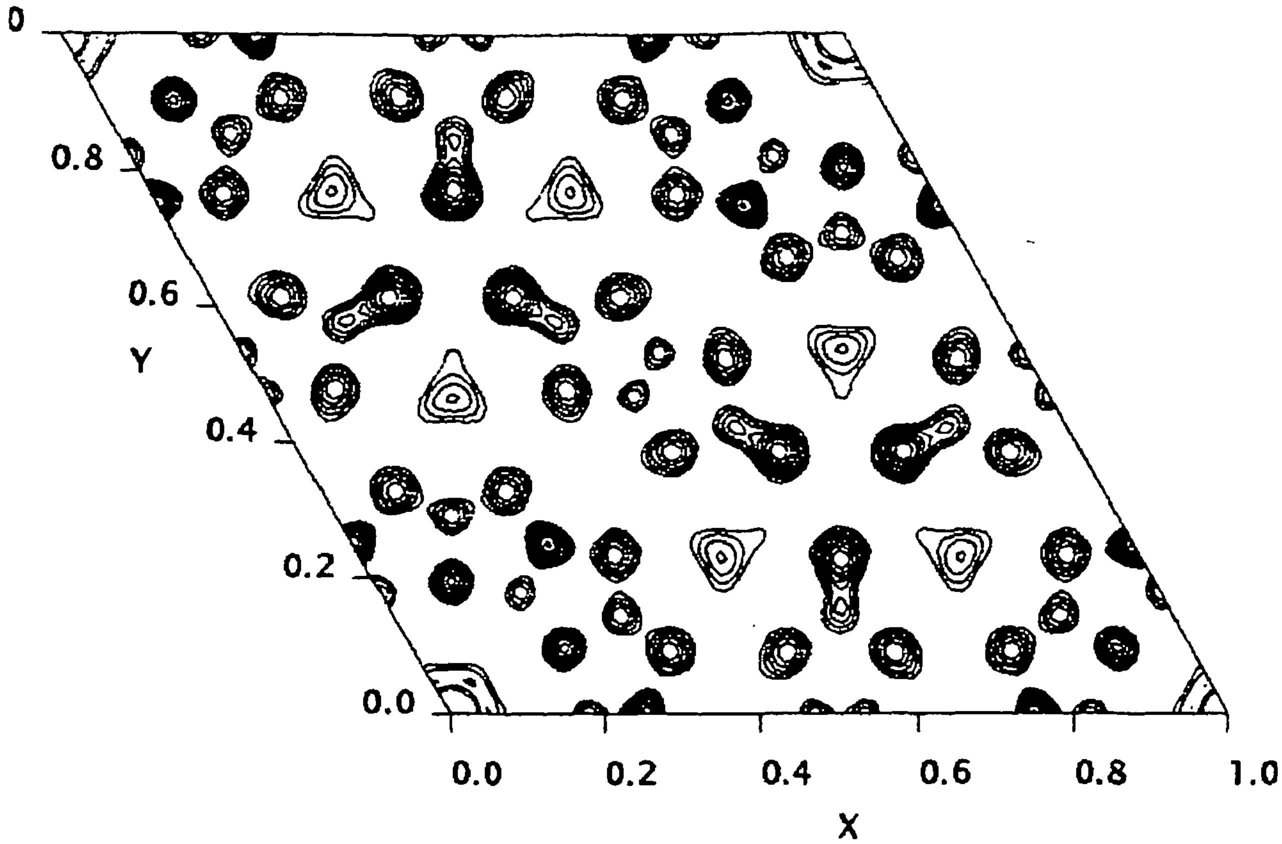

Fig. 4 Maximum Entropy contour map for the Si (111) 7×7 surface.

where here '≈' means probably true. (The probability increases as the product of the moduli of the three structure factors.) By first assuming the phases of some reflections, new ones are generated by these relationships, then by testing for self-consistency a diffraction pattern of 100 reflections can often be reduced to only 2–3 possible arrangements of atoms. (Further details can be found in the literature [29–34].) Despite dynamical complications there is growing evidence [35–37] that the same methods can be applied to transmission electron diffraction data—these methods rely upon probabilistic relationships which are rather lenient.

There are many reasons why this might not work for surfaces, the most severe being that it is essentially impossible to measure the true surface contribution to the 1×1 or bulk diffraction spot intensities. (There are strong bulk contributions to the 1×1 intensities, so it is not correct to call these surface spots in transmission electron diffraction.) There is also the issue that kinematic diffraction for surfaces is not rigorously valid. However, it has turned out that deviations from kinematic behaviour and the absence of measurements for many of the intensities do not make the approach invalid—in fact it seems to work rather better than for bulk electron diffraction and is quite simple [38–40]. As an example, Fig. 4 shows a Maximum Entropy map of the surface potential for the Si (111) 7×7 surface [40]. While not all the atoms are in the correct positions, and the heights of the various peaks are not accurate, there is still enough information for an approximate first analysis of the atomic positions. (Frequently the initial maps will contain more possible sites than exist, and they may be displaced from the true sites by 0.02–0.05 nm. One places atoms at the strongly defined sites and uses classic Fourier difference and other techniques to complete the structure, followed by a full refinement against the measured diffraction intensity data.)

Phase extension from HREM images

Given that one can obtain atomic scale information from both HREM images, and, independently from images, one can also combine the two. The HREM image defines the phases of some of the larger spacings, and one can then use these phases via Σ_2 (and other relationships) to determine the phases of spots that appear in the diffraction pattern but cannot be resolved in the image (due to signal-to-noise and resolution limitations). This is rather easy to do, and as an example Fig. 5 shows the results where the phases from the HREM image of the Si (111) 7×7 surface [28] have been combined with diffraction data [7] to give a map of the surface potential with a

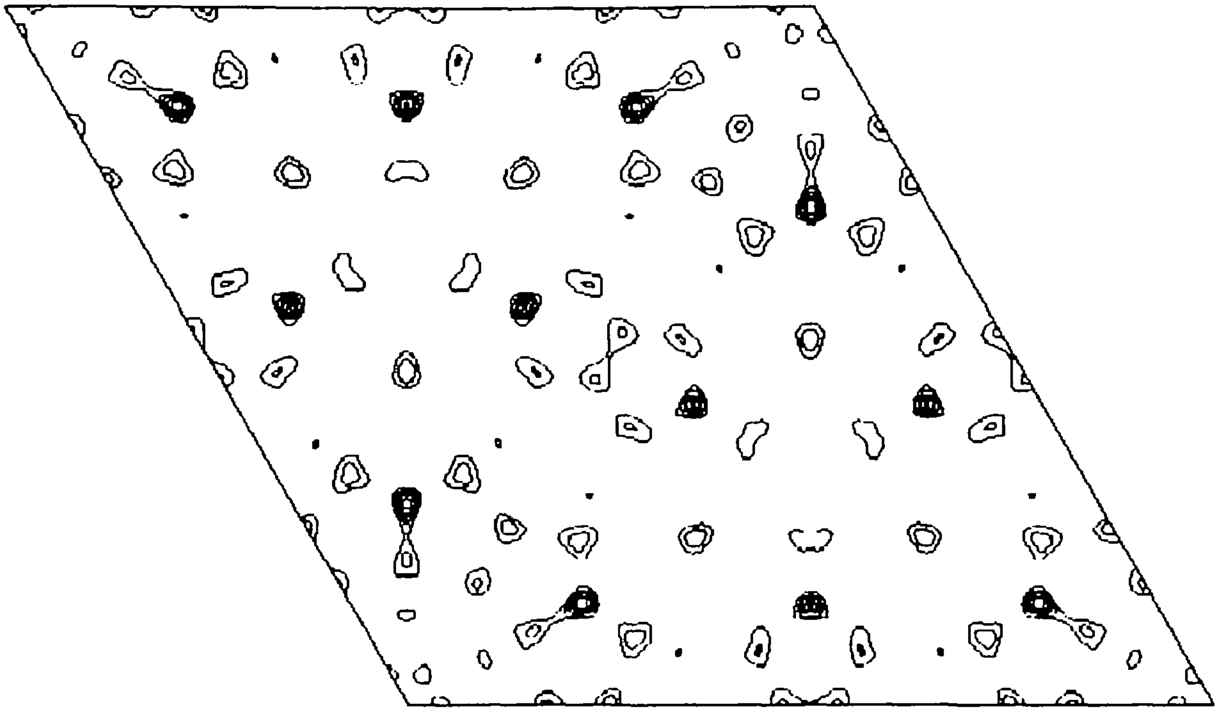

Fig. 5 Contour map of the Si (111) 7×7 surface generated using the phases from an HREM image and the amplitudes from a diffraction pattern.

resolution of better than 0.1 nm [40]. The strong features are the sites of the adatoms, strong because there is an overlap of the adatom with a silicon atom in the second layer below. All the other features match well with the locations of atoms in the structure, although due to the limited number of beams included (and exclusion of the bulk 1×1 and (220) reflections) the relative heights of the peaks are not correct.

Discussion

The results discussed herein imply a rather good future for electron microscopy studies of surfaces at the atomic scale, generating information at much higher resolution levels than is currently available. There is still room for development, for instance utilization of maximum entropy approach to the filtering of the images might lead to better results than Wiener filters (for large spacings). This, together with higher brightness sources (field emission electon gun), will be very valuable for looking at surface defects, still an open topic. Perhaps the main current limitation for high resolution is astigmatism and tilt correction; for a well-ordered surface there is no diffuse elastic scattering (amorphous regions) available. One also does not have any idea whether the final image will (after processing) show anything useful, a problem that can in principle be solved by using a CCD camera for image acquisition and real time filtering. (The latter is just about technically feasible.) What levels of information can be achieved with energy filtering or by the use of small probes remain open questions.

Direct methods for interpreting diffraction pattern information also has room for many improvements. For instance, there is a classic technique called a Wilson-plot [41] for determining the Debye-Waller term in a bulk crystal, but the four times that it has been tried for surfaces (twice at Northwestern, once in Buffalo and once in Glasgow) it gave negative values which are physically unreasonable. (This is almost certainly because the weaker intensities cannot be correctly modelled using kinematic theory, and the effects of measurement errors.) Some modified method needs to be developed. To date we have applied direct methods to three surfaces where the structures were already known, and three where they were not; a larger data base needs to be developed with the final target of 'black-box' algorithms, perhaps two to three years away.

While the application of these techniques for surfaces will remain the realm of a few groups with relatively specialized instruments, the same is not true for a buried interface. Here the main problem will be sample preparation. Both surface contamination layers and the density of point defects (from ion-beam thinning) have to be kept low, otherwise the interface information will be buried by noise from these two sources. This is probably the reason why there are very few papers using electron microscopy in a plan-view geometry to investigate atomic scale interface structure. (There are a number of recent papers using X-ray diffraction to look at buried interfaces, e.g. [42–43].) Sample preparation is not an insoluble problem, and we confidently predict that results will start to appear within a year or two.

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