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Direct structure determination of systems with two-dimensional periodicity

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Abstract. We describe a new x-ray method for the direct measurement of structures which have two-dimensional (2D) periodicity, and are positionally correlated with an underlying substrate crystal. Examples include reconstructed crystal structures at interfaces, layered heterostructures, crystalline–amorphous interfaces, and self-assembled structures on crystalline substrates. The structure is obtained by determining the complex scattering factors along the Bragg rods and Fourier back-transforming them into real space. The method for determining the complex scattering factors has two variations. The first is generally applicable. It involves the measurement of the derivative of the diffraction phase along the Bragg rods and the subsequent determination of the diffraction phase using the known structure of the substrate. The second is applicable to 2D systems, with an unknown structure, that are buried within a crystal with a known structure. In this case the diffraction phase is determined without the need to measure its derivative first. We experimentally demonstrate both variations by determining the diffraction phase along one Bragg rod of a GaAs sample with four buried AlAs monolayers. Using simulated data along the Bragg rods within a volume in reciprocal space, we show that the method yields the three-dimensional structure of 2D systems with atomic resolution.

1. Introduction

Many structures of current interest, from both a scientific and technological standpoint, can be characterized as two-dimensional crystals. Such systems are fully or partially periodic in two dimensions, aperiodic in the third, and positionally correlated with an underlying substrate crystal. Examples include reconstructed crystal structures, layered heterostructures, crystalline–amorphous interfaces (e.g., Si–SiO_2), and self-assembled structures crystallized on a substrate. These systems are interesting because their physical properties differ markedly from those of bulk materials. Their study has been hampered by a lack of characterization tools that can probe this type of structure with atomic resolution. In this paper we present a new x-ray approach which addresses this problem.

Various x-ray methods have been used to investigate 2D structures. These include reflectivity and diffuse scattering [1, 2], high-resolution x-ray diffraction along Bragg and truncation rods [3], multiple diffraction [4], and standing waves [5]. In all these methods, it is necessary to first postulate a structural model and then refine its parameters to obtain the best fit with experiment. Interface structures are often quite complex and guessing a reasonable structural model can be both difficult and unreliable. Two direct methods, proposed in the past, are anomalous reflectivity [6] and x-ray holography [7]. These methods are of limited use for

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2D structures. The former only provides in-plane-averaged results. The latter provides the average structure around probe atoms that are typically located at inequivalent sites. In special cases when the system has inversion symmetry, the problem is greatly simplified because the scattering factors are real. This has been utilized to obtain the scattering factors of Fe/Ru superlattices and to calculate their structure by Fourier back-transformation [8].

Recently, using the tangent formula of Rius *et al* [9], Torrelles *et al* [10] developed a method for obtaining directly the projection of a reconstructed crystal surface on the surface plane from the Bragg-rod diffraction intensities on the equatorial plane in reciprocal space. The method has been generalized [11] to obtain the three-dimensional structure using the intensities on additional points along the Bragg rods. The problem of the so-called direct methods and of this method is that it involves the refinement of a large number of phases. Thus, the computation complexity grows at least as the square of the number of atoms. The method proposed here is also direct: it does not require an *a priori* conjecture of the structure, it is general and does not depend on the symmetry properties of the system, and it provides the three-dimensional structure of the 2D system; however, it is much simpler and its computational complexity scales linearly with the number of atoms.

2. The method

The method that we have developed is quite general but it will be easier to explain using a specific example. As shown in figure 1, we consider a system composed of a three-dimensional semi-infinite crystal, GaAs, containing embedded crystalline monolayers of AlAs. The electron density of the unknown 2D structure is the difference between the ideal semi-infinite crystal and the actual sample. In this example they are the ideal semi-infinite GaAs crystal and the sample containing the AlAs, respectively. Note that if the GaAs is distorted relative to its ideal structure, the difference between the ideal and the actual distorted structure is also part of the unknown 2D structure.

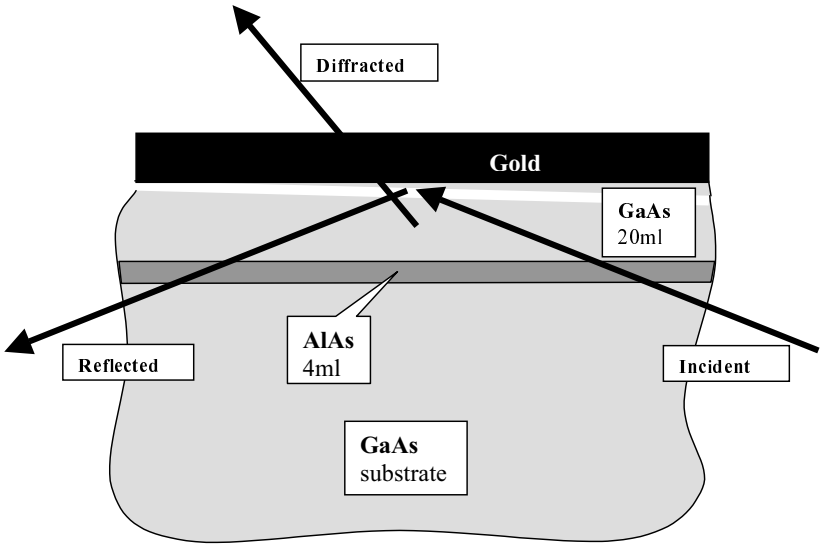

Figure 1. A schematic diagram of the sample and scattering geometry.

The 3D crystalline lattice (GaAs) defines a two-dimensional grid on x–y planes parallel to the interface. We first consider a 2D structure that is fully periodic with respect to this grid. The complex scattering factor (CSF) of the ideal semi-infinite *substrate* crystal, $S(k_z)$, is known and non-zero along a set of Bragg (truncation) rods which are oriented parallel to the surface normal (z-axis). The CSF of the *unknown* 2D structure, $U(k_z)$, also contributes to the scattering intensity along these Bragg rods. Since the transverse and longitudinal coherence lengths of the incident x-ray beam that we use are much larger than the thickness of the unknown 2D structure, the contributions from the substrate and the 2D structure interfere with each other coherently and the diffraction interference pattern that we measure is proportional to the absolute value squared of the *total* CSF $|T(k_z)|^2 = |S(k_z) + U(k_z)|^2$. The moduli of the three CSFs for a representative data set are shown in figure 2. For the purposes of illustration we used here a simulated data set based on the known atomic structures of GaAs and AlAs.

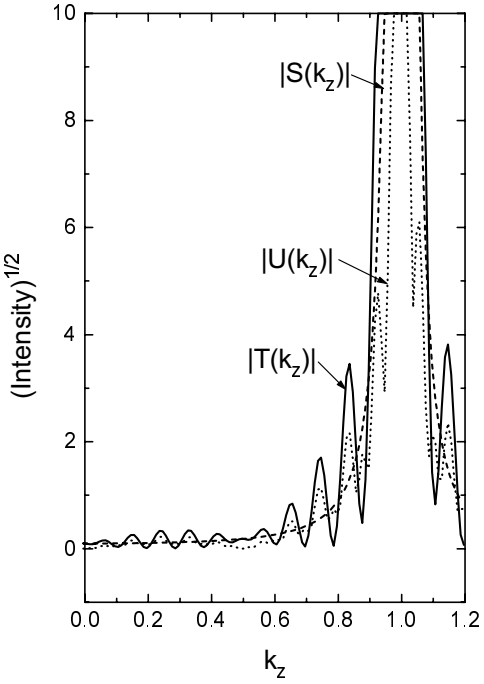

Figure 2. An example of the moduli of the complex scattering factors of the semi-infinite GaAs substrate $|S(k_z)|$, of the actual sample with four AlAs monolayers $|T(k_z)|$, and of the difference between the two, $|U(k_z)|$, over a fraction of a Bragg rod. The large peak at $k_z = 1$ corresponds to a Bragg point.

The method that we present here has two variations. The first is generally applicable and it consists of two steps. First we measure the *phase derivative* $\partial\phi/\partial k_z$ of the total CSF along the Bragg rods. This is accomplished using the two-beam diffraction interference method [12, 13]: we evaporate a thin gold film on the sample. A monochromatic x-ray beam enters the sample from the side (see figure 1) and, since gold is a heavy atom, it undergoes, at small incidence angles, total external reflection. Under these conditions the incident and reflected beams are diffracted in pairs of coherent and exactly parallel beams [12, 13]. The beams in each pair interfere with each other coherently, providing the phase derivative along the Bragg rods [12, 13].

The second step is to determine the phase itself. In principle, one could integrate the measured phase derivative. This approach has two problems. First, it is necessary to know the absolute phase at least at one point on each Bragg rod. More seriously, even a small amount of noise in the experimental data produces large errors in the phase, rendering it useless.

We propose here an efficient iterative approach that determines the phase from the measured diffraction interference patterns and the phase derivative itself without the need for integration. We first consider two points along a Bragg rod at a small separation Δk_z from each other. The total CSFs at the two points can be expressed in terms of the substrate CSF and unknown CSF as follows:

$$S_1 + U_1 = |T_1|\,\mathrm{e}^{\mathrm{i}\phi_1} \tag{1}$$

$$S_2 + |Q|\,\mathrm{e}^{\mathrm{i}\phi_Q} U_1 = |T_2|\,\mathrm{e}^{\mathrm{i}(\phi_1+\Delta)}. \tag{2}$$

Here, indices 1 and 2 correspond to k_z and $k_z + \Delta k_z$, respectively, $S = |S|\mathrm{e}^{\mathrm{i}\phi_S}$, and $U = |U|\mathrm{e}^{\mathrm{i}\phi_U}$; Q is the complex ratio between U_2 and U_1, and $\Delta = \phi_2 - \phi_1$. $|T|$ and Δ are directly determined from the experimentally measured scattering intensity and phase derivative, and S is the known CSF of the semi-infinite substrate crystal. We now approximate $|Q| \approx 1$ and solve equations (1) and (2) for U_1, ϕ_1, and ϕ_Q. At each point k_z there are two solutions. The correct solution is determined from the requirement that U_1 should vary smoothly along the Bragg rod. In this way we can calculate U_1 for all values of k_z. We can now use the function $U(k_z)$ to calculate a better approximation for $|Q|$ and to iterate again the solution of equations (1) and (2). In all our simulations this procedure converged after less than six iterations.

The second variation of the method applies to systems where the thickness of the unknown 2D structure is small compared to its distance from the surface, z_0. In this case, it is possible to determine $U(k_z)$ without measuring the phase derivative. Shifting the zero point of the real-space z-coordinate changes the k_z-dependence of ϕ_U, ϕ_Q, ϕ_S. We choose to place the zero point within the unknown 2D layer. We assume that we either know or can approximately guess this position. The results are insensitive to 20% changes in z_0. It is easily seen that in this case ϕ_U varies with k_z much more slowly than ϕ_S. Thus, $|\phi_Q| \ll \phi_{S2} - \phi_{S1}$ can be well approximated by zero and the complex ratio Q can be approximated with unity. We can now solve equations (1) and (2) for U_1, ϕ_1, and ϕ_2 and proceed with the iterations as before.

This procedure provides $U(k_z)$ for all relevant Bragg rods in reciprocal space. Its three-dimensional Fourier back-transformation into real space provides the 3D real-space x-ray dielectric function $\varepsilon(\vec{\rho}, z)$, which is related in a known way to the electron-density function. Here, $\vec{\rho}$ is the position vector in the crystalline-substrate-defined 2D unit cell and z is the distance in the direction normal to the plane of the 2D structure.

It is important to notice that the phase at each pair of points along the Bragg rods is determined using information related only to that pair of points. Thus in contrast to the method of Torrelles *et al* [11], computation time is linear in the number of atoms.

The method that we developed is also applicable if the unknown 2D structure is not fully periodic with respect to the 2D grid defined by the underlying substrate crystal. In this case, we define an average x-ray dielectric function:

$$\tilde{\varepsilon}(\vec{\rho}, z) = \frac{1}{N} \sum_j \varepsilon(\vec{\rho} + \vec{r}_j, z). \tag{3}$$

Here, $\vec{\rho}$ is the in-plane vector coordinate within one 2D unit cell defined by the substrate crystal and $\vec{r}_j$ is the in-plane coordinate of the jth unit cell. It can be readily shown that the Fourier transform of the averaged dielectric function $\tilde{\varepsilon}(\vec{r}, z) = \tilde{\varepsilon}(\vec{\rho}, z)$ is precisely proportional to the CSF of the system along the Bragg rods. (Notice that in this case the CSF away from the

Bragg rods is non-zero.) Thus, measuring the amplitude and phase of the CSF $U(k_\eta, k_\xi, k_z)$ along the Bragg rods and Fourier back-transforming the results into real space will directly yield the average dielectric function $\tilde{\varepsilon}(\vec{\rho}, z)$. The measurement and the analysis method are the same as for the 2D fully periodic systems.

Although the average dielectric function does not provide the positions of the individual atoms, it does provide the probability of finding an atom of a certain species at a point $(\vec{\rho}, z)$ in the 2D unit cell. For example if the atoms in a monolayer at a distance z from the surface occupy their ideal positions, $\tilde{\varepsilon}(\vec{\rho}, z)$ will have peaks at these positions. However, if the atoms are displaced due to reconstruction and the unit cell near the interface doubles, $\tilde{\varepsilon}(\vec{\rho}, z)$ will have double the number of peaks at positions $\vec{\rho}$, that correspond to the positions in the doubled unit cell projected on the undistorted 2D unit cell defined by the substrate crystal. Thus, measuring the average dielectric function $\tilde{\varepsilon}(\vec{\rho}, z)$ can provide detailed information on the reconstructed structures at interfaces as a function of the distance from the interface. We expect that measuring $\tilde{\varepsilon}(\vec{\rho}, z)$ will also be useful in studying crystal–amorphous material interfaces. Close to the interface the crystal is distorted and the electron density is not fully periodic but it does retain partial periodicity. This periodic component corresponds to the strain-induced displacement of atoms averaged over all 2D unit cells. Furthermore, one expects that the crystal will induce some degree of order into one or two monolayers of the amorphous material. Thus, measuring $\tilde{\varepsilon}(\vec{\rho}, z)$ can provide important information on the local distortions and on the degree of order as a function of the distance from the nominal interface.

3. Simulations

To test our method we have carried out both experiments as well as an extensive set of simulations. The simulations all led to the same conclusions, so only a few representative examples of the simulations will be presented. These representative simulations all involved a GaAs crystal with a number of AlAs monolayers buried at various distances from the surface. The AlAs monolayers and the crystal surface were assumed to be perpendicular to the [110] direction. We further assumed that the sample has an evaporated gold layer as shown in figure 1. We then calculated the diffraction intensity along the Bragg rods, assuming the scattering geometry shown in figure 1, for three x-ray incidence angles $\theta = -0.089^\circ, -0.178^\circ, -0.355^\circ$. In calculating the diffraction intensity we took into account both the incident x-ray beam and the beam reflected at the sample–gold interface. To these simulated data we added noise typical of that encountered in the experiments described further below. From here on, the data were treated as experimental data and the sample as unknown (except for the known substrate crystal). The simulated data were then analysed in order to recover the sample structure. Using the two-beam diffraction interference method [13] we calculated the phase derivative. The phase itself and the unknown complex scattering factor were obtained using the method described above both with and without the phase derivative. Finally the CSF was Fourier back-transformed resulting in the difference between the ideal GaAs electron density and the electron density of the unknown sample.

In figure 3 we present the results from an analysis of three simulated data sets. The data were simulated along one Bragg rod only: from $[-5\,-1\,1]$ to [151]. The Fourier back-transformation was done in one dimension yielding the difference between the electron density of GaAs and the actual sample averaged over each monolayer. In figure 3, curves a and b show the electron-density difference for a system of four AlAs monolayers buried under twenty monolayers of GaAs analysed with and without the phase derivative, respectively. As seen, both analyses yield monolayer-resolved structures and very little noise. Curves c and d represent the electron-density difference for a similar structure but here we also have three

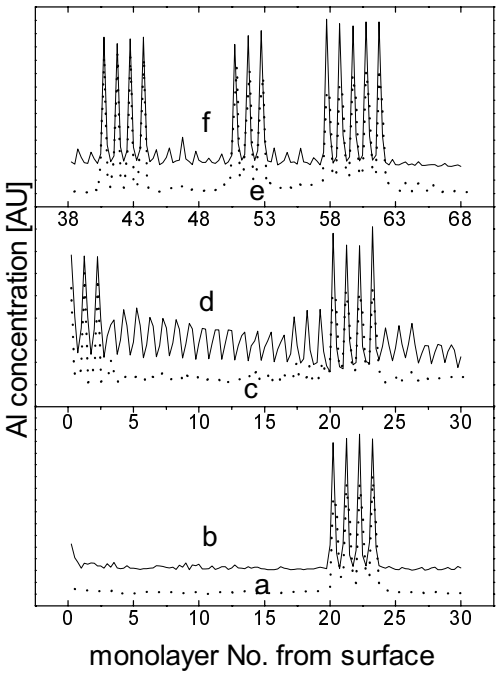

Figure 3. Electron-density differences between an ideal GaAs semi-infinite crystal and GaAs/AlAs samples as functions of the distance from the sample surface. The samples consist of alternating GaAs and AlAs monolayer sequences proceeding from the outer surface to the cleaved GaAs substrate; (a, b) 20, 4; (c, d) 0, 3, 17, 4; (e, f) 40, 4, 6, 3, 4, 5. Graphs a, c, e were obtained using the phase derivative while graphs b, d, f were obtained without it.

AlAs monolayers at the surface. Notice that in this case the unknown region extends from the surface to 5 nm below it, so its thickness is not small compared to its distance from the surface. Thus the approximation made in analysing the data without the phase derivative is not valid. Indeed as expected, the analysis with the phase derivative gives good results while the results obtained without it are rather poor. Curves e and f show the reconstructed structure of a 22-monolayer-thick unknown region buried 40 monolayers underneath the surface. In this case both variations work well. This result shows that the method allows us to reconstruct rather thick structurally unknown layers with monolayer resolution.

We have also carried out three-dimensional simulations. In these simulations we generated the diffraction data along 49 Bragg rods and analysed the data for each rod as before. This provided us with the scattering factor $U(k_\eta, k_\xi, k_z)$, where k_η, k_ξ are the x- and y-components of the (η, ξ) discrete in-plane reciprocal-lattice vectors. We then Fourier back-transformed this function in three dimensions to obtain the three-dimensional dielectric function. An example of the results is shown in figure 4. The structure that we used was again GaAs with four monolayers of AlAs buried under twenty monolayers of GaAs. In figure 4(a) we show the difference between the electron density of GaAs and AlAs as a function of position in the plane of the AlAs monolayer closest to the surface. The peaks are at the Al-atom positions. The in-plane structure of the next AlAs monolayer is shown in figure 4(b). As expected, the structure is the same but shifted by 0.5 and 0.353 unit-cell units in the $\langle 001 \rangle$ and $\langle 1\bar{1}0 \rangle$ directions, respectively. These results show that the structure has been retrieved with both in-plane and out-of-plane atomic resolution.

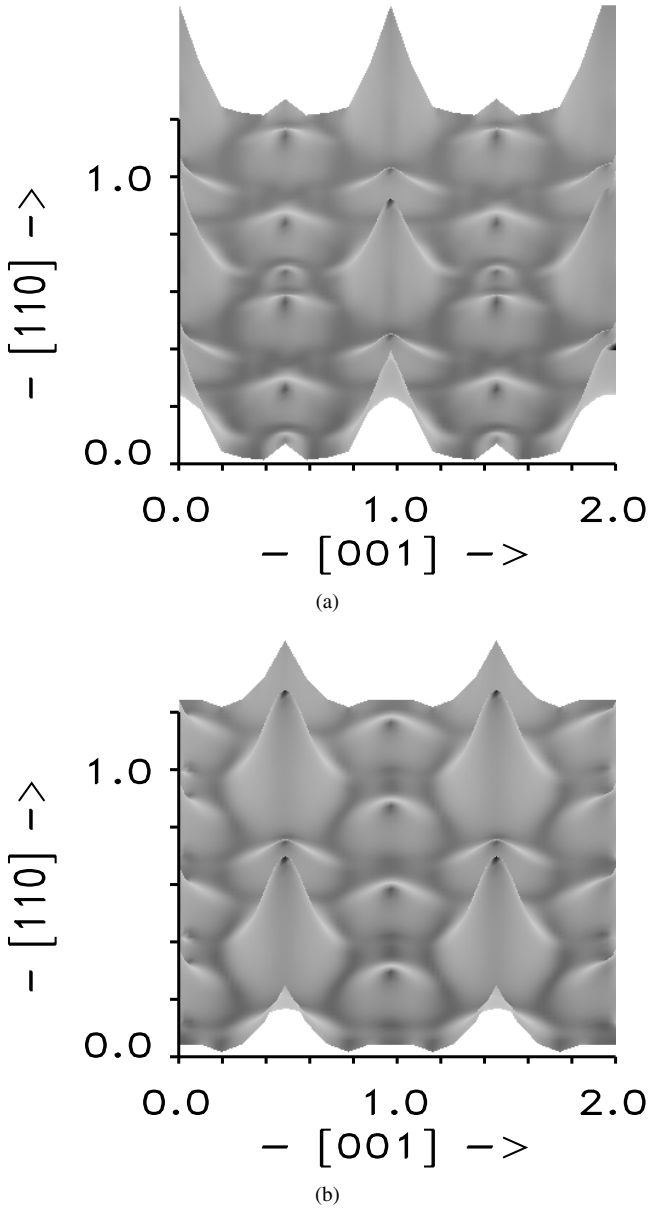

Figure 4. The electron-density difference between an ideal GaAs semi-infinite crystal and the GaAs/AlAs sample, corresponding to figure 3, curve a, as a function of the in-plane position, for two AlAs monolayers: (a) the monolayer closest to the surface and (b) the next monolayer.

4. Experimental demonstration of the method

The method has been experimentally demonstrated on two samples. A GaAs crystal was cleaved along a (110) plane in vacuum, in an MBE growth chamber. We grew on it nominally four monolayers of AlAs followed by a cap layer of twenty monolayers of GaAs. The number of monolayers was controlled *in situ* using the usual reflected high-energy electron diffraction

(RHEED) method. The crystal was then cleaved into a number of samples. On one of the samples, sample 'b', we evaporated 200 nm of gold while another, sample 'a', was not coated. Each sample was mounted on a two-axis tilt stage, which was mounted on the ϕ-circle of a four-circle goniometer. This arrangement allowed us to scan the diffraction intensity along a Bragg rod keeping the angle of incidence constant. A precision slit (0.5×0.03 mm^2) was mounted on the χ-circle of the goniometer along the incident beam path. This allowed us to minimize the footprint of the incident beam. The diffraction intensity was very carefully calibrated. Tests showed that we could rely on the ratio between the diffraction intensities at two points on the same or different Bragg rods to within $\pm 2\%$. This calibration is crucial in order to obtain good results.

The diffraction profiles were measured along one Bragg rod from $(-5\ -1\ 1)$ to (151) on beamline X25 of the National Synchrotron Light Source. The diffraction from sample 'a' was measured with an angle of incidence of $+0.1^\circ$ while sample 'b' was measured for three angles of incidence $\theta = -0.089^\circ, -0.178^\circ, -0.355^\circ$. From these measurements we determined the phase derivative along the Bragg rod of 'b' as explained in reference [13]. The data were then analysed using the method discussed above, resulting in the CSF along the Bragg rod. This was then Fourier back-transformed in one dimension resulting in the difference between in-plane averages of the GaAs and the AlAs electron densities as a function of the distance from the crystal surface.

Figure 5 shows this difference for both samples. Sample 'b' was analysed using the

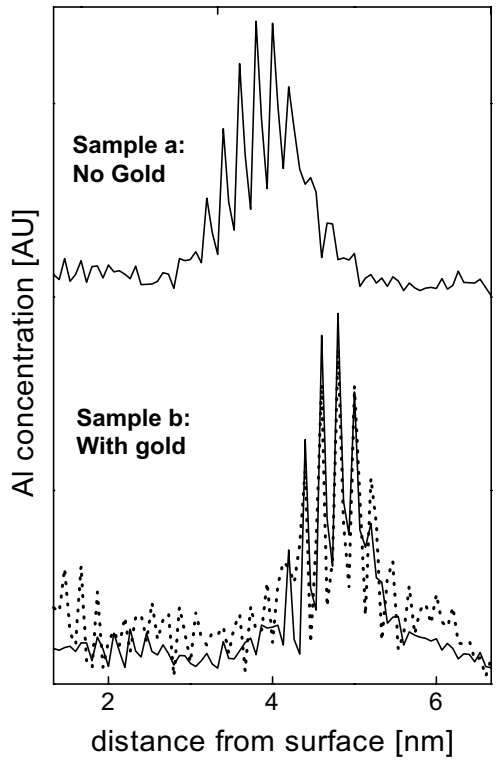

Figure 5. The experimentally obtained electron-density difference between an ideal GaAs semi-infinite crystal and two GaAs/AlAs samples. Solid line: analysis of both samples without the phase derivative; dotted line: analysis of sample b with the experimentally determined phase derivative.

phase derivative results (first variation) and both samples were also analysed without the phase derivative using the second variation of our method. The solid curves represent the results obtained without the phase derivative while the dotted line represents the results obtained with it. The results of the two analyses are in good agreement with each other. The electron density obtained with the phase derivative is noisier because it involves measuring several diffraction profiles at different incidence angles and using differences between the profiles. Each peak corresponds to one monolayer in which the Ga has been partially or fully replaced by Al. We believe that the four largest peaks correspond to the four monolayers nominally grown as AlAs. It seems that Al has penetrated into a small number of adjacent nominally GaAs monolayers. This is clearly seen in two monolayers on the left, closer to the surface. The growth seems to have also affected the cleaved crystal although not as much. The results clearly show that our method provides the phase along Bragg rods and the structure is obtained with monolayer resolution.

5. Summary and conclusions

We have presented a general method for determining the three-dimensional structure of systems that are periodic in two dimensions, aperiodic in the third, and are commensurate with an underlying three-dimensional crystal. The method does not require any *a priori* model of the structure. It can handle structures with large 2D unit cells and large layer thickness, and it is non-destructive. Using simulation of the data along one Bragg rod, we have demonstrated that the system layer structure can be reconstructed with monolayer resolution. Furthermore, we showed that the full three-dimensional structure of a system can be reconstructed with atomic resolution from simulated data along Bragg rods within a volume in reciprocal space. Finally it has been demonstrated that the complex scattering factor can be experimentally determined along a Bragg rod. Using these results the layer structure of the test samples was reconstructed. These same CSFs, when determined along the Bragg rods within a volume in reciprocal space, can be used to determine the three-dimensional structure.

We believe that the method presented here will facilitate structure determination of a variety of restricted-dimensionality systems, including epitaxially grown thin films, crystal–amorphous interfaces, and reconstructed structures, and structural phase transitions at interfaces.

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