X-Ray Standing-Wave Determination of the Clean InP(110) Surface Reconstruction

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The x-ray standing-wave technique through detection of surface-sensitive Auger electrons has determined the surface reconstruction of clean InP(110). Using the back-reflection diffraction geometry from (220) planes, we find the perpendicular displacements of the surface P and In atoms to be $+0.18 \pm 0.1$ and -0.48 ± 0.08 Å, respectively, from their unrelaxed bulk positions. The use of low-energy x rays combined with a novel method of data analysis opens the general problem of surface reconstruction to study by this technique.

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Much progress in understanding the geometric aspects of surface structure has been made since the invention of the scanning tunneling microscope (STM) [1]. However, the STM does not readily provide information on distances perpendicular to the surface. These distances in principle can be obtained from elastic low-energy electron diffraction (ELEED) [2], but the complexity of data analysis that employs a multiple-scattering theory is a severely limiting factor, and the method has been applied to only a handful of model systems. ELEED is also not sensitive to displacements parallel to the surface plane.

The x-ray standing-wave (XSW) technique is an ideal method of surface structural determination to complement the STM because it can easily determine perpendicular distances [3]. XSW can also provide complete geometries and parallel displacements if more than one diffracting plane is used. Extension of the method to clean surfaces would significantly complement STM studies and provide a complete description of clean-surface geometry with which to compare state-of-the-art calculations and the complex theoretical analysis which must accompany ELEED data.

To date, XSW has been used to study the structure of surface or interface atoms which differ in atomic number from those in the bulk. In such cases, distinct core-level, Auger, or fluorescence yields from the different elements are used to discriminate between the surface and bulk signals. For studies of clean surfaces, elemental discrimination is of no use, and the surface sensitivity of Auger electrons can serve. Durbin *et al.* [4] attempted such a measurement of the clean Si(111) 7×7 structure; however, their interpretation was challenged in a later XSW study by Patel *et al.* [5], who suggested that most of the low-energy Auger electrons and background observed in the former were produced by the higher-energy electron background that emerged from deep within the bulk. Thus, the resulting yield was actually representative of the bulk extinction behavior of the XSW field, which can appear similar to a surface contraction. It has also been argued that the hot electrons from the bulk (up to 10000 eV) present in their study created more surface Auger electrons than the x-ray field itself, rendering any such effect unmeasurable [6].

In this Letter, we present new x-ray standing-wave data from the InP(110) surface which demonstrates conclusively that the XSW technique can, in fact, determine displacements at clean surfaces. The methods employed in this study have numerous advantages over previous work.

First, the InP(110) surface has been studied by a variety of techniques, and it is believed to exhibit a reconstruction in which only rehybridization and relaxation occur [2]. This situation is less complex than the Si(111) 7×7 surface, and it is therefore more suitable for an initial investigation.

Second, in the soft-x-ray energy range there are no high-energy hot electrons (~10 keV) exiting through the surface from the bulk. Hot electrons can emerge from a depth as large as an x-ray extinction length, and can excite a significant amount of shallow core-level vacancies at the surface which contribute to the Auger signal.

Third, the InP(110) surface has two atoms in its surface unit cell, P and In, both of which have low-energy high surface-sensitive Auger peaks with which to measure the surface displacements independently. This surface therefore possesses an internal check of the data analysis method, namely, the relative difference in the atomic coordinates of the surface P and In atoms. The elemental discrimination of Auger spectra makes separate determination of the atomic positions routine for XSW.

Fourth, in the back-reflection diffraction geometry, the width of the crystal rocking curve becomes very wide, allowing the technique to be applied to even mosaic metal surfaces in addition to all the semiconductor surfaces such as the III-V, II-VI, and group IV's [7].

Furthermore, we present a simplified method of analysis which allows the determination of the surface relaxation without prior knowledge of the energy depen-

dence of the inelastic electron background or of the effective escape depth of the P and In Auger decays.

This experiment should therefore clarify the existing controversy in the literature [4,5] and establish the x-ray standing-wave technique as a new experimental method for the study of surface reconstructions.

The x-ray standing-wave experiments were performed on beam line X24A [8] of the National Synchrotron Light Source in a standard ultrahigh-vacuum chamber equipped with a double-pass cylindrical-mirror analyzer (CMA). Data from the freshly cleaved InP(110) surface were collected in a fixed-angle normal-incidence diffraction geometry by scanning a pair of Si(111) monochromator crystals through the InP(220) Bragg back-reflection condition, which occurs near 2987 eV. A conventional ultrahigh-vacuum sample manipulator was sufficient for sample alignment.

In a single XSW scan, the back-reflected photon intensity and the P LVV(~120 eV) or the In MNN(~400 eV) Auger yield are measured simultaneously as a function of photon energy around the Bragg condition. Similar data are recorded with the CMA kinetic energy set above the P (~150 eV) or the In (~450 eV) Auger lines. This is necessary because the P and In Auger peaks ride on top of a background of inelastically scattered electrons which also is strongly modulated by the standing-wave characteristic of the bulk substrate. The reflectivity spectra were measured by the incident-flux monitor, which consisted of an 80%-transmitting Ni grid and a channeltron, upstream of the sample. As the energy is swept through the Bragg condition, the back-reflected beam intensity from the crystal at normal incidence is observed on top of the signal from the incident flux. The detection of the reflectivity peak is critical for the analysis because it provides fiducial information on the energy resolution and energy calibration as well as control of the sample alignment.

Figure 1 shows the InP(220) reflectivity curve along with the best fit to the data points. The fit is the result of convolving the theoretical reflectivity [9] with a Gaussian of width 0.57 eV and adjusting it for a small energy offset. Shown also is the photon energy dependence of the secondary electron signal recorded with the CMA kinetic energy set above the In Auger line. This background spectrum is compared to a least-squares fit by the function [9]

$$Y = 1 + R + 2\sqrt{R}\cos(\phi - 2\pi\nu),$$

which is appropriate for the XSW signal from atoms located near a crystal surface, i.e., for cases where extinction effects are negligible. The pertinent fitting parameter for the standing-wave pattern is ν, the coherent distance in units of the reflecting-plane spacing. ϕ is the phase of the standing wave which is defined through the reflectivity R by

$$E_H/E_0 = |E_H/E_0|e^{i\phi} = \sqrt{R}e^{i\phi}.$$

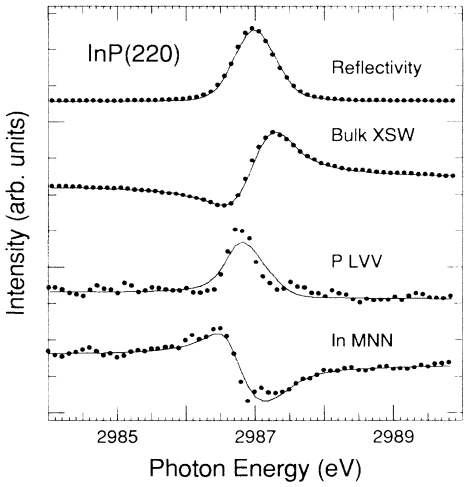

FIG. 1. Photon energy dependence of the reflectivity, the background XSW, the P LVV ratioed XSW, and the In MNN ratioed XSW near the InP(220) Bragg condition. The solid lines are the best fits to the data points (see text).

E_0 and E_H are the incident and reflected fields which are solutions of Maxwell's equations. The best fits for both the In and P background signals were obtained for $\nu = 1.01$, which is indistinguishable from the expected value of 1 for atoms at bulk lattice sites close to the surface. We note that if extinction effects were present, the above simple theory would find a spurious contraction in coherent position of the background wave [10]. Extinction effects are negligible in our measurements due to the low photon energy used. The extinction depth in InP (a few microns) is much larger than the depth of escape of the highest-energy electrons (a few hundred angstroms) present in this study [11].

In contrast to the inelastic background signal, the signal recorded at either the P LVV or the In MNN Auger peaks include components of different origin. The background signal underlies the Auger peak itself. This background is presumed to be identical to that recorded just above the peak except for a scaling factor to account for the upward slope of the background with decreasing kinetic energy. The elastic portion of the Auger peak includes contributions from the surface layer and the top few near-surface layers. To isolate the characteristic signal of the surface layer, one approach would be to model each of the above processes and estimate their relative magnitude. This, however, requires accurate knowledge of the complicated energy dependence of the inelastic background and of the electron escape depth of the Auger electrons from the near surface at the observation angle of the spectrometer. We have performed such analysis [12], but prefer instead to present here a novel approach which is less model dependent.

The key to this analysis is the above experimental result that the background signal is matched by the

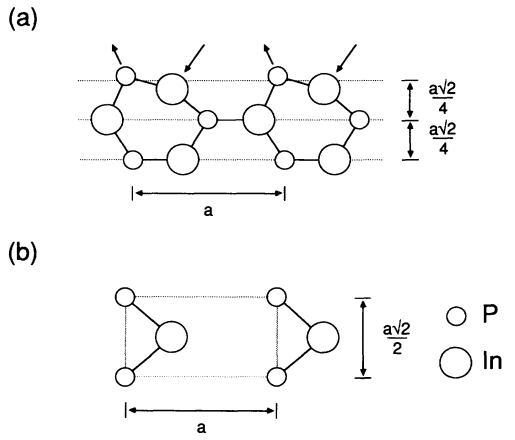

FIG. 2. Schematic of the clean InP(110) surface relaxation: (a) side view and (b) top view. The dashed lines denote the (220) Bragg planes in (a) and the surface unit cell in (b).

standing-wave behavior of a bulk lattice site. While this is not true in general for electron spectra stimulated by x-ray standing waves at arbitrary photon energy, it is demonstrated in this case, and it will hold for cases when the photon energy is low. When this circumstance is realized, all contributions to the electron spectrometer signal at the Auger peak, with the crucial exception of the surface-layer signal directly stimulated by the x-ray standing waves, will match the behavior of the substitutional position. Thus, the total signal T recorded at the Auger peak is found from $T=S+\alpha B$, where S is the surface signal of interest, and B is the background signal measured above the Auger peak. α is a scaling constant which accounts for the additional contributions to T. It is clear that the ratio of the two standing-wave patterns recorded at and above the Auger line will produce the ratio of the surface to bulk signals plus a constant: $(S+\alpha B)/B=S/B+\alpha$. If we fit the ratio with $Y(v)/Y(1)+\text{const}$, the fit will produce the surface-atom position, which is independent of the Auger escape depth and the energy dependence of the inelastic background. Information on these effects is contained in the constant. This method has the additional advantage that if electrons emanating from the bulk do in fact lead to a significant amount of surface Auger decay, their signal is processed as if it were part of the direct bulk wave.

The P and In ratioed data are shown in Fig. 1 with the best fits as described above. Clearly, the ratioed data are quite different for the P and In signals [13]. From these data, it is immediately evident that the surface P atom is upwardly displaced while the surface In atom is downwardly displaced from the bulk plane. Had the surface not been reconstructed, these data would be constant versus photon energy. We find the best fits for these displacements to be $+0.18\pm0.1$ and -0.48 ± 0.08 Å, respectively. For a bond-length-conserving rotation [14], we find the angle ω between the plane of the surface P-In chain and the plane of the unreconstructed (110) surface to be $27\pm5°$. This reconstruction is shown in Fig. 2. Table I compares our experimental results with theoretical values from various groups [14] and the ELEED determination [15]. Our data favor Chadi's energy-minimization calculation.

TABLE I. Comparison of the XSW determination of the P and In perpendicular surface displacements with theory and ELEED analysis.

	Displacement (Å)		
ω (deg)	P	In	
28.1	+0.06	−0.63	ELEED
26.5	+0.18	−0.47	Chadi
25.3	+0.21	−0.46	Chang *et al.*
31.8	+0.17	−0.58	Mailliot *et al.*
27 ± 5	$+0.18\pm0.1$	-0.48 ± 0.08	XSW

The only assumption used in the above analysis is that the standing-wave pattern recorded above the Auger peak approximates the bulk wave which we have experimentally demonstrated. If more than one atomic layer is displaced from its bulk site, then the above analysis will yield the escape-depth-weighted average of the sum of the displacements. (Note that in all standing-wave experiments of overlayer sites a similar situation holds in that the final coherent position includes the sum of all the surface relaxations.) It is possible to fit the data with more than one position, but such analysis is outside the scope of the present measurement, and the second-layer displacements are assumed much smaller than the first [14]. It is important that the amplitude of the surface signal be comparable to and its line shape different from the bulk signal in order to be detectable above the experimental noise and artifacts due to monochromator instability. In future work these criteria can be better assured by collecting electrons at shallower takeoff angles and by recording the Auger signal and background simultaneously at each photon energy.

In conclusion, we have demonstrated the utility of the x-ray standing-wave method in the determination of a clean-surface reconstruction. We have independently measured the perpendicular displacements of the P and In atoms at the clean InP(110) surface and have found them to be $+0.18\pm0.1$ and -0.48 ± 0.08 Å, respectively, from their unrelaxed bulk positions. These displacements agree with theoretical calculations for the bond-length-conserving rotation.

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[12] Taking $\lambda_P = 8$ Å and $\lambda_{In} = 15$ Å, smooth-line interpolations of the inelastic backgrounds, no hot-electron considerations, and 26° for the average acceptance angle of the CMA at normal incidence produced the displacements $\Delta_P = +0.15$ Å and $\Delta_{In} = -0.46$ Å, both of which are within the quoted uncertainty of the ratio method.

[13] For both the P and In Auger lines, the Auger signal to background was ~1:1, and the contrast in the ratio is ~10%.

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