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1996 J. Phys.: Condens. Matter 8 15

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An x-ray standing-wave study of H₂S adsorption on InP(110)

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Received 15 September 1995

Abstract. The sulphur adsorption site for H₂S-dosed InP(110) has been determined using normal-incidence x-ray standing waves (NIXSW) using the (220), (022) and (113) Bragg planes for triangulation. Photoabsorption was monitored by photoelectron emission from the S 1s, P 1s and In 3d_{5/2} core levels. The sulphur was found to be located in the phosphorus sites of the continued-layer structure, bonding to the surface indium. Using Auger electron emission for surface-sensitive NIXSW, it was found that H₂S adsorption lifts the relaxation of the clean surface.

1. Introduction

Exposure to hydrogen sulphide can result in an ordered overlayer on the cleaved (110) surface of III–V semiconductors [1]. The adsorption process appears to be very similar on InP, GaP and GaAs, although the reactivity of GaAs is markedly lower than that of the phosphides [2, 3]. Soft x-ray photoelectron spectroscopy (SXPS) shows that two adsorption regimes exist, a high-dosage regime in which there is some surface disruption, and a low-dosage range (between 1 and 5 langmuir) where the clean surface can be regenerated by annealing [1, 3, 4, 5]. In this latter regime the S 2p core-level spectrum shows only one component, corresponding to one adsorbed sulphur species; the anion (P, As) core-level spectrum loses its surface component and develops a new, chemically shifted component at 0.6 eV higher binding energy than the bulk component [2, 3]; the cation (In, Ga) core-level spectrum shows only a reduction of the surface component [3]. The distinct anion core-level shift has led to the suggestion that the H₂S interacts with the surface anion [2].

There is, however, an alternative explanation for the observed changes in the core-level spectra. The ideal (110) surface of a III–V semiconductor is shown in figure 1(a). This structure is known to relax to that shown in figure 1(b). The anion has moved out of the plane so its remaining three bonds are roughly at right angles, with a lone pair of electrons facing away from the surface. The cation has moved inwards so its three bonds are roughly planar at 120° angles, with an empty dangling bond facing outwards from this plane [6]. The H₂S molecule itself has a lone pair of electrons located on the sulphur. It seems more likely that this would interact with the empty cation orbital rather than the filled anion dangling bond. This interaction explains the reduction of the surface component in the cation core-level spectrum. The shift to higher binding energy in the surface anion spectrum can then

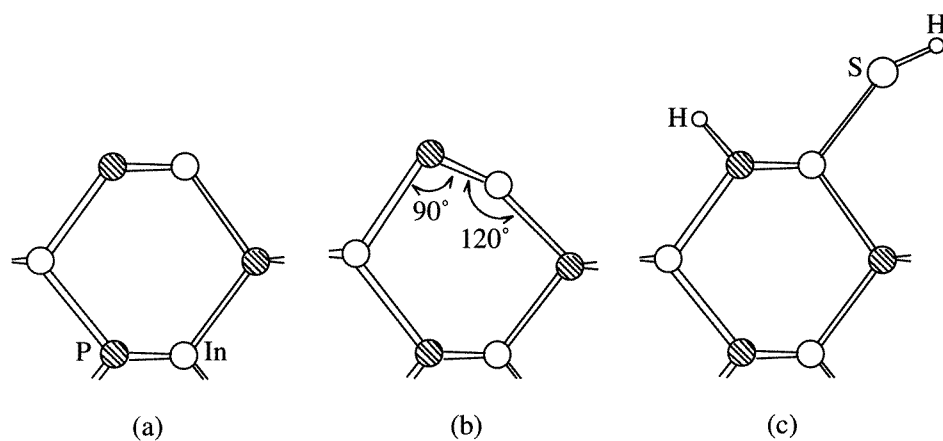


Figure 1. (a) A side view of the ideal (110) surface of a III-V semiconductor; (b) relaxation of the clean surface; (c) the dissociative adsorption model for H₂S.

be explained via a proton exchange between the H₂S and the anion dangling bond upon adsorption—in effect a dissociative adsorption of H⁺ and SH⁻ at anion and cation sites, respectively, as shown in figure 1(c). This model has some support from the fact that the observed reactivities of the different III-V semiconductors scale with the proton affinity of the anion dangling bond [3].

If this interpretation is correct, the adsorbed sulphur should be located in the vicinity of the continued-layer phosphorus site. Normal-incidence x-ray standing waves (NIXSW) provide a method well suited to the determination of an adsorbate position on a surface [7], and are used in this work to determine the sulphur atom position. Furthermore, it seems likely that this dissociative adsorption will de-relax the semiconductor surface as shown in figure 1(c). The influence of the adsorption on the surface relaxation is studied here with surface-sensitive NIXSW, using the evaluation method described by Woicik *et al* [8].

2. Experimental details

Pre-notched n-InP samples were cleaved in UHV at base pressures of around 3×10^{-10} Torr and then dosed with 2–5 L of H₂S (purity 99.6%). All experiments described here were performed at beamline 6.3 of the Daresbury Synchrotron Radiation Source in the UK. This beamline has a double-crystal monochromator which (for Ge(111) crystals) has a photon energy range from 2000 to 8000 eV. The UHV chamber contained a VG LEED optics to check the sample alignment and a VSW HA100 hemispherical electron analyser. There was some uncertainty in measuring dosage because of the location of the ion gauge away from the main chamber, so the actual dosages may have been lower than the nominal values. Measurements were repeated on two cleaves to test the reproducibility of the results.

A NIXSW experiment monitors the atom-specific photoabsorption of the x-ray standing wave field set up in the crystal at the Bragg condition for constructive interference. As the wavelength of the incident x-rays is scanned across the Bragg condition, the phase of this standing wave changes and the resulting absorption profile is characteristic of an atom's distance relative to the bulk scattering planes.

To determine an unknown adsorbate position accurately, a set of three Bragg planes are

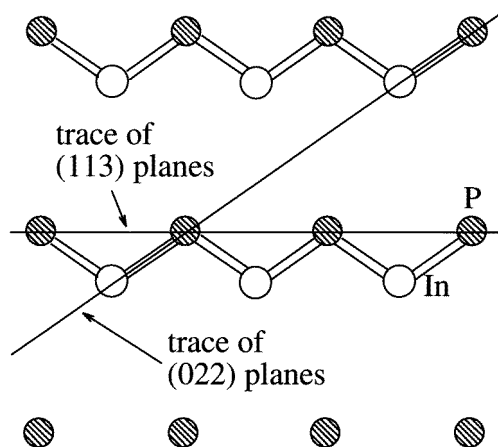


Figure 2. A plan view of the (110) surface showing the azimuthal orientation of the traces of the (022) and the (113) planes. The polar angle between the (022) and the (110) planes is 60° and the polar angle between the (113) and (110) planes is approximately 65° .

needed for triangulation (two sets of planes would be sufficient to distinguish between the In and the P sites of the continued layer; the third plane provides a more accurate value for the adsorbate–substrate bond length). The planes used in this work were the (220) planes parallel to the cleaved surface, the (022) planes at 60° to the surface and the (113) planes at 65° to the surface. The azimuthal orientation of the traces of these latter planes in the (110) surface plane are shown in figure 2. The Bragg energies for {220} and {113} planes are 2980 eV and 3497 eV, respectively. Photoabsorption was monitored using the In $3d_{5/2}$ (binding energy 435 eV) and the P 1s (binding energy 2139 eV) photoemission peaks. To check for possible photoelectron diffraction effects in the P 1s spectra, the P NIXSW profiles obtained in this way were compared to alternative profiles monitored by the intensity of the P KLL Auger electron emission peak at 1806 eV. Since the two profiles were virtually identical, the P 1s photoemission signal was used because of its higher intensity. For the adsorbate the S 1s (binding energy 2467 eV) photoemission peak was used rather than the S KLL Auger at 2100 eV for the same reason. It should be noted that the use of the photoemission signals also overcomes any potential difficulties associated with secondary-electron ionization events which can contribute to the measured Auger electron signal.

However, in spite of the secondary-electron contributions, low-kinetic-energy Auger signals can be advantageous in a variation of NIXSW which probes the geometry of surface *substrate* atoms. Photoelectrons at low kinetic energies have a higher surface sensitivity, but show stronger photoelectron diffraction effects. As shown in figure 1(b), the planes of surface anions and cations are displaced above and below the ideal (110) surface plane, respectively. Low-energy Auger emission provides the surface sensitivity needed to selectively monitor the photoabsorption using these surface atoms. The Auger lines used in these experiments were the In MNN Auger line at 394.5 eV and the P LVV Auger line at 114.1 eV. To separate the surface Auger emission stimulated by the standing-wave field from the emission stimulated by secondary electrons, the evaluation method described by Woicik *et al* [8] was used.

For NIXSW measurements the samples were aligned by setting the monochromator energy slightly above the computed value for the Bragg condition. The reflected beam

could then be observed on a phosphorescent screen mounted around the entrance port for the light. By alternately varying the sample position and reducing the monochromator energy the diffracted beam was aligned so that it was reflected back into the beamline. This could be observed through the increase (of about 10%) in the drain current from an aluminium foil flux monitor in the beamline. For the (113) planes the sample was deliberately misaligned (so that the reflected beam was tilted downwards by about 2°) to separate the (113) XSW profile from that of several other Bragg reflections visible at this energy and orientation.

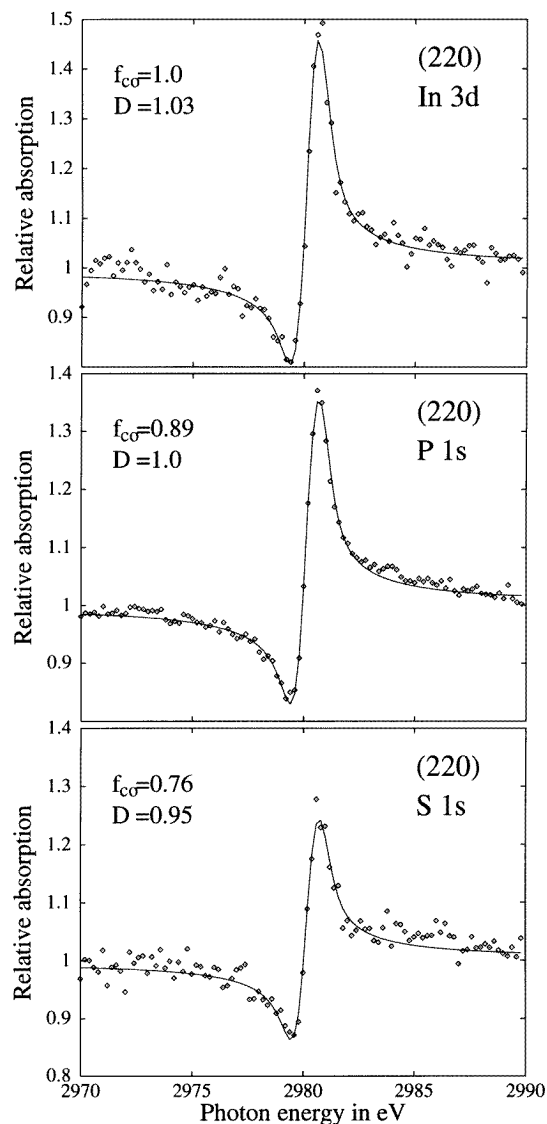


Figure 3. (220) NIXSW profiles from doped InP. The sulphur profiles strongly resemble the phosphorus and indium profiles. The coherent positions are given in units of the interlayer spacing.

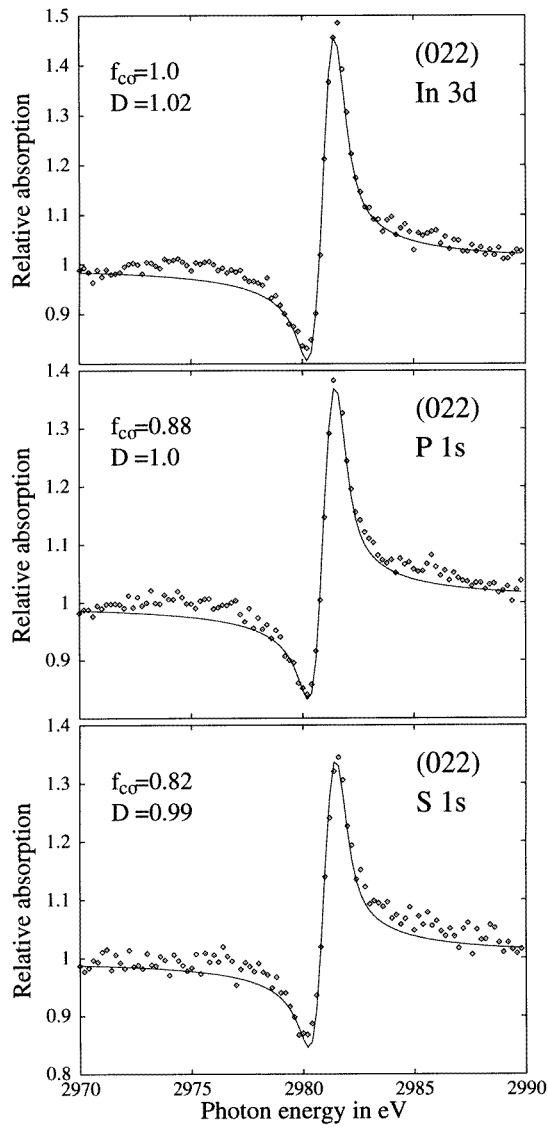


Figure 4. (022) NIXSW profiles from dosed InP. Again the sulphur profile strongly resembles both the bulk profiles. There is some nonlinear background in the spectra which could not be fitted completely. The coherent positions are given in units of the interlayer spacing.

3. Results

The NIXSW profiles for the two substrate species and for the sulphur adsorbate are shown in figures 3, 4 and 5 for the (220), (022) and (113) Bragg planes, respectively. The line fits were obtained by using an intensity profile of the form

$$I = (1 - f_{co})(1 + R) + f_{co} \left| 1 + \sqrt{R} e^{i(\varphi - 2\pi D)} \right|^2$$

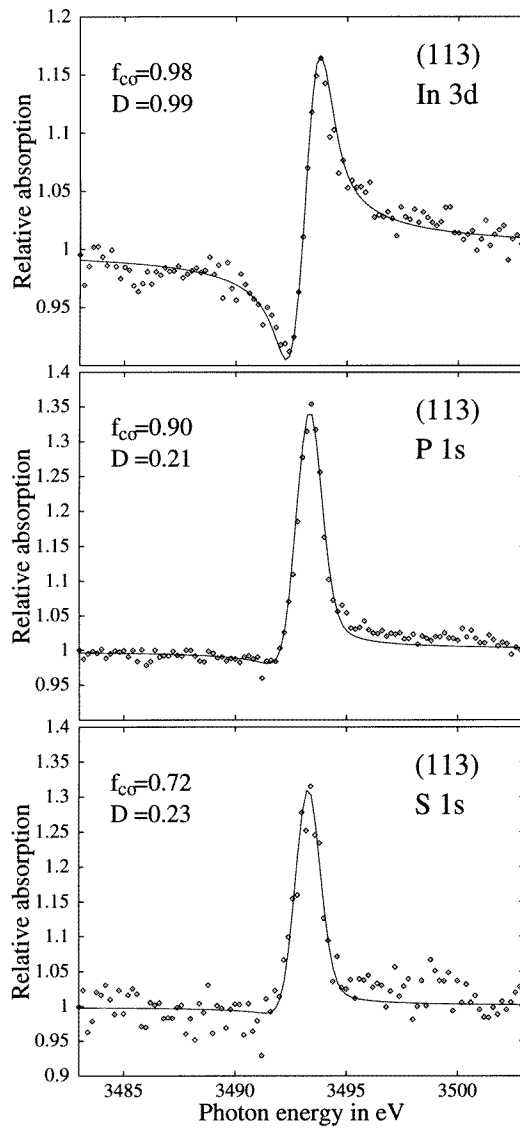


Figure 5. (113) NIXSW profiles from dosed InP. Here the sulphur profile resembles the phosphorus profile. The coherent positions are given in units of the interlayer spacing.

where R is the reflectivity and φ is the phase of the reflection; the fitting parameters were the coherent fraction f_{co} and the coherent position D of the absorber atoms. The resulting fit parameters are shown in the figures and listed in table 1. They were found to be reproducible on two different cleaves within an error of 0.03 for the coherent positions and 0.04 for the coherent fractions. Although the statistical errors in the individual fits are much lower (about 0.01 for both parameters), the scatter among repeated experiments is a truer measure of experimental error.

The absolute Bragg energy and the energy broadening of the profiles were determined by fitting NIXSW profiles obtained from the inelastic electron background. For the nonpolar

Table 1. NIXSW coherent fractions and coherent positions for H₂S-dosed InP(110). The coherent positions are given in units of the interlayer spacing. Bragg energy and energy broadening were found from off-peak spectra and are not listed here.

	(220) planes		(022) planes		(113) planes	
	D	f_{co}	D	f_{co}	D	f_{co}
In 3d _{5/2}	1.03	1.00	1.02	1.00	0.99	0.98
P 1s	1.00	0.89	1.00	0.88	0.21	0.90
S 1s	0.95	0.76	0.99	0.82	0.23	0.72

(220) and (022) planes this background is dominated by bulk emission with a coherent position very close to 1. For the polar (311) planes the In XSW profiles were used to determine the Bragg energy and the energy broadening, since the In atoms are very close to the effective Bragg scattering planes (see below).

The coherent fraction of the In absorption signal is very close to 1.00 for all three planes, as expected for the bulk signal. The phosphorus coherent fraction is consistently somewhat lower, around 0.90. This is possibly due to a greater surface sensitivity of the P 1s photoelectrons with a kinetic energy of approximately 800 eV compared to the In 3d_{5/2} photoelectrons with a kinetic energy of 2500 eV. The sulphur coherent fraction lies between 0.72 and 0.82 for the three planes. Since photoemission shows that only one sulphur species is present on the surface, these somewhat lower coherent fractions may indicate that the adsorbed molecule is vibrating on the surface; such a random movement would reduce the coherent fraction by a Debye–Waller factor.

It should be noted that in the (113) planes In and P atoms sit in two layers separated by $\frac{1}{4}d$ (d is the distance between the Bragg planes). The effective Bragg scattering plane is situated between these two layers, but is closer to the In layer, because indium is a much stronger photon scatterer than phosphorus. The position of the Bragg scattering plane was taken to be the mean position weighted with the atomic scattering factors (using only the real part) of P and In. This would give a coherent position of 0.20 for the phosphorus and 0.95 for the indium, in reasonable agreement with the experimental values (all coherent positions are given as fractions of the interlayer spacing).

Figures 3–5 show that the S profiles are very similar to those of the phosphorus for all three planes. This means that the sulphur either occupies a bulk-like substitutional site within the surface layer or a similar site above the surface in the continued-layer lattice. XSW cannot distinguish these two sites, but this question can be decided with the help of photoemission results. In the dosage range used in these experiments photoemission shows that the adsorbate can be removed completely and the clean-surface core-level and valence band spectra restored by cautious annealing to about 100 °C [3], so a substitution reaction seems unlikely. The resulting position of the continued-layer site relative to the (220) and (113) planes is shown in figure 6.

4. Substrate de-relaxation using surface-sensitive NIXSW

Figure 6 still shows the surface as relaxed, although it is quite likely that the saturation of both anion and cation dangling bonds will at least partly lift the surface relaxation. It is possible to observe the relaxation of the clean InP(110) surface with NIXSW, as was shown by Woicik and co-workers [8]; their method for extracting the signal arising from

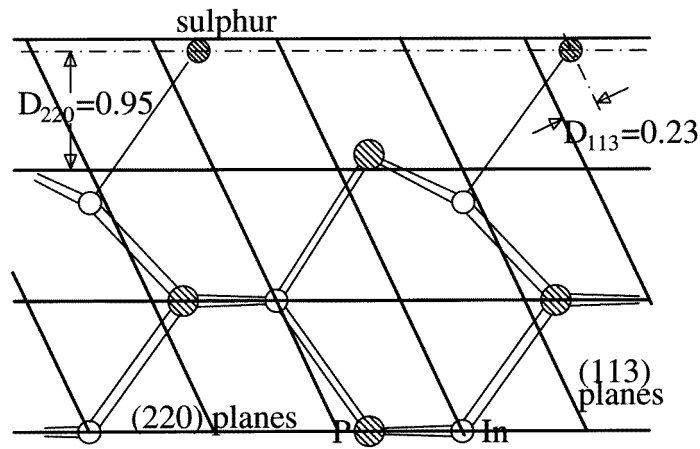


Figure 6. The position of adsorbed sulphur on the relaxed InP(110) surface with respect to the (113) and (220) planes determined with XSW. The position of the sulphur is very close to the bulk phosphorus sites in the continuing layer. The coherent positions are given in units of the interlayer spacing.

the surface atoms is used in this work.

To achieve surface sensitivity the low-energy P LVV Auger line at 114.1 eV and the In MNN Auger at 394.5 eV are used. At these kinetic energies electron escape depths are minimal, so the intensity ratio of surface and bulk signals should be at a maximum. Unfortunately the low-energy Auger emission is also stimulated by electrons *originating in the bulk*. An additional problem is the strongly sloping inelastic background in this kinetic energy region. All these signals, except the Auger emission from the surface atoms directly stimulated by the standing wave, will produce a bulk-like XSW profile.

To separate the two different profiles, Woicik *et al* recorded the XSW signal both on the Auger peak and on the inelastic background well away from the peak. The off-peak signal B is dominated by bulk emission. The on-peak signal T is the sum of the true surface signal S and several components which all have a bulk-like profile and thus can be written as the off-peak signal B scaled up by some factor α :

$$T = S + \alpha B.$$

When the on-peak signal is divided by the off-peak signal, the result is

$$\frac{T}{B} = \frac{S}{B} + \alpha.$$

The quotient T/B can now be fitted with $I(D)/I(0) + \text{constant}$ and the coherent position D of the relaxed surface atom determined.

Figure 7 shows the quotients of the on-peak and off-peak signals for the In MNN and P LVV Auger lines, for the clean and the dosed surfaces. For the In MNN the off-peak spectrum was recorded at a kinetic energy of 407.5 eV; the P LVV off-peak signal had to be measured further away at 170 eV, because for the dosed surface the S LVV Auger line is situated close to the P LVV line. The clean-surface profile ratios were fitted to standing-wave profile ratios as described above; the resulting coherent positions are 0.14 ± 0.03 for the phosphorus and 0.80 ± 0.03 for the indium. This is in very reasonable agreement with the experimental values of Woicik *et al* and lies within the range determined with other structural methods [9].

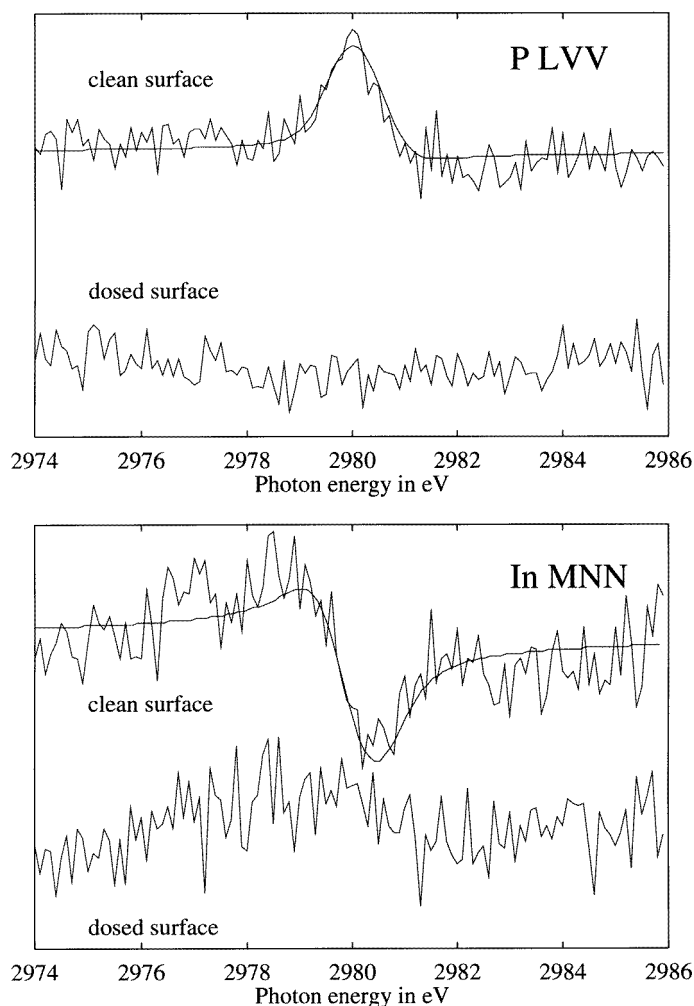


Figure 7. The ratio of on-peak and off-peak NIXSW profiles for the P LVV and the In MNN Auger. The clean-surface profiles reflect the surface relaxation, while on the dosed surface the ratio is practically a straight line.

On the dosed surface the quotients of on-peak and off-peak signals show almost no variation with photon energy, implying that there is essentially no difference between the lineshapes of the surface and bulk components. To ensure that this is not just due to an energy shift of the surface Auger emission, the two complete Auger spectra were recorded before and after dosage; the lineshape of the In MNN spectrum was found to be virtually unchanged by adsorption and the P LVV spectrum was reduced in intensity but not changed in shape. Thus figure 7 actually shows the lifting of the surface relaxation after H₂S dosage.

5. Conclusions

The positions of sulphur atoms on the H₂S-dosed InP(110) surface have been determined with NIXSW using three sets of Bragg planes for triangulation. It is found that the sulphur is

located in the continued-layer phosphorus site, bonding to the surface indium in agreement with the model proposed earlier [3]. The offsets from the ideal continued-layer phosphorus site are: $0.04 \pm 0.05 \text{ \AA}$ in the $(00\bar{1})$ direction, $0.02 \pm 0.08 \text{ \AA}$ in the $(\bar{1}10)$ direction and $-0.10 \pm 0.06 \text{ \AA}$ normal to the surface.

Using surface-sensitive NIXSW it has been shown that the relaxation of the clean InP(110) surface is lifted by the H_2S adsorption, presumably through the saturation of the anion and cation dangling-bond states, which brings the surface atoms back to tetrahedral coordination.

Acknowledgments

The authors acknowledge the support of the Large Scale Installations Plan and the HCM Network 'Structural and Electronic Properties of Surfaces and Ultra-Thin Films using Synchrotron Radiation' (contract No CT93-0358) for funding. Further support from the HCM network 'Chalcogen Modification of Semiconductor Interfaces' (contract No CT93-0317) is also acknowledged. The staff of the Daresbury Laboratory are thanked for their excellent technical support.

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