

Reflectance difference spectroscopy of mixed phases of indium phosphide (001)

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Reflectance difference spectra of mixed (2×1) and (2×4) phases of indium phosphide (001) have been recorded and benchmarked against scanning tunneling micrographs of the surface. The line shapes are found to be linear combinations of the spectra of the pure (2×1) and (2×4) structures, $\Delta r/r_{\text{mixed}} = x\Delta r/r_{(2\times 4)} + (1-x)\Delta r/r_{(2\times 1)}$, where x is the weighting factor. Thus, in the absence of adsorbates, the reflectance difference spectra can be used to estimate the surface composition, i.e., the fractional coverage of phosphorous is $\Theta_P = 1 - 0.81x \pm 0.06x$. © 2001 American Institute of Physics. [DOI: 10.1063/1.1337620]

Reflectance difference spectroscopy (RDS) is a useful, *in situ* probe of the condition of compound semiconductor surfaces during epitaxial growth.^{1,2} This technique is sensitive to the elemental composition of the surface as well as to submonolayer coverages of adsorbates.^{3–9} However, interpretation of RDS spectra is difficult, and the assignment of specific features is unclear in many cases. For example, it has been suggested that a correlation exists between the coverage of phosphorous dimers and the degree of CuPt_B-type ordering in InGaP and AlInGaP alloys grown by metalorganic vapor-phase epitaxy (MOVPE).^{10–13} The coverage of phosphorous dimers has been related back to a specific feature appearing in the optical spectra of the surface taken during growth.¹⁴ However, this feature has not been benchmarked against any other probes of the semiconductor surface structure, and consequently, this correlation must be viewed as a hypothesis that remains to be tested.

With regard to the simplest of phosphide-based materials, InP (001), two principal reflectance difference spectra have been identified.^{14–18} These correlate with the (2×1) and (2×4) reconstructions as identified by reflection high-energy electron diffraction, low-energy electron diffraction, and scanning tunneling microscopy (STM). Comparison of the RDS spectra reported in the literature reveals a considerable discrepancy in the line shapes recorded for each surface phase.^{14,18} Recently, we have characterized the phase diagram for indium phosphide (001), and have found that there are four distinct reconstructions.^{19–21} These are the $c(2\times 2)/p(2\times 2)$, (2×1), $\sigma(2\times 4)$, and $\delta(2\times 4)$ at phosphorous coverages of 2.00, 1.00, 0.25, and 0.125 ML, respectively. It is common for two or more reconstructions to co-exist on the same surface, such as $c(2\times 2)$ and (2×1), or (2×1), $\sigma(2\times 4)$, and $\delta(2\times 4)$. These mixtures could account for the discrepancies in the RDS spectra reported in the literature.

In this letter, we report on RDS spectra of indium phosphide (001) surfaces containing mixed (2×1) and (2×4) phases. These spectra have been benchmarked against scanning tunneling micrographs of the surfaces. We find that the

spectra of the mixed phases are linear combinations of the line shapes of the pure phases, and as a result, may be used to estimate the phosphorous surface coverage.

Indium phosphide films were grown with trimethylindium (TMIn) and tertiarybutylphosphine (TBP) at 525 °C and 20 Torr total pressure in a horizontal MOVPE reactor.²² The samples were cooled to room temperature while maintaining the TBP supply, and then transferred directly to an ultra-high-vacuum surface-analysis system. Room-temperature reflectance difference spectra were acquired before and after heating the samples to 400 °C for a few minutes. The spectra were recorded on a J-Y NISEL RDS spectrometer, and have been base-line corrected to remove any artifacts unrelated to the samples. In addition, scanning tunneling micrographs were obtained of the InP(001) surfaces using a Park Autoprobe VP STM at a sample bias of –3 V and a tunneling current of 1 nA.

We found it was convenient to monitor the optical signal at 2.9 eV during heating. As the sample temperature was increased from 25 to 400 °C, the positive peak at 3.1 eV in the (2×1) RDS spectrum shifted to 2.9 eV.²³ Then, while at 400 °C, this peak rapidly fell in intensity as the phosphorous desorbed from the surface and the (2×1) was converted into the (2×4) reconstruction. The value of the peak intensity provided an accurate gauge of the degree to which the surface had undergone the phase transition.

In Fig. 1, a scanning tunneling micrograph is presented of the indium phosphide surface following partial desorption of the phosphorous. The surface is covered 75% with the (2×1) and 25% with the $\sigma(2\times 4)$. The (2×1) is evident as a series of closely spaced gray rows running parallel to the [110] direction. The $\sigma(2\times 4)$, on the other hand, appears as shallow pits with more widely spaced gray rows separated by black trenches that extend along the $[\bar{1}10]$ direction. Samples with greater amounts of (2×4) were produced by heating for slightly longer times at 400 °C. The percentage of each reconstruction present on a surface was determined by carefully cutting up the printed STM image, and weighing the paper corresponding to the different phases. The values reported in this letter have been averaged over five separate images of each surface.

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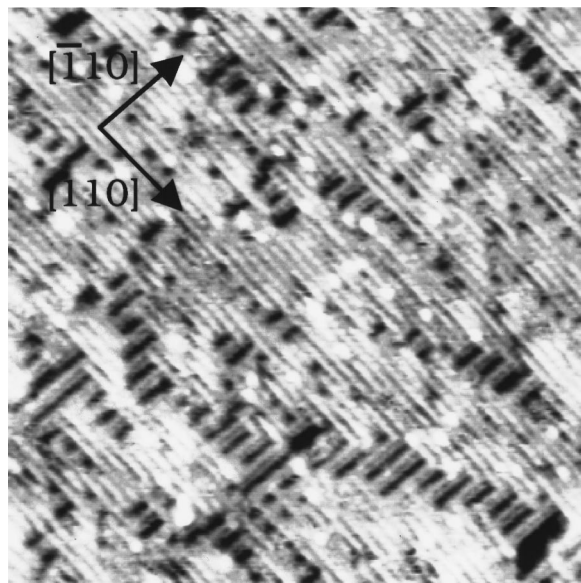


FIG. 1. Filled-states scanning tunneling micrograph of the InP(001) surface with a phosphorous coverage of 0.8 (image area = $430 \times 430 \text{ \AA}^2$).

Shown in Fig. 2 are reflectance difference spectra of a series of InP (001) surfaces having structures ranging from that obtained directly out of the MOVPE reactor to a pure (2×4) phase. When the sample is removed from the reactor,

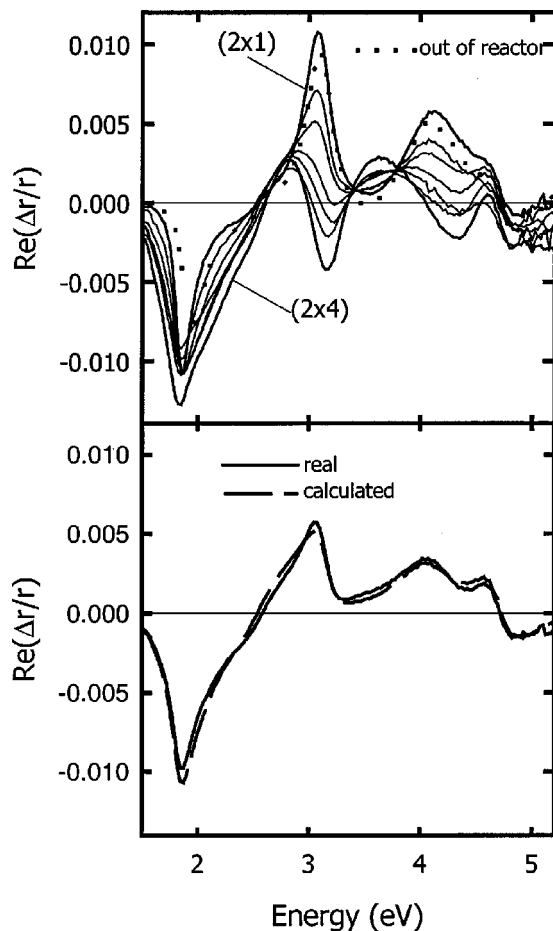


FIG. 2. Reflectance difference spectra of InP(001): (a) surfaces obtained directly following growth and after annealing at 300–400 °C for different periods of time; and (b) real and calculated spectra of a surface containing a mixture of (2×1) and (2×4) domains.

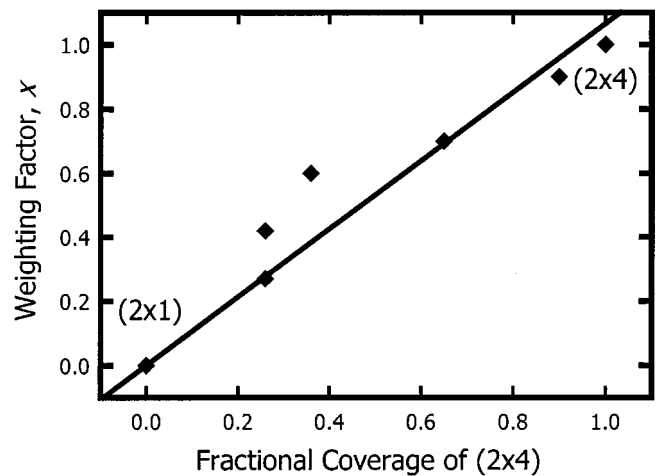


FIG. 3. Dependence of the weighting factor from the RDS spectra on the fractional coverage of the surface by (2×4) domains.

the surface is covered with phosphorous dimers, alkyl groups, and hydrogen atoms adsorbed on top of a monolayer of phosphorous atoms.^{20,21} The P ad-dimers exhibit localized $c(2 \times 2)/p(2 \times 2)$ domains. These adsorbates reduce somewhat the overall intensity of the spectra (dotted line). Heating to 300 °C for several minutes desorbs these species and produces a sharp (2×1) RD spectrum, as shown in Fig. 2. Further annealing of the samples at 400 °C produces a series of transitional spectra, and ultimately the (2×4) RD spectrum.

As the (2×1) reconstruction is gradually converted to the (2×4) , the following changes occur in the optical spectra: (1) The negative peak at 1.8 eV becomes broader and increases in intensity from -0.009 to -0.013 . (2) The positive peak at 3.1 eV falls from an initial intensity of 0.011 to 0.000, and is replaced by a negative peak at 3.2 eV, which reaches a final intensity of -0.004 . (3) The broad positive band at 4.2 eV disappears and is replaced by broad and narrow peaks at 3.6 and 4.6 eV. To determine if the intermediate spectra result from a superposition of the line shapes of each phase, the following formula was applied:

$$\frac{\Delta r}{r}(\text{mixed}) = x \frac{\Delta r}{r}(2 \times 4) + (1-x) \frac{\Delta r}{r}(2 \times 1). \quad (1)$$

In Eq. (1), $\Delta r/r(\text{mixed})$ is the calculated spectrum, $\Delta r/r(2 \times 4)$ and $\Delta r/r(2 \times 1)$ are the (2×4) and (2×1) spectra shown in Fig. 2, and x is a weighting factor. This weighting factor equals the fractional contribution of the (2×4) line shape to the overall spectrum. We have found that excellent agreement is achieved between the calculated and real RD spectra of the transitional surfaces. An example of one such fit is shown in Fig. 2(b).

In Fig. 3, the RDS weighting factor is plotted against the fractional surface coverage of (2×4) domains. A linear relationship is obtained. These data indicate that the value of x extracted from the RD spectrum can be used to identify the distribution of (2×1) and (2×4) domains on the surface, and in turn, the average phosphorous coverage. The phosphorous coverage is given by the following equation:

$$\theta_p = 1 - 0.81x + 0.06x^2 \quad (2)$$

Here, the fractional P coverage on the (2×4) is taken to be intermediate between the $\sigma(2 \times 4)$ and $\delta(2 \times 4)$, which equals 0.19. The uncertainty accounts for the variation between the two phases, $\Theta_p = 0.25$ and 0.125, respectively.

When the indium phosphide surface is heated to desorb the phosphorous atoms, the surface undergoes two phase transitions, from (2×1) to $\sigma(2 \times 4)$ and from $\sigma(2 \times 4)$ to $\delta(2 \times 4)$. In comparing the RDS data, we have found only two characteristic line shapes, i.e., we do not observe distinctly different spectra for the $\sigma(2 \times 4)$ and $\delta(2 \times 4)$. The former surface is terminated with a single phosphorous dimer straddling four indium dimers in the second layer, while the latter surface is terminated with an In-P heterodimer straddling four indium dimers.²¹ It may be that the P-P and In-P dimers exhibit the same optical response. However, further experiments are needed to resolve this issue.

Previous studies of compound semiconductor surfaces have proposed that the optical spectra of intermediate phases result from the superposition of the pure phase spectra.²³⁻²⁵ We have shown that this is indeed the case for InP(001), and that the linear response of the RDS spectrum can be used to determine the phosphorous coverage. However, this is not the case for gallium arsenide (001). Desorption of arsenic atoms from GaAs results in a series of phase transitions from $c(4 \times 4)$ to (2×4) to (4×2) .²⁶ Reflectance difference spectra of intermediate structures between the $c(4 \times 4)$ and (2×4) are not simple combinations of the pure reconstructions.⁸ The reason for this is that arsenic desorption from the $c(4 \times 4)$ leads to out-diffusion of gallium atoms, and the formation of metastable $(2 \times n)$ domains on top of the surface.^{8,27} In addition, the $c(4 \times 4)$ regions become disordered due to the presence of the gallium adatoms. Evidently, the Ga species contribute new features to the RDS spectra that are not present in either the spectrum of the $c(4 \times 4)$, or that of the (2×4) . By contrast, phosphorous desorption from InP(001) involves only the loss of phosphorous dimers, without indium out-diffusion and the formation of metastable structures.

The results presented above establish the relationship between the atomic structure of InP(001) surfaces and the RDS spectra they produce. Surfaces containing mixtures of (2×1) and (2×4) domains exhibit line shapes that are linear combinations of the spectra of the pure phases. Consequently, one can extract from these spectra an estimate of the phosphorous coverage. This approach could be used for real-time monitoring of surface composition during vapor-phase epitaxy, provided the optical response is not affected by other factors, such as by temperature and the presence of adsorbates.

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