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In situ monitoring of the surface reconstructions on InP(001) prepared by molecular beam epitaxy

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Reflection anisotropy spectroscopy (RAS) and reflection high-energy electron diffraction (RHEED) were applied to study clean InP(001) surfaces prepared by molecular beam epitaxy (MBE). At phosphorus beam equivalent pressures (BEPs) between 3.5×10^{-7} and 3.5×10^{-6} mbar and substrate temperature (T_s) falling from 590 to 150 °C, (2×4), (2×1), (2×2), and $c(4\times4)$ RHEED patterns are observed. The main RAS features, observed at 1.7–1.9 and 2.6–2.9 eV are assigned to In and P dimers, respectively. The above reconstruction sequence is associated closely with transformations identified in RAS signatures that are induced by progressively increasing the P surface coverage. The RAS results also imply the existence of $(2\times4)\alpha$ and $(2\times4)\beta$ phases. A surface-phase diagram for MBE-grown (001) InP, in the whole range of T_s and phosphorus BEPs is proposed. © *1997 American Institute of Physics.* [S0021-8979(97)00113-8]

As evidenced by well established surface characterization techniques such as reflection high-energy electron diffraction (RHEED), the (001) GaAs surface exhibits a variety of reconstructions depending on the substrate temperature (T_s) and the overpressures of the group III and group V elements. The surface-phase diagrams of other important III–V materials like InP, InAs, GaP, and their ternary alloys have also been studied, but in much less detail. In the case of the InP(001) surface (2×2), (2×1), and (2×4) RHEED patterns have been observed under solid-source[1] and gas-source[2] molecular-beam epitaxy (MBE) conditions, as well as under chemical-beam epitaxy (CBE).[3] The microstructure of the (2×4) phase has been studied by low-energy electron diffraction (LEED),[4] time-of-flight scattering and recoiling spectrometry (TOF-SARS),[4] and more recently, by scanning tunneling microscopy (STM).[5–7]

The above mentioned charged-particle surface probes require vacuum ambients and are not compatible with growth techniques such as metalorganic vapor phase epitaxy (MOVPE), hence optical probes are called for. Reflection anisotropy spectroscopy (RAS) has been shown to meet the needs for a reliable *in situ* monitoring tool, applicable to ultrahigh vacuum, as well as to gas-phase environments. Identification of surface phases by RAS is made possible by relating a specific spectrum to known RAS ''signatures'' that are verified by other surface monitoring tools. Therefore, for the further development of the RAS technique, as well as for an adequate understanding of the surface conditions and their implications for the crystal growth process in general, it is crucial to set up a RAS database that includes the largest available variety of materials and growth conditions.

RAS spectra of InP under MOVPE[8] and CBE[8,9] conditions have been published recently. A combined RAS and RHEED study in a CBE environment has allowed the correlation of RAS features with the observed (2×4) and (2×1) surface reconstructions[8] prepared by varying the beam equivalent pressure (BEP) of the P precursor at a constant $T=500$ °C. A surface-phase diagram appropriate for MOVPE conditions in the narrow temperature range 470–550 °C has been proposed on the basis of a surface photoabsorpton (SPA) study.[10]

We have performed a combined, by RAS and RHEED, *in situ* investigation of the surface of a (001) InP layer after homoepitaxial growth in a MBE chamber. The temperature was varied from 150 to 590 °C, in a much wider temperature range than has been previously reported, and the phosphorus BEP was independently set to values between 3.5×10^{-7} and 3.5×10^{-6} mbar.

The growth took place in a VG Semicon V80H MBE machine equipped with solid sources for In and cracked P (P_2). With the only viewport available on the growth chamber dedicated to the RAS monitoring system, T_s was measured with the help of a thermocouple in contact with the substrate holder. Readings from the thermocouple were calibrated by preliminary pyrometer measurements. After cleaning the InP(001) substrates from the surface oxide under a P_2 BEP of 3.5×10^{-6} mbar, nominally 0.2-μm-thick layers were grown on-axis at 510 °C. RHEED was monitored immediately before and after the RAS scans, which typically took about 3 min to complete, as well as being verified in separate temperature runs, undertaken for RHEED purposes only. Several RHEED patterns were observed with falling

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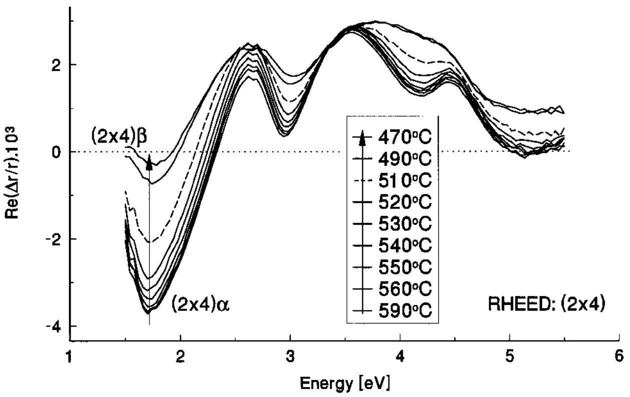

FIG. 1. RAS in the highest T_s range (P-BEP$=3.5\times10^{-6}$ mbar), corresponding to the (2×4) RHEED pattern. The spectra behave differently in the temperature regions separated by the dashed line at 510 °C, indicating the presence of two phases: (a) (2×4) and (b) (2×4).

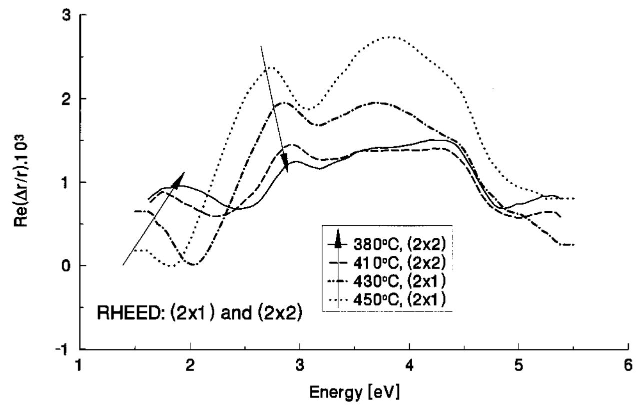

FIG. 2. RAS in the intermediate T_s range (P BEP$=3.5\times10^{-6}$ mbar), corresponding to the transitional (2×1) and (2×2) reconstructions. The 1.7 and 2.6 eV peaks from Fig. 1 move continuously to higher energies, and the region between 3 and 4.5 eV becomes flat.

temperature: (2×4), (2×1), (2×2), and $c(4\times4)$. The usually clear and sharp (2×4) pattern was observed to deteriorate for $T_s>570$ °C, indicative of surface roughening. Although considerably weakened below 500 °C, the ×4 periodicity was still observable down to 470 °C. At lower T_s (2×1) and (2×2) patterns were observed over a comparatively short temperature range and with a diffuse boundary between the two. At a P_2 BEP of 3.5×10^{-6} mbar and $T_s=370$, 360, and 340 °C weak $c(4\times4)$ RHEED patterns were observed. The existence of half- and quarter-order streaks on the images recorded under these conditions was additionally verified by digital enhancement and noise reduction by averaging over consecutive scan lines. To our knowledge, this is the first report of the observation of a $c(4\times4)$ reconstructed (001) InP surface. The RHEED pattern quality degraded rapidly below 340 °C.

RAS was applied in the range 1.5–5.5 eV by means of an in-house constructed system of the ''optical bridge'' design of Aspnes *et al.*[11] To suppress the sensitivity to strain in the viewport window, the spectra were recorded as the real part of the normalized anisotropy

$$\frac{\Delta\dot{r}}{\dot{r}}=2\frac{\dot{r}_{1\bar{1}0}-\dot{r}_{110}}{\dot{r}_{1\bar{1}0}+\dot{r}_{110}}, \tag{1}$$

where $\dot{r}$ is the complex reflectance with the incident light polarized along the direction specified by the subscript.

Figure 1 shows the evolution of the RAS spectra for T_s in the range where the (2×4) RHEED pattern is observed. The two most prominent features are the negative peak at 1.7 eV and the positive peak at 2.6 eV. Between 590 and 510 °C the spectra shift parallel to one another towards positive values, preserving the overall shape. A change in this behavior occurs at about 510 °C (dashed spectrum). The 1.7 eV peak decreases towards the zero, whereas no further changes take place in the intensity and position of the 2.6 eV peak. Simultaneously, the ''three-buckle'' shape flattens between 3.5 and 4.5 eV resulting in a ''camelback'' overall spectral shape.

The spectra in the transitional region between 490 and 420 °C, where (2×1) and (2×2) RHEED patterns are observed, are grouped together in Fig. 2. The characteristic trend here is the continuous shift of the 1.7 and 2.6 eV structures to higher energies and the transformation of the camelback into an almost flat region between 3 and 4.5 eV. At the lowest temperature in this range, a positive structure has appeared at around 1.9 eV, close to the position of the formerly negative 1.7 eV peak.

The spectra corresponding to the lowest T_s range are shown in Fig. 3. The RAS signal is positive and no essential spectral shifts are observed for the peaks at 1.9 and 3 eV. The prominent enhancement of the anisotropy between 3.5 and 4.5 eV transforms this initially flat region into a dominant bulge.

In analogy with results from GaAs,[12] it is assumed that the main RAS features at 1.7–1.9 and 2.6–2.9 eV are due to In dimers and P dimers, respectively. This is in agreement with the interpretation of RAS from MOVPE InP.[8] Under solid-source MBE conditions no combination of T_s or P_2:In flux ratio has been reported[1] to yield a (4×2) pattern on the (001) InP surface, which agrees with our observations. A (2×4) RHEED pattern has been observed for static con-

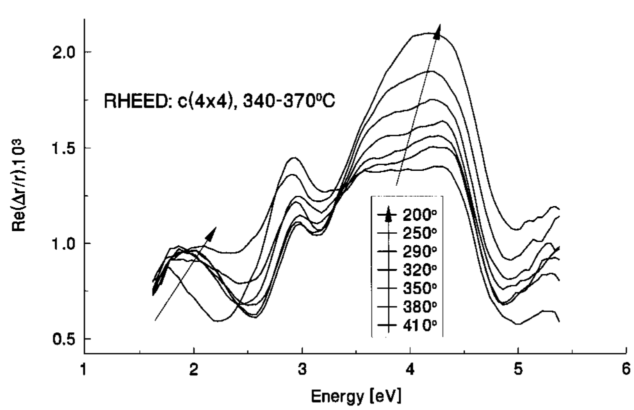

FIG. 3. RAS in the lowest T_s range (P BEP$=3.5\times10^{-6}$ mbar). The $c(4\times4)$ RHEED pattern is observed only between 340–370 °C. The RAS signature consists of positive peaks at 1.9 and 3 eV together with the flat region between 3.5 and 4.5 eV that evolves into a prominent bulge.

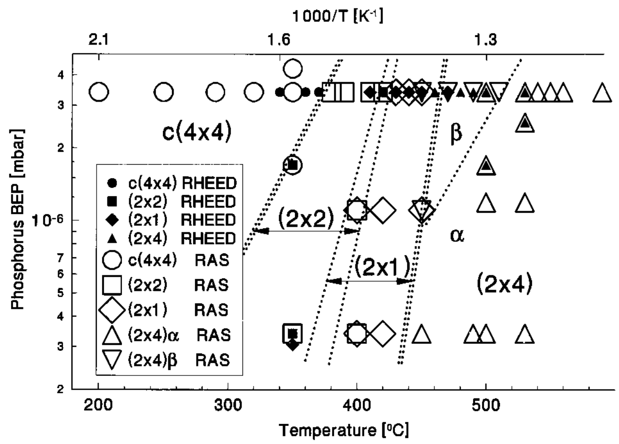

FIG. 4. Surface phase diagram of (001) InP under MBE conditions. The closed and open symbols indicate RHEED and RAS results, respectively. The tentatively drawn lines separating the phases show a diffuse boundary between the (2×1) and (2×2) reconstructions.

ditions with III/V ratios less than, as well as more than, unity and consequently both P-stabilized as well as In-stabilized (2×4) reconstructions have been considered.[2] In the case of migration-enhanced growth the (2×4) pattern became clearer and sharper in the In-supply period, which allowed the authors to propose a model for an In-stabilized (2×4) phase. Our results do not comply with the In-stabilized model, because P dimers should be absent on such a surface.[2] We observe (Fig. 1) strong signals from both dimer types in the range 590–510 °C, as should be expected for the $(2\times4)\alpha$ phase (two P dimers along the [110] with two exposed In dimers along the [110] in the lower layer, 50% P coverage), in analogy to the microstructure model proposed for GaAs.[13] As a result of increasing P coverage, the P dimer peak grows at the expense of the In dimer one until the $(2\times4)\beta$ phase, which does not involve In dimers (every fourth P dimer missing, 75% P coverage), becomes dominant at 510–470 °C. The existence of $(2\times4)\alpha$ and $(2\times4)\beta$ phases on InP(001) has been also shown by STM.[7]

X-ray photoelectron spectroscopy has revealed[7] excessive P on the (2×1) surface. In agreement with the observed transitional character of the (2×1) and (2×2) phases, they should correspond to a P coverage of around 100%, which is known to be energetically less stable.[7]

For surfaces with a still higher group-V coverage, in the range 340 °C$<T_s<$370 °C, we observe a $c(4\times4)$ RHEED pattern. At $T_s<$340 °C the blurring of the RHEED image coincides with the bulging of the $c(4\times4)$ RAS spectrum between 3.5 and 4.5 eV. Such behavior has been observed in GaAs,[12] and interpreted as ''disordering'' of the $c(4\times4)$ phase. Therefore we can speculate that for the lowest T_s and highest P BEPs a significant reduction of the long-range order takes place.

The absence of a $c(4\times4)$ reconstruction in MOVPE InP was concluded by Kobayashi *et al.*[10] on the basis of their observation that the P dimer SPA signal does not change its sign, despite evidence of excess P on the surface. Although our observations confirm that the P dimer does not change its $[\bar{1}10]$ orientation for any of the RAS experimental points, we have proof that this behavior coexists with the $c(4\times4)$ phase. One possible explanation may be the different nature of the optical and RHEED probes. While RHEED samples long-range order, optical techniques are sensitive to local electronic transitions. However, it is worth emphasizing that the expectation of a sign reversal in the group V dimer signal is based mainly on studies related to GaAs. Recently, direct analogies between different III–V compounds have been questioned by suggestions that the microstructure of the (2×4) reconstruction of GaAs and InP(001) surfaces may differ substantially. STM images[6] of the latter surface, prepared in the absence of a group V amosphere, reveal threefold-coordinated structures interpreted by the authors as trimer units of P adatoms. Our results do not call for the involvement of P trimers in any of the observed InP(001) reconstructions. It is possible[14] to build a microstructure model for the InP(001) $c(4\times4)$ surface that is based on P dimers oriented along [110], as well as on 175% P coverage, and that satisfies the electron counting rules.[15] Thus, while retaining some basic features from the GaAs(001) case, this microstructure would also comply with the RAS signature. To establish the model in detail, however, additional proof from other surface monitoring techniques and theoretical calculations is needed.

In conclusion, we report for the first time on the $c(4\times4)$ reconstruction of (001) InP. As a result of a combined RHEED and RAS study, we proposed a surface-phase diagram of the InP(001) surface under MBE conditions. The RAS signatures corresponding to different regions of this diagram were identified.

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