Optical Properties of Ordered As Layers on InP(110) Surfaces

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The structure of arsenic monolayers on InP(110) surfaces has been investigated by combining optical spectroscopy with calculations of the surface atomic structure and optical properties. A highly ordered surface structure is obtained after As deposition at room temperature followed by annealing at 300 °C. From the excellent agreement between the experimental and theoretical results we conclude that the ordered structure consists of an InAs monolayer on the substrate surface.

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The adsorption of group-V overlayers on III-V (110) surfaces is of large interest for fundamental studies of interface formation. Among those, much work has been dedicated to the study of Sb monolayers on III-V (110) surfaces which are known to form an exceptionally well-defined, atomically abrupt and ordered (1 × 1) overlayer [1]. This prototype system for surface studies has been thoroughly investigated by means of optical spectroscopic techniques such as reflectance difference spectroscopy (RDS), spectroscopic ellipsometry (SE), and surface resonant Raman spectroscopy [2–4]. The studies have demonstrated the large potential of optical techniques for surface analysis and, moreover, gave insight into the microscopic origin of the surface optical properties by comparison with theoretical work. In contrast, much less is known about the interaction of As with III-V (110) surfaces. Arsenic adsorbates on GaAs(100) surfaces have been studied in the past by optical methods because of their role in the epitaxial growth process [5]. However, studies of As on InP(110) surfaces have been restricted to low-energy electron diffraction (LEED) and photoemission investigations by Tulke and Lüth [6] and Chassé, Neuhold, and Horn [7], and theoretical calculations of their atomic structure are not available.

The question to be addressed here is whether As remains on the substrate surface forming well-defined surface monolayers, as in the case of antimony and bismuth terminated III-V surfaces [8–11], or whether a significant chemical reaction with the substrate top layers occurs, such as observed for the (100) InP surface [12]. For this purpose we present an investigation of arsenic monolayers on InP(110) surfaces (hereafter InP:As) combining a spectroscopic study of the surface optical properties with microscopic calculations of the atomic structure and optical spectra. In agreement with Refs. [6] and [7] we detected a poorly ordered InP:As phase (phase A), obtained after As deposition at room temperature (RT) and a highly ordered phase (phase B) with coverage in the monolayer range, formed after annealing at temperatures above 300 °C. One can reversibly go from one phase to the other by changing the As coverage by either thermal desorption (A → B) or As deposition (B → A). The structure of the ordered phase B was further investigated by performing ab initio total energy calculations of the ground state geometries and of the optical properties for different surface configurations. The excellent agreement between the experimental and theoretical results indicates the formation of an InAs ordered top monolayer through a P-As exchange reaction. The reversibility implies that this reaction takes place immediately after As deposition at RT with annealing leading to surface ordering and desorption of excess As.

The optical experiments were performed in a UHV setup (base pressure <5 × 10⁻¹⁰ mbar) using (110) surfaces of InP substrates (semi-insulating or Sn doped with [Sn] = 5 × 10¹⁸ cm⁻³) obtained by the double-wedge cleaving technique in UHV. The As surface layers were prepared by exposing the cleaved InP surfaces held at RT to the direct flow of As₄ molecules from an evaporation cell. Relatively long exposure times were used (up to 15 min under an As background pressure of 8 × 10⁻⁷ mbar) in order to assure saturation coverage of the InP surfaces. The pseudodielectric function (ε) of the surfaces was measured in situ using a rotating analyzer ellipsometer and the surface anisotropy was recorded using a RDS spectrometer with an acoustooptical modulator [13].

To access the surface electronic properties we determined the surface excess function (SEF) from the difference between the ellipsometric data of the clean and As-covered surfaces [14]. Assuming the surface layer to have an effective dielectric function ε + Δε (ε is the substrate dielectric function) and an effective thickness d, much smaller than the light wavelength, the SEF corresponds to the product Δed, and describes optical properties induced by As deposition. The imaginary part of the SEF for As-covered InP(110) surfaces prepared under different conditions is displayed in Fig. 1(a).
open circles show the SEF obtained after As deposition. The spectrum is dominated by the contributions of the $E_1 = 3.15$ eV, $E_1 + \Delta_1 = 3.30$ eV, and $E_0 = 4.7$ eV critical points of bulk InP [15]. The minima in the SEF at the InP critical points $E_1$ and $E_0$ evidence the removal of the substrate-specific oscillator strength upon As deposition. A rough estimate of the As layer thickness from the minima yields values between 2.5 and 7.5 Å, thus indicating that the As coverage remains in the range of a few monolayers after RT deposition.

The positive peaks denoted by $S_A = 2.50$ eV, $S_B = 2.85$ eV, $S_C = 3.8$ eV, and $S_D = 4.45$ eV in Fig. 1(a) are associated with the As-terminated surface. The broad structures $S_A$ and $S_C$, observed after As evaporation [open circles in Fig. 1(a)], indicate a low degree of surface ordering of the as-deposited surface. This result is consistent with the increased background of the LEED (1 × 1) pattern reported for this phase [7]. After annealing at 200 °C (thin line), new sharp lines $S_B$ and $S_D$ appear in the SEF, which are characteristic of the ordered phase $B$ (300 °C, thick line).

The changes in the dielectric function upon annealing are followed by dramatic modifications in the optical anisotropy. Figure 2 displays the real part $\text{Re}[\text{RDS}] = \text{Re}[\{r_{[1\bar{1}0]} - r_{[001]}\}/r]$, of the relative difference in the complex reflection coefficients, $r$, for polarizations along the $[1\bar{1}0]$ and $[001]$ surface directions, as measured by the RDS technique. Below the InP $E_1$ critical point the imaginary part of the substrate dielectric function is small, and $\text{Re}[\text{RDS}]$ is directly proportional to the imaginary part of the dielectric anisotropy $\text{Im}[(\Delta \varepsilon_{[1\bar{1}0]} - \Delta \varepsilon_{[001]})]$. Since bulk InP is essentially optically isotropic, the anisotropy is surface specific and sensitively dependent on the configuration of the As atoms on the surface. The anisotropy of the clean InP(110) surface is positive with structures in the range of the bulk critical points $E_1$ and $E_1 + \Delta_1$, and a small peak at 2.9 eV due to a surface state of the clean sample [3,16]. The latter disappears after As deposition [Fig. 2(b)], and a broad minimum between 2.5 and 3 eV becomes the main feature of the spectrum. The spectrum is characteristic of the disordered phase $A$, which is stable up to 200 °C [Fig. 2(c)]. After annealing at 250 °C [Fig. 2(d)] additional strong lines, $SB = 2.85$ eV and $SD = 4.45$ eV, appear in the spectrum. These lines, characteristic of the high temperature phase $B$, become the dominant features for annealing temperatures above 300 °C [Fig. 2(e)]. Phase $B$ becomes fully established only after annealing at 315 °C, and remains thermally stable up to temperatures of at least 375 °C. We verified that the anisotropy of clean InP surfaces remains unchanged upon annealing, thus confirming that the changes in Fig. 2 are related to the presence of As.

An additional interesting feature of the As-covered InP surface is the reversible transition between phases $A$ and $B$ through annealing and As-deposition cycles illustrated in Figs. 3(a) and 3(b). The thin curves reproduce the results of Fig. 2 and display the optical anisotropy directly after As deposition [Fig. 3(a) and after subsequent annealing.
anisotropy for the exchange-reacted (solid squares) and for the ECLS As overlayer (empty squares). The \( \text{Re}[\text{RDS}] = \text{Re}[n_{[10]} - n_{[00]} / \Sigma \] for InP:As (110) surfaces (a) after As deposition (phase A) and (b) after annealing at 315 °C (phase B). Thick lines: RDS spectra of the same sample obtained (a) after As redeposition and (b) after a second annealing treatment at 315 °C. (c) Calculated reflection anisotropy for the exchange-reacted (solid squares) and for the ECLS (empty squares) surface geometries.

at 315 °C [Fig. 3(b)]. Arsenic was then redeposited on the sample under the same conditions as the original deposition. The anisotropy spectrum, displayed by the thick line in Fig. 3(a), reverts to that of phase A. After reannealing at 315 °C the anisotropy trace of phase B is again obtained, as indicated by the thick line in Fig. 3(b), thereby characterizing the reversible transition back to phase B.

Our approach to elucidate the structure of phase B started with the determination of the equilibrium atomic structure for different As configurations by means of \textit{ab initio} total energy calculations, which were based in the density-functional theory on the local-density approximation (DFT-LDA) [10]. The minimum of the total-energy functional with respect to both the electronic and atomic degrees of freedom was found by employing a molecular dynamical approach [17]. We considered two classes of structural models for the well-ordered phase B. The first involves the formation of an exchange-reacted InP\(_2\)As\(_{1-x}\) monolayer through As substitution of the P atoms of the topmost substrate monolayer. Such a model, with \( x \sim 0.5 \), was proposed by Tulke and Lüth [6] and later adapted by Chassé et al. [7] to explain the intensity dependence of the photoemission core level signals of In and P in As-terminated InP(110) surfaces. Evidence for an exchange-reacted surface has also been reported for As on InP(100) surfaces [12]. In order to explain consistently the reversibility discussed above, the surface reaction must occur \textit{during} As evaporation at RT, and not during the subsequent thermal annealing, as proposed in Refs. [6] and [7]. The second class of models involves the formation of an ordered As monolayer \textit{on top} of the substrate, similar to that observed for the Sb and Bi-terminated III-V surfaces [11]. Also, earlier calculations indicate that As monolayers are thermodynamically stable on GaAs(110) [18,19].

For the total energy calculations of the exchange-reacted surface we assumed that all uppermost substrate P atoms were replaced by As. The resulting bonding geometry represents at least a metastable configuration. As for the free III-V (110) surfaces, we observe an appreciable buckling of the uppermost layer of 0.80 Å which lies approximately between the values determined by LEED for clean InAs(110) and InP(110) surfaces (0.88 Å [20] and 0.73 Å [21], respectively). The bonds between As and the uppermost (second layer) In are 2.49 (2.55) Å and therefore close to the sum of covalent radii. Also the In-P bond lengths around the exchanged surface anion are near their ideal bulk value.

For the ordered one monolayer structure we investigated a series of different overlayer geometries which were discussed for adsorption of group-V [10] and group-III [22] elements on III-V (110) surfaces. We tested in detail the epitaxial continued layer structure (ECLS), the epitaxial on top structure (EOTS), the \( p^3 \) structure, the epitaxial overlapping chain structure (EOCS), the irregular chain structure (IRC), and As dimers bonded to the substrate surface anion and cation (cf. Fig. 4 in Ref. [22]). We found the ECLS, where the As atoms continue epitaxially the substrate structure forming chains in the [0-11] surface direction, to be the most favorable adsorption structure for one monolayer coverage. This is in agreement with results for Sb adsorption on III-V (110) surfaces [10]. The adsorption energy per As atom adsorbed in the EOTS (IRC) is smaller by 0.29 (0.31) eV. The bond lengths in the ECLS \( d_{\text{As-As}} = 2.56 \) Å, \( d_{\text{As-In}} = 2.55 \) Å, and \( d_{\text{As-P}} = 2.35 \) Å are apart from the stretched As-As bond close to the sum of the covalent radii.

The band structure and optical properties for the ground state geometries discussed above were then determined using the empirical tight-binding method (ETBM). The calculations were performed in the slab geometry and employed a basis consisting of \( sp^3s^* \) orbitals [23]. The tight-binding overlap parameters for InP were taken from Ref. [23]; those for the interaction between As and the substrate atoms were obtained from those in InP and InAs following the procedure described in Ref. [9]. Further details of the calculations will be presented elsewhere [24]. The imaginary part of the dielectric function was calculated by integrating the matrix elements for optical transitions between the valence and conduction bands over the Brillouin zone [4,24].

Figure 1(b) displays the calculated SEF, obtained from the difference in \( \varepsilon_2 \) for the clean and As-terminated surfaces, for the exchange-reacted surface (filled squares), and for the ECLS As overlayer (empty squares). The
corresponding calculations for the optical anisotropy are presented in Fig. 3(c). In both cases the curves were smoothed by a Gaussian with 0.1 eV half-width and shifted uniformly by 0.2 eV towards higher energies in order to correct for the underestimation of the InP $E_1$ gap by the InP parametrization of Ref. [23]. Apart from small energy shifts, we observe a remarkable agreement between the experimental spectra and the calculated data for the exchange-reacted surface. The optical investigations presented here thus give clear and direct evidence for the formation of an InAs monolayer on the InP substrate. As expected from the structural similarity to the clean surface, the As and In-like dangling-bond states of the exchange-reacted surface are shifted towards the valence and conduction band, respectively, so that there are no surface states within the bulk gap. The $S_B$ structure in Figs. 1 and 3 appears to be related to the $E_1$ (2.4 eV) and $E_1 + \Delta_1$ (2.7 eV) transition of bulk InAs, shifted to higher energies due to the distortion of the In-As bonds and to admixture of InP $E_1$-like states.

The optical properties also allow us to draw conclusions about the low-ordered phase $A$. A close examination of the RDS spectra in Figs. 3(a) and 3(b) for phases $A$ and $B$, respectively, reveals a reversal in sign of the anisotropy between 2 and 4 eV, thus indicating a 90° rotation of the bonds contributing to the anisotropy. We attribute the sign reversal to the presence in phase $A$ of an additional As layer on the exchange-reacted surface with bonds in a plane perpendicular to the [1T0] direction. This new atomic configuration should yield an anisotropy contribution with a sign opposite to that of the first As layer. In addition, the adsorption of the As atoms is expected to reduce the relaxation of the InAs layer and thus its contribution to the anisotropy [25]. Further work is necessary to clarify the detailed structure of this phase.

In conclusion, we have reported on the optical properties of As films on InP(110) surfaces with thicknesses in the monolayer range. We have demonstrated that a well-ordered As phase forms on InP after annealing at 300 °C. This phase is attributed to the formation of an InAs exchange-reacted top layer on the InP(110) substrate during As evaporation, which becomes well ordered after annealing.

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