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Oxygen chemisorption on cleaved InP(110) surfaces studied with surface differential reflectivity

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We present surface-differential-reflectivity results on the oxidation of InP(110) surfaces in the energy range between 2.0 and 4.0 eV. Absorption kinetics is analyzed by following the reflectivity variation between 1×10^2 and 2×10^6 langmuirs of molecular oxygen at three selected spectral energies. Several well-defined steps of the oxidation process are clearly resolved and discussed in terms of the disappearance of intrinsic surface states, the creation of acceptor and donor defect states, and the growth of In_2O_3.

The InP(110) surface has recently been the subject of a great deal of both experimental and theoretical work. Angle-resolved photoemission,[1] inverse photoemission,[2] picosecond time-resolved photoemission,[3] surface differential reflectivity,[4] electron-energy-loss spectroscopy,[5] together with a strong theoretical effort,[6-8] have contributed to obtaining the energy position and the dispersion of filled and empty states of the clean surface. The same is not true for the oxidized surface, despite the scientific and industrial interest of InP as an alternative to GaAs for high-speed metal-oxide-semiconductor field-effect transistor (MOSFET) applications and as solar-cell material. In particular, the physics of the early stages of the oxidation of InP(110) surfaces is still controversial and a chemisorption model for oxygen capable of explaining the experimental results has not yet been proposed.[9]

In this framework surface-differential-reflectivity (SDR) spectroscopy can make an important contribution to a better understanding of the chemisorption process. SDR spectroscopy involves measuring the reflectivity of a sample when the surface is clean and after an exposure E to an external gas.[10,11] The experimental results are given in terms of $(\Delta R/R)(E)$, i.e., the relative variation of reflectivity between these two conditions:

$$(\Delta R/R)(E)=[R_{\text{clean}}-R_{\text{ox}}(E)]/R_{\text{ox}}(E)\ , \tag{1}$$

where $R_{\text{ox}}(E)$ refers to the case of oxygen as the contaminating gas. The variation of sample reflectivity is due to (i) the disappearance of surface states; (ii) the variation of the Franz-Keldish (FK) effect in the space-charge region; and (iii) the optical properties of the growing oxide layer. As is known, the FK effect consists in the variation of the optical properties of a crystal caused by an external electric field. Characteristic oscillatory structures appear in correspondence to bulk critical points.[12] In SDR experiments the change in band bending caused by the oxidation determines a change in the builtin surface electric field and thus a variation in the FK contribution to reflectivity. Since band bending is connected to the Fermi-level position, a monitoring of the FK amplitudes allows an estimate of the Fermi-level position as a function of oxygen exposure. A previous study on GaAs(110) and GaP(110) surfaces[13] has shown a detectable FK oscillation around 3.0 eV in GaAs(110) and 3.8 eV in GaP(110); the amplitude of the oscillation grows between 10^2 and 10^4 L ($1\text{L}=10^{-6}$ Torr s) of O_2 and then saturates. Such behavior was in qualitative agreement with the variation of the Fermi-level position as measured with photoemission;[14] a quantitative comparison was not made since the variation of Fermi-level position was not extrapolated from the SDR data.

In this paper we present SDR experiments performed at room temperature with unpolarized light on InP(110) surfaces exposed to oxygen. The experimental apparatus has been described in detail elsewhere.[10] InP n-type samples ($n=1\times10^{17}$ cm^{-3}) were cleaved in UHV environment (base pressure $<1\times10^{-10}$ Torr) with the double wedge technique obtaining reproducible flat mirrorlike surfaces. During oxidation the ion pump was valved off, to avoid release of activated gas caused by the prolonged use at relatively high pressure (10^{-5} Torr or higher). The ionization gauge was kept on during the oxidation in an encased position far from the sample. The $\Delta R/R$ experimental accuracy was better than 2×10^{-4}. Several samples, with the same doping, have been used together with different oxygen dosages, all giving the same results within the experimental error.

The reflectivity variation brought about by the oxidation of a clean cleaved InP(110) surface is measured as a function of the photon energy in the range 2.0–4.0 eV. Figure 1 shows $\Delta R/R$ for two different exposures [2×10^3 (dashed line) and 2×10^6 L O_2 (solid line)]. The lower exposure curve shows clearly characteristic FK oscillations around 3.15 eV, corresponding to a bulk saddle point of type M_1.[12] The figure shows that the FK oscillations almost disappear at the highest exposures, when presumably the band bending returns to its initial value.

In order to discriminate among the different contributions to $\Delta R/R$ we have measured the reflectivity variation as a function of oxygen exposure at three different photon energies: 3.14 eV (corresponding to the minimum of FK first oscillation),[12] 3.22 eV (corresponding to the maximum of FK first oscillation),[12] and 3.58 eV (a region

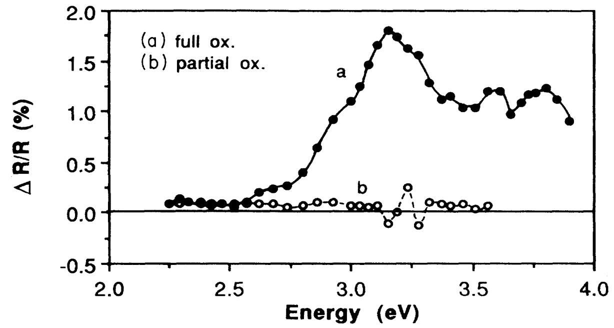

FIG. 1. Differential reflectivity for cleaved InP(110) surfaces. Curve *a* (solid line, solid circles) refers to a complete oxidation (2×10^6 L); curve *b* (dashed line, open circles) refers to the initial state of oxidation (2×10^3 L).

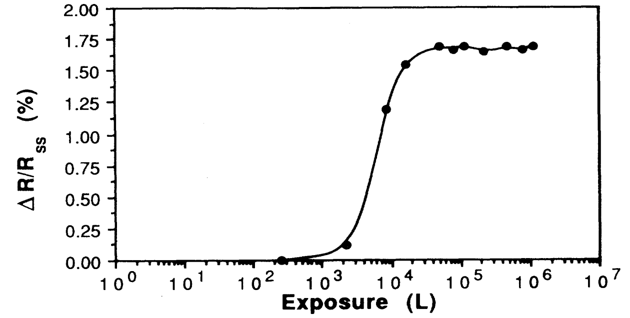

FIG. 2. Surface state contribution $(\Delta R/R)_{SS}$ vs oxygen exposure for cleaved InP(110) surfaces.

near the threshold of In_2O_3 absorption[15]). The choice of the photon energies for monitoring FK amplitude depends on the doping of the sample.[12] In our case we have chosen 3.14 and 3.22 eV after measuring $\Delta R/R$ on a sample with the same doping, as reported in Fig. 1, where FK minimum and maximum of the oscillation are clearly visible at those photon energies.

Below the threshold for oxide absorption it is possible to write, approximately,

$$\Delta R/R=(\Delta R/R)_{SS}+(\Delta R/R)_{FK}\;.$$

The value

$$(\Delta R/R)_{SS}=\tfrac{1}{2}[(\Delta R/R)_2+(\Delta R/R)_1]$$

(where 1 and 2 refer to 3.14 and 3.22 eV, respectively) gives directly the surface state contribution in the intermediate point where FK contribution is zero. On the other hand, the amplitude of FK oscillation can be obtained from

$$(\Delta R/R)_{FK}=(\Delta R/R)_2-(\Delta R/R)_1$$

and from the values of $(\Delta R/R)_{SS}$ at the energies 3.22 and 3.14 eV that can be obtained by interpolation between the values of $\Delta R/R$ at energies before and after FK oscillations. In the case of GaAs(110) and GaP(110), where there is no detectable first minimum in FK oscillation, we should measure the amplitude of the first maximum and/or the second minimum, without any difference for the evaluation of the Fermi-level variation.

The dependence of $(\Delta R/R)_{SS}$ and $(\Delta R/R)_{FK}$ as a function of exposure is reported in Figs. 2 and 3. The comparison of the two figures, particularly the difference of threshold and the different behavior at high values of exposure, shows clearly that the states that control the position of the Fermi level at the surface are not (or are not uniquely) the intrinsic surface states. The conclusion is also supported by curve *b* of Fig. 1 that shows remarkable FK oscillations, i.e., a strong variation of band bending occurring in the absence of appreciable disappearance of surface states. In this connection InP(110) behaves in the same way as GaAs(110) and GaP(110).[13]

From the value of $(\Delta R/R)_{FK}$ in Fig. 3, it is possible to calculate the change of band bending caused by oxidation using the theoretical approach of Seraphin and Bottka.[16] With the mean-field approximation[12] one obtains a change of band bending of approximately 0.3 eV after 8×10^3 L O_2, corresponding to the peak of the curve of Fig. 3. This value is in excellent agreement with that obtained directly by Spicer and co-workers[9] from photoemission experiments. Also the general behavior of band bending, which goes through a maximum and reverts towards the value of the clean surface for large exposures, agrees with the photoemission experiments. In the initial stage of oxidation (exposure less than 1×10^4 L), our data also agree with those obtained by Monch and coworkers[17] with the Kelvin technique. The latter results, however, show the reversal of band bending only at much higher exposures, in disagreement with SDR and photoemission data. The inversion of the Fermi-level movement can be due to native shallow donor defects that compensate the charge of the acceptor states, responsible for the initial increase of band bending.[18] At higher coverages (10^5 L) the acceptor states are completely compensated and the Fermi level reaches a pinning position evidenced by the plateau of Fig. 3. In this range oxygen molecules are chemisorbed as phosphorous oxides like P_2O_3, P_2O_5, and $InPO_4$.[19,20] At still higher exposures, In_2O_3 is formed, causing a further decrease of band bending associated with its intrinsic donor character. While

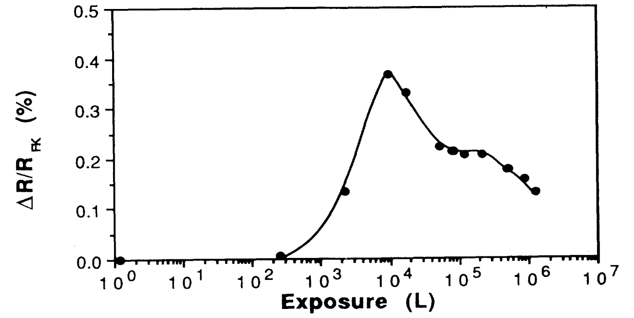

FIG. 3. Franz-Keldish contribution $(\Delta R/R)_{FK}$ vs oxygen exposure for cleaved InP(110) surfaces.

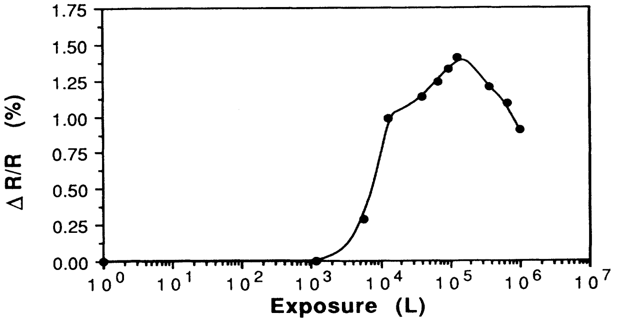

FIG. 4. Differential reflectivity at 3.58 eV vs oxygen exposure for cleaved InP(110) surfaces. The contribution of In_2O_3 absorption is evidenced at high exposures by the different behavior with respect to that of Fig. 2.

phosphorous oxides are transparent in our energy range, In_2O_3 is strongly absorbing above 3.5 eV.[15] Because of the definition of $\Delta R/R$ in Eq. (1) the presence of an absorption due to the oxide (In_2O_3) should give a negative contribution. This is clearly seen in the curve of Fig. 4 that reports $\Delta R/R$ at 3.58 eV as a function of exposure. The curve, in fact, presents a strong decrease in a region (above 2×10^5 L) where the surface states have already disappeared (see Fig. 2). An analysis similar to that reported for the FK oscillations is somewhat difficult since the spectrum of the oxide is unknown. The formation of other oxides (P_2O_3,P_2O_5, $InPO_4$) has to be excluded since they are absorbing at energies larger than 4.5 eV.[21]

In conclusion, the results obtained seem to imply a process of oxidation made of various steps: (i) creation of acceptor states that quickly modify the position of the Fermi level at the surface; (ii) disappearance of intrinsic surface states; (iii) creation of donor states responsible for the inversion of the Fermi-level movement; and (iv) growth of absorbing In_2O_3. A simultaneous experiment with photoemission, SDR, and Kelvin probe is in progress in order to directly verify the usefulness of SDR in terms of quantitative band-bending measurements.

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