

Possible derelaxation of *p*-type InP (110)

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(Submitted 15 July 1991)

Pis'ma Zh. Eksp. Teor. Fiz. **54**, No. 5, 283–286 (10 September 1991)

Measurements of the band curvature during the formation of an interface between *p*-type InP (110) and Ag at 10 K reveal a stage which is not seen at 300 K. It can be explained as resulting from a “derelaxation” of the surface.

The (110) surfaces of III–V semiconductor compounds produced by cleavage in high vacuum are known to undergo a spontaneous relaxation, in the course of which the group-III atoms are displaced toward the interior of the crystal, while the group-V atoms are displaced outward. During the relaxation, filled surface electronic states are forced out of band gap into the valence band, while vacant states are forced into the conduction band. It is for this reason that experiments on high-quality cleaved (110) surfaces of III–V semiconductors do not (except in the case of GaP) reveal a band curvature near the surface, in total agreement with theoretical predictions (e.g., Refs. 1–4). It has been shown in several places^{5–8} that the adsorption of submonolayer coatings of metals may cause a “derelaxation,” in the course of which surface states characteristic of the ideal surface are observed. In the case of *n*-type samples, this effect is seen, in particular, in a pinning of the Fermi level E_F^s at vacant electronic states (of the acceptor type) which have been “returned” to the band gap by the surface derelaxation. One might suggest that features of some sort would have been observed for *p*-type III–V semiconductors if the filled surface states of the derelaxed (ideal) surface lay above E_v . Analysis of the theoretical work reveals that this possibility is present⁴ in the case of InP(110). By measuring the change in the band curvature a result of the deposition of some adsorbate on a cleaved (110) surface of *p*-type InP, one might be able to test this suggestion.

We have carried out such measurements, using silver as the adsorbate. The measurements were carried out by UV photoelectron spectroscopy in an ESCALAB-5 electron spectrometer with a hemispherical energy analyzer and a capillary gas-discharge helium source of UV light. Atomically clean InP (110) surfaces were formed by cleavage directly in the high-vacuum chamber (the basic pressure was $\sim 5 \times 10^{-11}$ Torr). All values of θ , the degree of surface coverage by the Ag, are expressed in monolayers [the value is $\theta = 1$ if N , which is the number of Ag atoms per unit area, is equal to the number of substrate atoms in the (110) plane, i.e., if $N = 8.24 \times 10^{14}$ atoms/cm²]. The *p*-type InP test samples were doped to a concentration of 3×10^{16} cm⁻³. We studied the effect of the adsorption of Ag atoms on the UV photoelectron spectra near the Fermi level E_F^s . In particular, from the shift of this part of the spectrum as a whole one can follow the process by which Schottky barriers form, and one can determine the changes in the band curvature as θ is varied. Other experimental details are described in Refs. 6 and 9.

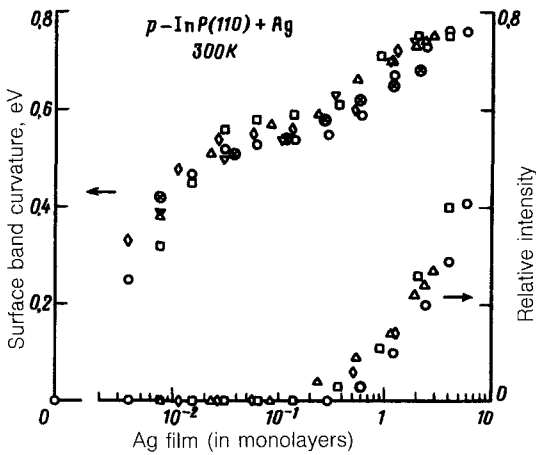


FIG. 1. Change in the position of E_F^s during the deposition of Ag on the (110) face of p -type InP at 300 K. The plot at the right reflects the change in the intensity of the metal states (the "step" at E_F^s).

Figures 1 and 2 show experimental results on the θ dependence of the band curvature during the deposition of Ag on the (110) face of a p -type InP substrate at 300 and 10 K. We see that at both 300 K and 10 K there are several stages in the changes in the Schottky barriers. These stages can be linked with changes in the UV photoelectron spectra and the morphology of the coatings which are forming. We first discuss the results obtained at 300 K (Fig. 1).

We see from Fig. 1 that in a first interval of coverage levels, $0 < \theta < 0.2-0.3$, the plot of the change in the band curvature versus θ at 300 K is a curve which exhibits saturation (above $\theta < 0.04$). The height of the Schottky barrier reaches ≈ 0.55 eV. No significant changes are seen in the spectra. This behavior can be explained under the assumption that surface states induced by the adsorption of individual Ag atoms (adsorption-induced gap states: AIGSs) appear when the adsorption begins. Filled surface states of the AIGS type probably correspond to the energy position $E \approx E_v + 0.55$ eV, which corresponds to a pinning of E_F^s up to $\theta < 0.04$ (Fig. 1). At the same time,

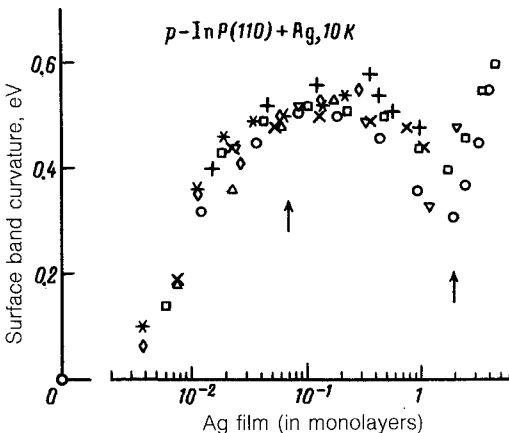


FIG. 2. Change in the position of E_F^s during the deposition of Ag on the (110) face of p -type InP at 10 K. The arrows show the point at which filled surface states of a derelaxed surface (the lower arrow) and metal states (the upper arrow) appear in the spectra.

we know¹⁰ that islands form. Their formation should be accompanied by the appearance of new surface states, which form as metallic clusters of silver “interact” with the substrate. We will call these states “metal-induced gap states” (MIGSs). At low degrees of coverage ($0 < \theta < 0.2-0.3$), the AIGSs apparently are predominant, while at higher degrees of coverage the MIGSs are. Indeed, Fig. 1 shows that beyond $\theta > 0.3$ it is possible to distinguish a second stage, in which there is a further increase in the band curvature. We see a good correlation with the formation of a “metal step” in the UV photoelectron spectra, near the Fermi level (the first curve in Fig. 1). This step is determined by an emission of electrons from a fairly large number of silver islands. Clearly, the MIGSs lie at a higher energy (with respect to E_v) than the AIGSs. Although our experimental procedure cannot give us correct measurements of the band curvature at large values of θ , such measurements were carried out in Refs. 11–14, where synchrotron radiation was used. There is a scatter in the experimental results. In Refs. 11–13, for example, it was reported that the states which arise as a result of the formation of a metal film lie near $E \approx E_v + 0.95$ eV, regardless of the substrate temperature, and that these states are surface states of a defect nature. Vitomirov,¹⁴ on the other hand, believes that the final value of the pinning depends on the temperature and is given by $E \approx E_v + 0.67$ eV at 300 K and $E \approx E_v + 0.55$ eV at 60 K. Calculations^{15,16} based on the Tersoff model yields values $E \approx E_v + (0.74-0.87)$ eV for MIGSs. The results in Fig. 1 are not an adequate basis for drawing a final conclusion about the particular states which pin E_f^s at the highest degrees of surface coverage in our experiments. However, we should immediately point out that even if surface states of a defect type are preferable, we can conclude that we are observing a correlation between the formation of these surface states and the appearance of a metal edge in the UV photoelectron spectra (the appearance of metal islands). The same conclusion follows from Ref. 17, where it was stated that the surface energy required for the formation of defects might be liberated in the course of the formation of metal clusters.

We turn now to the results found at 10 K. We see from Fig. 2 that three stages can be distinguished in the process by which an interface forms at a low temperature, in contrast with the case discussed above (for 300 K). The first stage corresponds to the coverage interval $0 < \theta < 0.2-0.3$. Here, as at 300 K, the AIGSs apparently play a leading role. These surface states should appear more clearly at 10 K because there is no diffusion of adsorbate along the surface. The stage at $\theta > 2$ is similar to the second stage in the 300 K case, discussed above. The pronounced increase in the band curvature at $\theta > 2$ is accompanied by the appearance of a metal step in the UV photoelectron spectra. At 300 K, this stage sets in far earlier, since metal islands begin to form even at low surface coverages ($\theta > 0.3$). The reason is the diffusion of the adsorbed atoms over the surface. In this stage, surface states of the MIGS type thus appear and become predominant as a result of the metallic nature of the coating.

A distinguishing feature of the low-temperature formation of the interface is the presence of an intermediate stage, at coverages $0.2-0.3 < \theta < 2$. This stage can be explained in the following way. At a low temperature, the adsorption of silver atoms which are distributed uniformly over the surface and which are not interacting with each other apparently leads to a derelaxation of the substrate surface: The atoms of the substrate surface return to the positions corresponding to an ideal (unrelaxed) surface. As a result, and in agreement with calculations of the electronic structure of an

ideal surface, the filled surface states should return to the band gap. They should lie near the top of the valence band, “creeping” somewhat into the band gap. These states appear to be the reason for the decrease in the band curvature in this intermediate stage. Another argument in favor of this suggestion comes from the following observation: After the first stage, beginning at $\theta \sim 0.1$ at 10 K, we find that states appear near E_F^s in the UV photoelectron spectra with intensities which increase with increasing θ . These stages disappear when the system is heated to 300 K. Similar states have been observed⁶ in the GaAs (110) + Ag system and have been explained as an emission of regions of a derelaxed (or “ideal”) surface from filled surface states.

Comparing our results with the results of Refs. 11–14, we immediately see that there is a good agreement in the case of the adsorption on the substrate at 300 K. At a low temperature, in contrast, no manifestation of the intermediate stage discussed above was seen on the θ dependence of the height of the Schottky barriers in Refs. 11–14. It is possible that the substrate temperature (60 K) in Refs. 11–14 was not low enough.

Finally, we note that in contrast with GaAs (110), for which numerous theoretical calculations have been carried out on the electronic structure of the ideal surface and the real surface (i.e., the relaxed surface), the InP (110) system has not received much attention. Consequently, the interpretation of the observations offered above is only tentative.

¹D. J. Chadi, Phys. Rev. B **18**, 1800 (1978).

²A. Kahn, Surf. Sci. **168**, 1 (1986).

³S. N. Molotkov and V. V. Tatarskiĭ, Fiz. Khim. Mekh. Mater. **10**, 59 (1990).

⁴G. P. Strivastava, I. Singh, V. Montgomery, and R. H. Williams, J. Phys. C **16**, 3627 (1983).

⁵C. R. Bonapace, D. Tu, K. Li, and A. Kahn, J. Phys. (Paris) **45**, 409 (1984).

⁶V. Yu. Aristov, I. L. Bolotin, and V. A. Grazhulis, Zh. Eksp. Teor. Fiz. **94**(12), 270 (1988) [Sov. Phys. JETP **67**, 2544 (1988)].

⁷C. M. Aldao, G. D. Waddill, I. M. Vitomirov, and J. H. Weaver, J. Vac. Sci. Technol. **A7**(3), 817 (1989).

⁸V. Yu. Aristov, I. L. Bolotin, and V. A. Grazhulis, Phys. Scr. **41**, 88 (1990).

⁹V. Yu. Aristov, I. L. Bolotin, V. A. Grazhulis, and V. M. Zhilin, Zh. Eksp. Teor. Fiz. **91**, 1411 (1986) [Sov. Phys. JETP **64**, 832 (1986)].

¹⁰V. Yu. Aristov, I. L. Bolotin, V. A. Grazhulis, and A. Ya. Nashel'skiĭ, Fiz. Khim. Mekh. Mater. **9**, 87 (1990).

¹¹R. Cao, K. Miyano, I. Linday, and W. E. Spicer, J. Vac. Sci. Technol. **A7**(3), 861 (1989).

¹²W. E. Spicer, R. Cao, K. Miyano *et al.*, Appl. Surf. Sci. **41/42**, 1 (1989).

¹³R. Cao, K. Miyano, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B **39**, 8465 (1990).

¹⁴I. M. Vitomirov, C. M. Aldao, and G. D. Waddill *et al.*, Phys. Rev. B **41**, 8465 (1990).

¹⁵J. Tersoff, Phys. Rev. B **32**, 6968 (1985).

¹⁶J. Menendez, Phys. Rev. B **38**, 6305 (1988).

¹⁷A. Zunger, Phys. Rev. B **24**, 4372 (1981).

Translated by D. Parsons