PHYSICAL REVIEW B VOLUME 13, NUMBER 10 15 MAY 1976

Photoemission studies of surface states and Schottky-barrier formation on InP[†]

P. W. Chye, I. A. Babalola,* T. Sukegawa,[‡] and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

(Received 23 October 1975)

Fermi-level pinning by empty surface states was observed on clean *n*-type InP using photoemission. Exposure to up to 10^7 langmuirs (1 L = 10^{-6} Torrsec) of oxygen did not remove the pinning. The Cs-InP Schottky-barrier pinning position showed good correlation with the pinning on the clear surface; however, the Cs-InP interaction was complex. The detailed movement of the Fermi level with increasing Cs coverage was complicated and could not be explained simply in terms of filling of empty surface states by Cs electrons. In addition, a large movement of the upper edge of the photoelectron energy distribution curves, that is, the valence-band edge at the Cs-InP interface, into the bulk band gap was observed. Thus, while empty surface states may be important in determining the Fermi-level pinning in Schottky barriers, other interactions will also have to be considered.

I. INTRODUCTION

Ultraviolet photoemission spectroscopy (UPS) has proven to be a powerful tool in the study of surface electronic states. Filled surface states have been observed directly using UPS,[1,2] and information on empty surface states may also be obtained by studying the pinning of the Fermi level at the surface by these empty states.[3] Continuous monitoring of the formation of Schottky barriers is also possible with UPS by following the changes in the photoelectron energy distribution curves (EDC's) and the Fermi-level pinning positions while small quantities of a metal (Cs) are being added to the surface.[4] This approach yields information during the formation of a Schottky barrier, whereas conventional Schottky-barrier experiments[5]—which are performed with the metal-semiconductor contact completed—do not, and thus fail to link states on the clean semiconductor surface and the metal-covered surface.

While UPS is able to locate the Fermi level to a high degree of accuracy and a considerable amount of information may be extracted from changes in the Fermi-level pinning, it is unable to shed light on the energy density of the pinning states except right at the lower edge.[6] Eastman and Freeouf[7] have developed a new spectroscopic technique for probing empty surface states, which they called photoemission partial-yield spectroscopy. While they are able to determine the density of states of the empty-surface-state levels, excitonic effects[8] may change the measured empty-surface-state position.

There has been a great deal of theoretical[3,9–11] and experimental[1–4,7,12–14] work on intrinsic and extrinsic surface states. On the clean surface, there is now general agreement that on Si (111) 2 ×1 surfaces there is a band of filled surface states extending about 0.3 eV into the band gap, with a peak 0.5 eV below the Fermi level. On the (110) face of III-V semiconductors such as GaAs, there are two kinds of surface states, filled and empty, associated with the two different kinds of atoms on the surface. The empty surface states are associated with the group-III atom and the filled surface states are associated with the group-V atom. The empty surface states lie in or near the band gap, while the filled surface states usually lie below the valence-band maximum (VBM). The work reported here on InP shows agreement with this general picture.

II. EXPERIMENTAL

The experimental setup was similar to one described previously.[4] Clean surfaces were obtained by cleaving the crystal (*n*-type InP, carrier density 6×10^{17} cm^{-3}), exposing the (110) face. A total of five cleaves were studied. A shield was mounted on the anvil to prevent the cleavage chip from flying forward onto or into the collector can. By substituting a copper emitter for the InP, the system may be calibrated so that the Fermi level could be determined to within ± 0.1 eV on the InP EDC's.[1] Oxygen exposures were made by leaking in research-purity oxygen obtained from Matheson Gas Products through a Varian leak valve and carefully monitoring the pressure with either a Redhead gauge for small exposures or a millitorr gauge at large ($p > 10^{-5}$ Torr) exposures. By passing current through channels containing cesium chromate and silicon, well-controlled amounts of Cs may be deposited on the semiconductor surface at room temperature. The deposition process was monitored by measuring the photoyield of the sample at photon energies near threshold. For the final exposure, light from a high-intensity *W* lamp was used, and the sample was cesiated to attain maximum yield. It was not possible to ascertain directly the amount of cesium deposited, but an estimate may be made by using the changes in work function in cesiated InP and published data relating cesium coverages to changes in work function for GaAs,[15] making the not unreasonable assumption that InP is quite similar to GaAs. One must, however, recognize that an error perhaps as large as a factor of 2 may be introduced. The coverage to give maximum "white-light" response is assumed to be the same as GaAs, which is about one-third of a monolayer, where a monolayer of Cs is defined to correspond to a Cs atom for each surface In or P atom. The coverages used throughout this paper are all estimated values based on the method outlined above. The work function may be obtained from yield-threshold measurements after correcting for the position of the Fermi level at the surface. This correction is necessary because yield thresholds are measured from the Fermi level. Photoyield of the sample was measured from threshold to 11.6 eV for each surface condition; corrections were made for the reflectivity of InP and the transmission of the LiF window. The reflectivity data were taken from Cardona's[16] measurements; the window transmission was measured separately. A calibrated Cs_3Sb photodiode was used as a standard in the yield measurements. The EDC's presented here, unless noted otherwise, are normalized according to yield; that is, the area of the EDC's are proportional to the sample yield at the corresponding photon energies.

III. RESULTS

The standard procedure at the start of a study of surface states is to first prepare a clean surface either by cleaving in vacuum, by heat cleaning, or by ion bombardment and annealing. One then attempts to identify structure in the data which may not be explained by bulk electronic transitions. By following the changes in this structure as the surface environment is altered by the adsorption of gases, one can try to associate the structure with the clean surface. In photoemission, it is possible to follow the movement of the surface position of the Fermi level as the crystal doping is varied from degenerate *p* type to degenerate *n* type. By studying the changes in pinning of the Fermi level, one can gain useful information as to the nature of the surface states in the forbidden energy gap, that is, where these states (filled or empty) are located and their density distribution. It is desirable to study as many crystals with different levels of doping as possible; however, since the group-III-V semiconductors are quite similar and there is good knowledge of the surface state distributions in some typical III-V semiconductors such as GaAs, one may feel fairly confident about obtaining a good picture of the surface-state distributions in InP despite having studied a number of cleaves on one degenerate *n*-type crystal.

A. Clean and oxidized surface

Figure 1 shows the EDC's at five different photon energies obtained from clean InP. All the structures in the EDC's appear to arise from bulk direct transitions, since the initial and final state energies change with photon energy. By varying the incident photon energy, these structures may be moved around to enhance small structures in the EDC's and thereby facilitate the identification of surface states, whose initial-state energy does not vary with photon energy. In Si, a peak with constant initial-state energy at different photon energies was observed; in InP, none could be found. The very faint shoulder near the high-energy edge of the EDC at a photon energy of 10.2 eV is not visible at photon energies more than 0.5 eV above or below and is not due to emission from surface states. Rather, this is due to a direct transition from the top of the valence band near the Γ point in the Brillouin zone. The same tran-

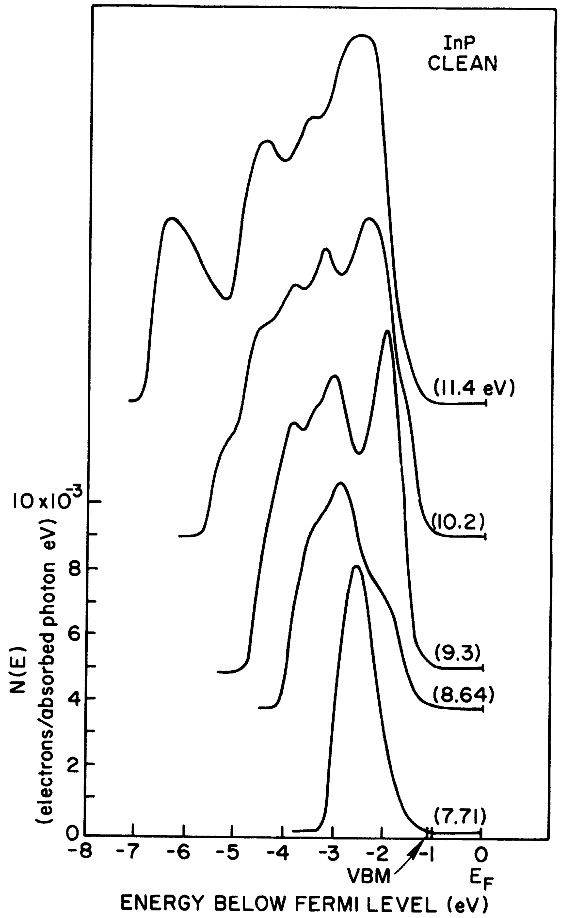

FIG. 1. EDC's for clean 6×10^{17} cm^{-3} *n*-type InP as a function of photon energy.

sition is visible in GaAs.[4] The VBM is therefore readily found by locating the high-energy cutoff position of emission in the 10.2-eV EDC. A sampling of EDC's at various energies reveals that the high-energy cutoff position lies closest to the Fermi level at photon energies near 10 eV, so this is further evidence that one has indeed located the VBM relative to the Fermi level at the surface. The surface position of the Fermi level is found to be pinned at 1.1 eV above the VBM—in rough agreement with Fischer[17]—putting the bottom of the pinning states at about 0.25 eV below the conduction band minimum (CBM), InP having a forbidden energy gap of 1.34 eV. The accuracy in these values, as mentioned previously, is to within ± 0.1 eV. Note the absence of prominent structure near the VBM which remains stationary relative to the Fermi level when the incident photon energy is varied, indicating an absence of sharp surface density of filled states at or near the forbidden gap, which would give rise to a peak or shoulder with a constant initial-state energy. The peaks here move with varying photon energy.

This situation is very similar to that in GaAs,[3] where the surface Fermi level is pinned at 0.7 eV below the CBM and, on the degenerate *p*-type sample, the surface Fermi level is at the bulk position indicating absence of filled surface states in the band gap. Application of Harrison's bond orbital model based on experiments by Gregory *et al.*[3] shows the existence of two bands of surface states with an energy difference of several electron volts between them. The empty surface states are associated with the Ga and the filled surface states with the As atoms. A recent refinement[18] of the model of the GaAs surface includes a displacement of the outer layer of atoms. The As atoms move out, and the Ga atoms move in towards the lattice by almost a lattice constant. The dangling electrons on the As atom then become mostly *s*-like, and the empty states associated with the Ga atom become mostly *p*-like. Eastman and Freeouf[7] also produced evidence in a measurement on GaSb that the empty surface states are associated with the group-III surface atoms and the filled surface states with the group-V surface atoms. Calculations by Joannopoulos and Cohen[9] also show a splitting of the surface states associated with the fundamental gap of about 3 eV, with the lowest surface-state band primarily localized on the surface As atoms and the highest surface-state band localized primarily on the Ga surface atoms. Recent calculations by Calandra and Santoro[10] also show agreement. This picture naturally extends to InP as well, with the empty and filled surface states associated with the In and P, respectively. Previously, Gregory *et al.*[3] made similar associations in GaAs. On exposure to oxygen, the oxygen atoms are expected, to a first approximation, to bond to the P atoms and further lower the filled surface states and leave the empty surface states, and thus the Fermi level pinning, largely unaffected. The behavior of InP under oxidation is shown in Fig. 2. The EDC's are presented with the various peaks lined up. The crystal was very insensitive to oxygen, a normal behavior among the III-V semiconductors in this $h\nu$ range. The main effects up to 10^7 langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr sec) of oxygen were a lowering of the leading peak and a rise in the background emission. Note, in particular, that there are no structures which disappear with light oxidation, as in the case of Si,[1] where the highest-lying structure associated with the filled surface states disappeared upon exposure to about 10^3 L of oxygen. This lack of oxygen-sensitive structures indicates that the filled surface states probably form a broad band lying several eV below the VBM. The Fermi level position, to within experimental resolution (± 0.1 eV), remained constant up to 10^7 L. At 10^8 L, the EDC underwent a much larger change, and the structures began to become smeared out.

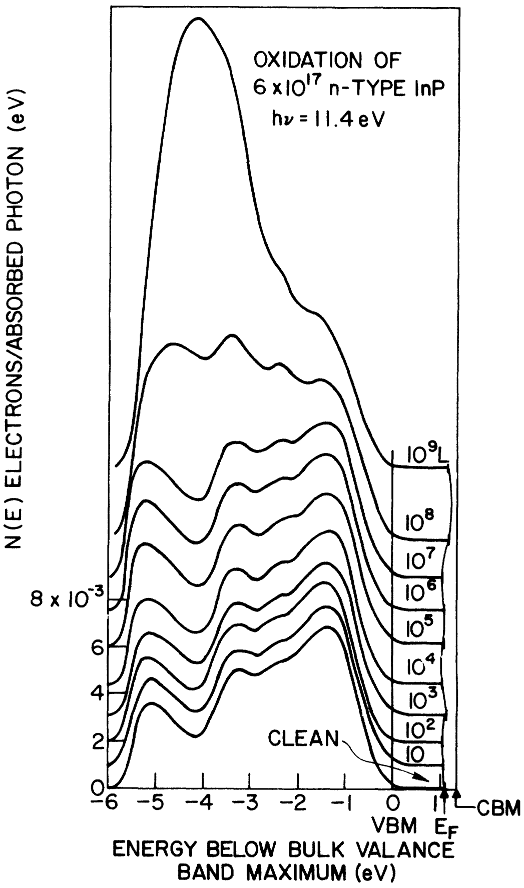

FIG. 2. EDC's for $6 \times 10^{17}\ \mathrm{cm}^{-3}$ *n*-type InP at a photon energy of 11.4 eV as a function of oxygen exposure.

At 10^9 L, a large oxygen peak had built up and most of the peaks were gone. Here, it has become rather difficult to line up the EDC's in the same manner as previously; nonetheless, it appears that the Fermi level pinning had not changed significantly even at this large exposure. This is consistent with the picture of oxygen initially bonding to the P atoms and leaving the empty surface states largely unaffected. In contrast, the Fermi level pinning in *n*-type Si is completely destroyed by exposure to 10^3-L O_2,[1,19] the pinning position rising from midgap to the bulk position. The Si "dangling-bond" electrons bond with the oxygen atoms to remove the intrinsic surface states and form new interface states.

B. Cesiated surface

Deposition of Cs permits one to study the metal-semiconductor interface and Schottky-barrier pinning. Conventional Schottky-barrier work does not shed much light on the origin of the pinning states, as studies are made with the metal already on the semiconductor surface. With UPS, we may study the Fermi level pinning as the metal is added in fractions of a monolayer. Since UPS probes about 20 Å into the bulk at around 10 eV, it is possible to use bulk semiconductor structures as a reference in following changes in the electronic structure at the surface. Cesium is particularly suitable for such studies as it is strongly polarized and the repulsion between the atoms prevents formation of islands on the surface, enabling it to wet the semiconductor well and provide a uniform coverage over the surface.[20]

One cleave of the sample was carefully cesiated in nine separate steps until maximum yield was achieved. Cesiation of a different cleave produced similar results. Sets of EDC's were taken after each exposure and the Fermi level position determined using the Cu backdoor as a reference. Figure 3 shows the movement of the surface Fermi level and the VBM at the surface relative to the bulk peaks, as obtained from the 10.2-eV EDC's. The VBM is determined from the extrapolated upper edge of the EDC taken at energies (around 10.2 eV) where direct excitations from the top of the valence band near Γ is visible as a faint shoulder in the EDC. The extrapolation is done by drawing a straight line along the leading edge of the EDC, cutting off the high-energy tail. An example of this extrapolation is given in Fig. 4. The high-energy tail may be caused by a number of reasons to be discussed later. In Fig. 4, a set of EDC's taken at 10.2 eV for various stages of cesiation is shown. The bottom trace is taken from the clean surface; the cesiated EDC's are stacked above it and labeled with the coverages. The coverages are estimates based on GaAs as discussed in Sec. II. The EDC's are shown with the peaks arising from bulk transitions lined up. The large background of scattered electrons may cause a shift in the position of the peaks, but the effect is small for the leading peaks because there are few scattered electrons at high energies. A subtraction of estimated background electrons confirms this. The Fermi levels at the surface and the extrapolat-

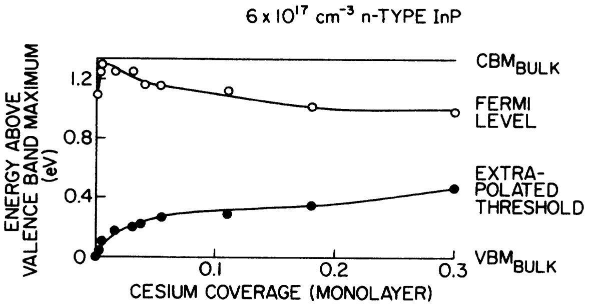

FIG. 3. Positions of the surface Fermi level and the extrapolated upper edge of the EDC's relative to the bulk band edges, plotted as a function of cesium coverage.

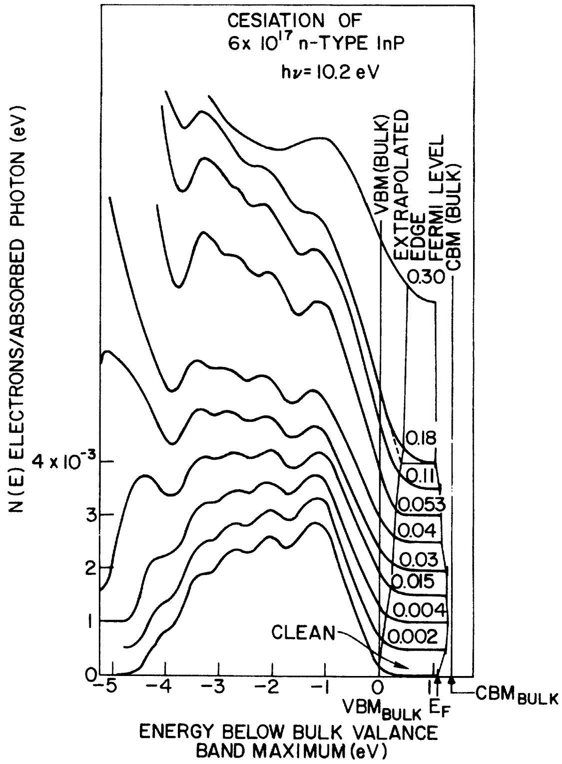

FIG. 4. EDC's at a photon energy of 10.2 eV as a function of cesium coverage. The method of locating the extrapolated upper-edge position is demonstrated on the second uppermost EDC. The EDC's are labeled with the cesium coverage in monolayers.

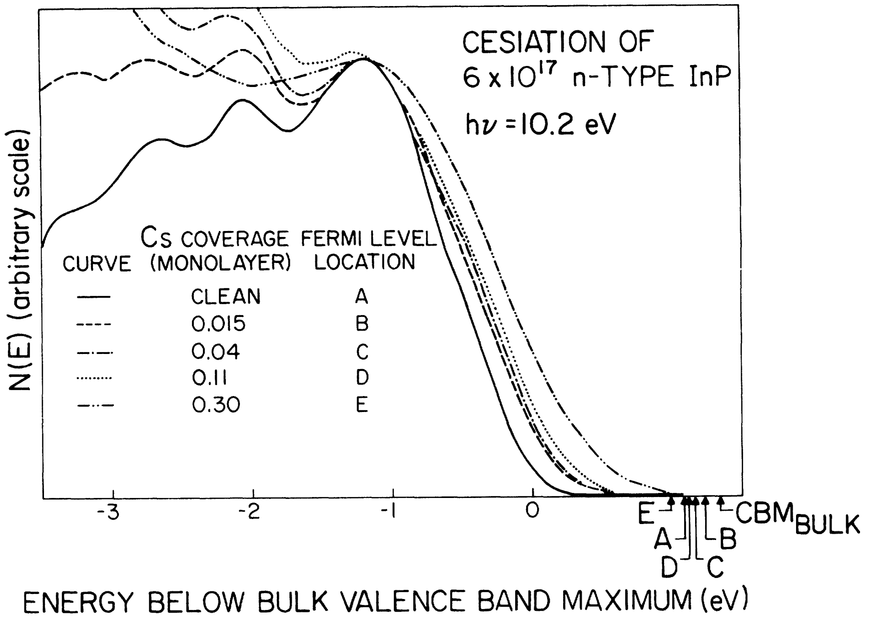

FIG. 5. High-energy portions of the EDC's at a photon energy of 10.2 eV as a function of cesium coverage, showing a large movement of the leading edge of the EDC's.

ed upper-edge positions are also shown, with lines drawn through the various points. Figure 5 shows the front (high-energy) portions of EDC's for various cesium coverages and are scaled so that the leading peak heights are identical. The movement upwards in energy (into the band gap) of the upper edge of the EDC with Cs is quite apparent. By the time maximum yield has been reached, the movement has reached 0.5 eV. The Fermi level, on the other hand, first showed an upward movement with very light (< 1/100 monolayer) cesium coverage, then started dropping with further deposition of Cs, and by the last cesiation it has dropped to 0.1 eV below the pinning position on the clean surface. Heavy cesiation also caused the structures in the EDC's to disappear, so that only the broadened first peak is still visible by the ninth cesiation. There was also considerable high-energy tailing in the EDC's. Although the disappearance of structure at 0.3 monolayer made comparison with lower coverages difficult, the movement upward of the upper edge of the EDC's was quite apparent even at coverages as low as 0.015 monolayer, when all the peaks in the EDC were clearly visible. At a coverage of 0.11 monolayer, when the upper edge had moved by almost 0.4 eV, all the bulk peaks in the EDC were still visible, thus making comparison with EDC's at lower coverages easy. The same sort of behavior is observed at lower photon energies. Yield data for the various cesiated surfaces are shown in Fig. 6. The threshold on the clean surface is 5.78 eV, in close agreement with Fischer's[17] value of 5.69 eV and Williams and McGovern's[21] value of 5.6 eV. The minimum threshold obtained was 2.03 eV, which, when taking the upward movement of the valence-band edge and the downward movement of the Fermi level into account, gives a value for the work function of 1.5 eV, which is also close (within 0.1 eV) to Fischer's value. The various thresholds for the different cesiations were obtained from these curves, and the threshold lowering was used in estimating the cesium coverages.

InP is an interesting material in Schottky-barrier studies in that it deviates quite far from the $\frac{2}{3}$ rule of Mead *et al.*,[5] who discovered that the Schottky-barrier height with Au is approximately two-thirds of the band gap down from the conduction-band edge. The final pinning position found here falls at or slightly below the bottom of the empty surface states; in GaAs, the Fermi level with Cs coverage is also pinned about 0.1 eV below the bottom of the empty surface-state band. It is likely that the final pinning position in the formation of Schottky barriers is closely related to where the pinning occurs on the clean surface, since for two different materials, one of which follows the $\frac{2}{3}$ rule and one of which does not, the same association between the clean-surface Fermi level location and the pinning position may be made.

Eastman[7] and Freeouf also found a correlation between the empty surface-state band and the Schottky-barrier pinning position for a number of III-V materials. We agree with this to first order. However, it appears that the Cs interacts with the semiconductor surface in such a way as to lower the pinning position to below the bottom of the empty surface-state band and move the valence-band threshold in the EDC (Fig. 3) to higher energy, and Schottky-barrier pinning cannot be sim-

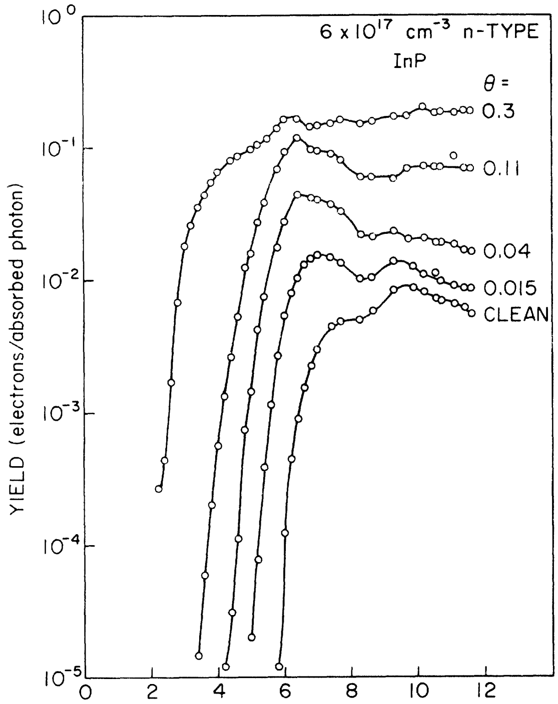

FIG. 6. Spectral yield curves for InP as a function of cesium coverage ϕ in monolayers defined in terms of Cs surface atoms per InP surface atom. $\theta=0.3$ corresponds to the maximum Cs coverage which can be obtained in a monolayer.

ply explained in terms of filling the empty surface states on the clean surface. Eastman and Freeouf based their conclusions on results on a number of III-V semiconductors, including GaSb, where they found the empty surface states to extend about 0.4 eV below the CBM so that the Schottky-barrier pinning position corresponds closely to the bottom of the empty surface states. However, experiments by Chye *et al.*[22] indicate an absence of empty and filled surface states in the band gap in GaSb. Moreover, the Fermi level moved by almost the entire band gap when Cs was added to the surface, indicating that a simple filling of empty surface states is an inadequate explanation. In arriving at at their conclusions, Eastman and Freeouf also had to rely on the existence of a "tail" of empty surface states with a low density of states which might change when different metals were added to the sample surface. Gregory and Spicer[6] have found no evidence of such a tail. Moreover, it has recently become clear that there is a variation in the location of the Fermi level on clean *n*-type GaAs samples studied in various laboratories.[3,7,23-25] Since the Fermi level can be pinned by as few as 10^{12}–10^{13} (surface states)/cm^2, one must be careful in assuming that the pinning position on *n*-type III-V semiconductors is associated with the bottom of the empty intrinsic surface states. While the pinning position on InP was very reproducible, and near the top of the band gap, suggesting that the pinning states were intrinsic (one might expect pinning owing to surface roughness and defects to vary from cleave to cleave, and might also expect impurities to pin the Fermi level somewhat further down in energy), at present it is impossible to rule out pinning by extrinsic states associated with various factors such as surface roughness or impurities. The large movement of the VBM on InP is indication of a strong interaction between the Cs and the semiconductor surface. Small amounts of Cs go on the surface as positive ions and creates a negative space-charge layer, causing the initially bent bands to straighten, giving rise to an upward movement of the Fermi level. As more and more Cs is added, the strong interaction causing the extension of emission into the band gap cannot be simple explained. One possible mechanism is the type suggested by Inkson[26]—i.e., when a metal is put on a semiconductor, it gives rise to an image potential which attracts electrons in the conduction band, causing the conduction band to bend downward, and attracts holes in the valence band, causing the valence band to move upward, resulting in a narrowing of the band gap. The data presented here do not support this picture unequivocally, but a similar sort of mechanism may be at work. More theoretical work dealing with the interaction of Cs with semiconductors is clearly needed before the data can be completely explained. One might ask if the interaction and broadening of the leading peak in the EDC's might be due to experimental artifacts. The resolution of the energy analyzer can be tested by observing the Fermi edge broadening of the EDC's taken off the copper backshutter. In all cases, the width of the 10%–90% edge height was between 0.2 and 0.3 eV (increasing with increased Cs coverage), too small to account for the observed broadening of the first peak in the EDC's. A second possibility is contamination owing to outgasing during cesiation. This is unlikely, for in GaAs, where the same broadening with cesiation was observed, contamination caused a decrease in the broadening in the first peak rather than an increase. It might also be argued that the broadening is a peculiarity of a particular cleave, as some cleaves exhibited sharper structure than others; for example, the Γ transition used to determine the top of the valence band is visible as a faint shoulder on some cleaves but not on others. However, since Cs was applied to two different cleaves, one with a clearly visible shoulder from the Γ transition and the other without such a shoulder, and since the same behavior under cesiation was observed on both, this possibility may be ruled out. Uneven coverage of Cs over the surface would cause a nonuniformity in work function over the surface, but this would only broaden the low-energy edge of the EDC's. Uneven coverage would also lead to differences in band bending over the surface. This difference is, however, small, as can be seen from Fig. 3, which shows Fermi level pinning changes and hence band bending changes as a function of coverage. In any case, with heavy Cs deposition, the nonuniformity should disappear, and with that, the broadening. Emission from the entire band-bending region may, at first glance, explain the broadening; however, on GaAs, differently doped crystals show the same broadening,[4] and on one sample doped 1.5×10^{17} p type, the band-bending length, estimated using the depletion approximation, is much greater than the electron escape depth. The same is true for the InP sample here. Therefore there must be some mechanism other than the unscreened acceptors causing a band bending sharp enough to yield the observed broadening, which again points to mechanisms such as Inkson's If there were a sharp band bending upward near the surface caused by the metal image potential, then the resulting EDC's would be broadened and structureless, and there would be emission from within the band gap, as was observed. This sharp upbending of the bands would bring the valence-band edge over a very short distance (several atomic layers) to the Fermi level at the surface and could explain the high-energy tail up to the Fermi level observed in the EDC's taken from the heavily cesiated sample. This high-energy tail is unlikely to be produced by emission from metallic Cs,[27] because a superposition of an InP EDC and a Cs EDC does not lead to anything like the heavily cesiated InP EDC. Moreover, the yield from the high-energy tail is much higher than the yield from metallic Cs. Metallic Cs has a very short electron escape depth and low yield at 10.2 eV.[28,29] For example, $n(E)$ at the peak near the Fermi level in the Cs EDC's is more than two orders of magnitude smaller than $n(E)$ at the first bulk peak in the InP EDC's. It is therefore unlikely that emission from bulk Cs changes the high-energy edge of the EDC significantly.

IV. CONCULSIONS

A careful study of an n-type InP crystal has demonstrated the absence of emission from filled surface states with strongly peaked density of states. A broad band of filled surface states may lie below the valence band maximum, however. Fermi level pinning owing to a band of empty surface states extending 0.25 eV into the band gap was observed. The compound was insensitive to oxygen exposure, and the Fermi level pinning position changed little with oxidation up to exposures as large as 10^7-L O_2. This is consistent with the model proposed by Gregory *et al.*,[3] where the empty surface states may be associated with the group-III element, and the filled surface states associated with the group-V element, with the two bands of surface states separated by a rather large band gap. The oxygen bonds onto the group-V atoms and leaves the empty surface states undisturbed for the first exposures of oxygen. The downward band bending in InP that was observed with the arrival of the first small fraction of a monolayer of Cs was due to the presence of Cs^+ ions on the surface. With more Cs, there was a definite upward movement of the upper edge of the EDC's, and the Fermi level moved downward and stabilized at or just below the pinning position on the clean surface. This indicates that the Cs interacts with the semiconductor in some complicated manner beyond a simple donation of electrons to the empty surface states. The Schottky-barrier model of Inkson[26] which predicts a closing of the band gap near the surface owing to image potentials would partly explain the phenomenon. It is clear, however, that much more theoretical and experimental work has to be done before this phenomenon may be understood completely.

---

†Research supported by the Advanced Research Projects Agency of the Department of Defense and monitored by Night Vision Laboratory, US AEC under Contract No. DAAK 02-74-C-0069.

*Present address: Physics Dept., University of Ibadan, Nigeria.

‡Present address: Research Institute of Electronics, Shizuoka University, Hamamatsu, Japan.

[1] L. F. Wagner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).

[2] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

[3] P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, Appl. Phys. Lett. 25, 511 (1974).

[4] P. E. Gregory and W. E. Spicer, Phys. Rev. B 12, 2370 (1975).

[5] C. A. Mead and W. G. Spitzer, Phys. Rev. 134, A713 (1964); C. A. Mead, Solid State Electron. 9, 1023 (1966).

[6] Gregory and Spicer (Ref. 4) have studied GaAs samples with different doping levels and concluded that the empty surface density of states have a very sharp cutoff at the lower edge.

[7] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).

[8] G. P. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).

[9] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974); J. R. Chelikowski and M. L. Cohen (unpublished).

[10] C. Calandra and G. Santoro, J. Phys. 8, L86 (1975).

[11] J. A. Applebaum and D. R. Hamann, Phys. Rev. B 6,

2166 (1972); J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973).

[12] R. Ludeke and L. Esaki, Phys. Rev. Lett. 33, 653 (1974).

[13] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 31, 102 (1973).

[14] R. Ludeke and A. Koma, Crit. Rev. Solid State Sci. 5, 259 (1975).

[15] T. E. Madey and J. T. Yates, Jr., J. Vac, Sci., Technol. 8, 39 (1971); H. Clemens and W. Monch, Crit. Rev. Solid State Sci. 5, 273 (1975).

[16] M. Cardona, J. Appl. Phys. 36, 2181 (1965); 32, 958 (1961).

[17] T. E. Fischer, Phys. Rev. 142, 519 (1966).

[18] W. A. Harrison (private communication).

[19] L. F. Wagner and W. E. Spicer, Phys. Rev. B 9, 1512 (1974).

[20] R. L. Bell, *Negative Electron Affinity Devices* (Oxford, London, 1973).

[21] R. H. Williams and I. T. McGovern, Surf. Sci. 51, 14 (1975).

[22] P. Chye, I. A. Babalola, T. Sukegawa, and W. E. Spicer, Phys. Rev. Lett. 35, 1602 (1975).

[23] A. Huijser and T. van Laar, Surf. Sci. 52, 202 (1975).

[24] J. H. Dinan, L. K. Galbraith, and T. E. Fischer, Surf. Sci. 26, 587 (1971).

[25] G. W. Gobeli and F. G. Allen, Phys. Rev. 137, A245 (1965).

[26] J. C. Inkson, J. Phys. C 5, 2599 (1972); 6, 1350 (1973).

[27] A possible explanation of the "edge shift" would involve the assumption that the emission from a $\frac{1}{3}$ monolayer of Cs was 10^2 greater than that from metallic Cs. This is not supported by Eastman and Grobman's work [Phys. Rev. Lett. 30, 177 (1973)], where the emission of Pd on Ag was found to increase by about a factor of 10 in going from submonolayer to several-monolayer coverage.

[28] N. V. Smith and G. B. Fischer, Phys. Rev. B 3, 3662 (1971).

[29] P. E. Gregory, P. Chye, H. Sunami, and W. E. Spicer, J. Appl. Phys. 46, 3525 (1975).