PHYSICAL REVIEW B VOLUME 13, NUMBER 2 15 JANUARY 1976

Photoemission study of surface states of the (110) GaAs surface*

Paul E. Gregory and W. E. Spicer
Electrical Engineering Department, Stanford University, Stanford, California 94305

(Received 2 September 1975)

A detailed photoemission study of the cleavage face of GaAs shows that there are no empty surface states in the lower half of the energy gap, but empty surface states extend down to about the middle of the energy gap. The empty surface states cause Fermi-level pinning and band bending on *n*-type GaAs, but the bands are approximately flat for *p*-type GaAs. No evidence for filled surface states is found below the valence-band maximum, indicating that any filled surface states below the valence-band maximum have no strong structure and may be strongly mixed with bulk valence-band states. Several theoretical calculations of the surface states for GaAs (110) have been reported which find an empty surface state in good agreement with the results reported here, but the calculations also find a high density of surface states located approximately 0.5 eV below the valence-band maximum, in poor agreement with our results.

I. INTRODUCTION

Measurements of the energy distribution of surface states on semiconductor surfaces are of great theoretical and practical importance. In the past few years, ultraviolet photoemission spectroscopy (UPS) has emerged as a very powerful tool for studying surface states on atomically clean semiconductors.[1-3] UPS measurements can provide a direct indication of the energy distribution of surface states, information that is difficult to obtain by any other technique.

In this paper we report the results of a UPS study of the surface states on the GaAs (110) surface, prepared by cleaving in ultrahigh vacuum. At the time this study was begun, two previous UPS studies of surface states on GaAs (110) had been published,[2,4] but the studies were in disagreement as to the presence of filled surface states in the energy gap. We decided to undertake a detailed UPS study of the GaAs (110) surface to resolve that disagreement. We have now studied a total of 12 cleavages on four different GaAs samples. Our results show that there are no filled surface states within the energy gap, in good agreement with the results of Ref. 4. It has now been reported that the filled surface states reported in Ref. 2 were not reproducible and more recently reported results are in agreement with the results reported here.[5,6]

We have previously given brief reports of our results,[7,8] and have given an overview of our results with suggestions of how the results might be extended to other faces and other III-V materials.[9] In this paper we present more data than could be reported in the short earlier reports, new data not available at the time of those reports, and a more detailed analysis of the data than has been previously presented.

II. EXPERIMENTAL DETAILS

The experiment was performed in an ion-pumped, stainless-steel vacuum chamber capable of pressures of 2×10^{-11} Torr or better. Monochromatic uv light for photoemission was provided by a McPherson 225 monochromator with a hydrogen discharge lamp having a hot filament.[10] The uv light entered the sample chamber through a LiF window. Measurements were made in the photon energy range $5.6 \leq h\nu \leq 11.8$ eV, the high-energy limit being determined by the LiF-window cutoff, and the low-energy limit by the work function of the GaAs sample.

Two *n*-type and two *p*-type GaAs single crystals of different doping were studied. The dopings of the samples and the sample designations are given in Table I. A clean (110) surface was exposed by cleaving the sample between a tungsten carbide blade and annealed copper anvil in ultrahigh vacuum. The (110) surfaces studied were 1×1 cm in area. Approximately 1.3–3 mm of material was removed in each cleave, and the samples were long enough so that each sample could be cleaved several times. The number of cleaves of each sample that were studied is listed in Table I. In this paper, a particular cleaved surface will be referred to by sample designation and cleavage number. For example, 19*p* cleave 2 refers to the second cleavage studied from sample 19*p*.

Electron energy distribution curves (EDCs) and yield spectra were measured for each sample. EDCs were measured with the ac retarding potential technique.[11] Yield was measured relative to a Cs_3Sb photocell with known response.[12] The yield has been corrected for the GaAs reflectivity measured by Phillip and Ehrenreich[13] as tabulated by Eden.[14] The GaAs EDCs presented in this paper are normalized so that the area under an EDC is proportional to the yield at the photon energy used to measure the EDC.

The position of the Fermi level at the sample surface was determined by measuring EDCs from a copper emitter which could be interchanged with the GaAs sample. The copper emitter was formed

TABLE I. Description of samples studied.

Sample designation	Type	Doping (cm^{-3})	Dopant	Calculated bulk Fermi-level position[a]	Number of cleaves studied
19*p*	*p*	3×10^{19}	Zn	0.055 eV below VBM	2
17*p*	*p*	1.5×10^{17}	Zn	0.11 eV above VBM	4
14*n*	*n*	6×10^{14}	O	0.17 eV below CBM	4
18*n*	*n*	1.7×10^{18}	Si	0.068 eV above CBM	2

[a] CBM is the conduction-band minimum; VBM is the valence-band maximum.

by *in situ* evaporation, simultaneously with the evaporation of copper on the inside surface of the energy analyzer. This method of determining the Fermi-level position has been described previously,[15] but we will review the method here since the surface Fermi-level position is an essential part of the data of this paper.

Figure 1(a) shows schematically the energy of the filled states and work functions for a semiconductor emitter, a metal emitter, and the collector surface (metal) of the electron energy analyzer, along with EDCs from the two emitters. ϕ_s, ϕ_m, and ϕ_c are the work functions of the semiconductor emitter, metal emitter, and collector, respectively. In Fig. 1(a) the collector is shown biased at V_{E_F}, the retarding potential necessary to just retard an electron emitted from the Fermi level. As is shown, V_{E_F} is given by

$$V_{E_F} = h\nu - \phi_c$$

for both emitters. The work functions of the metal and semiconductor emitters determine the low-energy edge of the EDCs, but do not influence the position of the Fermi level on the EDC.

Figure 1(b) shows that the value of retarding potential at the Fermi level for the semiconductor is the same value as the Fermi-level retarding potential determined from the metal EDC, if both EDCs have been measured at the same photon energy. In practice the Cu EDCs are usually measured at one or two photon energies, and the position of the Fermi level for other photon energies is corrected for the difference in photon energies. EDCs from the copper emitter for this system have been previously published.[16]

The measurement of the Fermi-level position for the EDCs is very important in this work because surface states can cause band bending in the GaAs, and a measurement of the band bending gives important information regarding the energy of the surface states. The band bending causes the position of the valence-band maximum (VBM) relative to the Fermi level to be different at the surface than it is in the bulk GaAs. The bulk position is known from the doping, and the surface position can be determined from the EDCs.

The surface position of the bands is measured by UPS because the probing depth in UPS is short compared to the band bending length. The probing depth is determined by the hot electron escape depth. The escape depth has not been measured for GaAs, but values for other materials[17] suggest that for 10-eV electrons the escape depth is 10–25 Å. On the other hand, the band bending lengths for the GaAs samples studied here is >200 Å for 0.5-eV band bending, except for sample 19*p* where it is about 50 Å. We have detected band bending

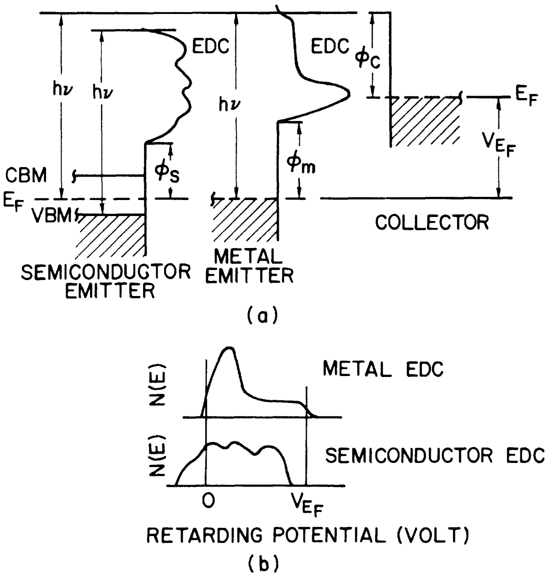
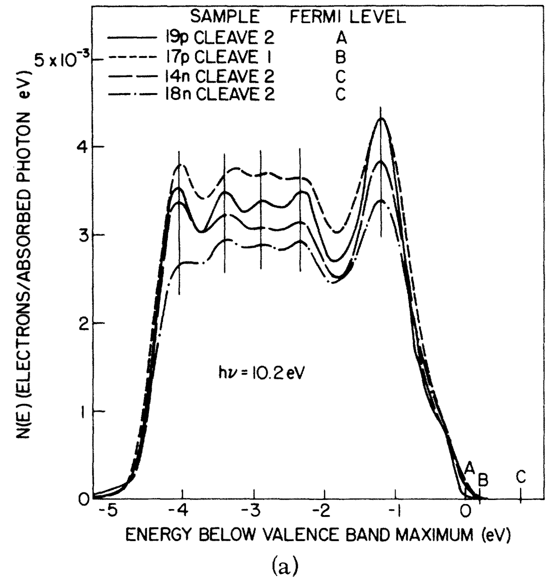


FIG. 1. (a) Energy relations between emitter and collector surface, when biased so as to barely retard an electron emitted from the Fermi level of the emitter. Two emitters are shown, a semiconductor and a metal. ϕ_s is the semiconductor work function, ϕ_m the metal emitter work function, and ϕ_c the collector work function. V_{E_F} is the retarding potential required to barely retard an electron from the emitter Fermi level and $h\nu$ is the photon energy. EDCs are indicated above the emitter work functions. (b) EDCs from (a), plotted vs retarding potential. The Fermi level appears at the same retarding potential for both the metal and semiconductor EDCs, so the metal EDC Fermi-level position can be used to locate the Fermi-level position on the semiconductor EDCs. The width of the EDCs, measured from the left edge to the Fermi level, is determined by the photon energy and the emitter work function.



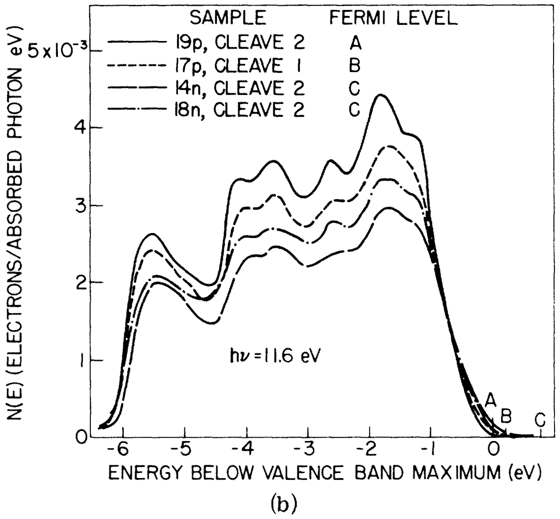


FIG. 2. (a) EDCs for four GaAs samples of different doping levels for $h\nu = 10.2$ eV. Notice how the peaks of the EDCs are aligned, but the Fermi levels are not a aligned. The Fermi level for the two n-type samples, $18n$ and $14n$, is pinned by a band of empty (acceptor) surface states in the upper half of the band gap. (b) EDCs for the same samples as (a), for $h\nu = 11.6$ eV.

changes caused by[18] Cs and oxygen[19] adsorption that are very similar for samples $19p$ and $17p$. This fact suggests that the 50-Å band bending length for sample $19p$ is long compared to the electron escape depth.

The position of the Fermi level on the Cu EDC is determined by taking the midpoint of the straight-line portion of the upper edge of the EDC. The absolute error in the determination of the Fermi-level position may be as large as ±0.1 eV, but the Fermi-level position measured by this technique is reproducible to better than 0.05 eV. The difference in Fermi-level position relative to the VBM at the surface for several samples is determined by aligning EDCs for the different samples and measuring the difference in Fermi-level positions, as is shown in Fig. 2. The major error in this procedure comes from the difficulty in knowing how to align the EDCs. Fortunately, as Fig. 2 shows, GaAs EDCs have a large number of sharp peaks to use in aligning the EDCs. In this paper the EDCs are usually aligned relative to the peak located 1.2 eV below the VBM in the GaAs EDCs measured at $h\nu = 10.2$ eV. This peak is used because it is sharp and very reproducible. As discussed below, this alignment brings the other peaks into good alignment also.

III. RESULTS AND DISCUSSION

A. Surface states in band gap

As we will show, the distribution of surface states on the GaAs (110) surface consists of an empty band of surface states in the upper half of the band gap, with a lower edge 0.75 ± 0.05 eV above the VBM, while any filled surface states lie below the VBM. We will present data on surface states within the band gap in this section, and data regarding surface states below the VBM in Sec. III B.

Figure 2(a) shows EDCs for the four GaAs samples studied, measured for $h\nu = 10.2$ eV, aligned at the peak 1.2 eV below the VBM. This alignment brings the other peaks into close alignment also. Figure 2(b) shows EDCs for the same samples for $h\nu = 11.6$ eV, with the same relative Fermi-level spacing as in Fig. 2(a); the peaks are well aligned in Fig. 2(b) also. The shape of the EDCs for the four samples is very similar at a given photon energy for the range of photon energies investigated here, for all 12 cleavage faces studied. The significant difference in the EDCs is the position of the Fermi level for the different samples. As Fig. 2 shows, the Fermi-level position is about the same for the two n-type samples, but is different for the two p-type samples.

The fact that the surface Fermi-level positions for the p-type samples are different than for the n-type samples is an important indication of the surface-state distribution within the band-gap region. As will be dicsussed in Sec. III B, the upper edge of the EDCs for $h\nu \approx 10.2$ eV lies at the VBM. The fact that the surface Fermi-level for sample $19p$, cleave 2, lies at the extrapolated edge of the EDC, that is, at the VBM, demonstrates that there cannot be any filled intrinsic surface states in the lower portion of the band gap. If any filled surface states were present in the lower half of the band gap, they would pin the

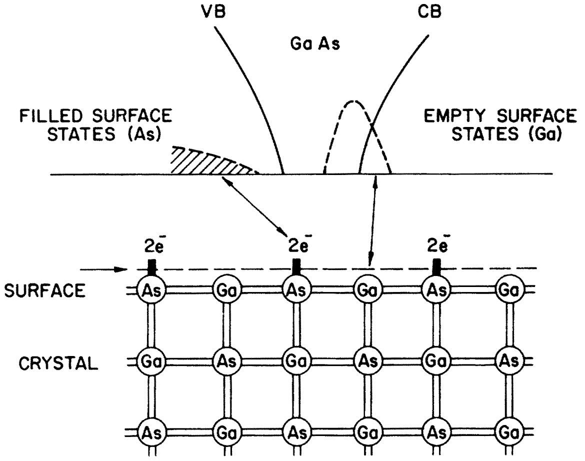


FIG. 3. Surface-state model for the GaAs (110) surface. A band of empty surface states extends down the middle of the energy gap, but the lower half of the band gap has no surface states. We find the position of the lower edge of the empty surface-state band to be 0.75 ± 0.05 eV above the VBM. The distribution of empty surface states is drawn to suggest the results of Ref. 5. We show the filled surface-state band only to indicate that it is below the VBM, and does not have strong structure; we have seen no structure which could be attributed to filled surface states below the VBM. The Ga character of the empty surface states and As character of any filled surface states is suggested by several theoretical and experimental results (see Refs. 6, 7, and 21–25).

Fermi level at a higher energy on the *p*-type GaAs. In the case of Si, where there are filled surface states within the band gap, the Fermi level is pinned at approximately 0.35 eV above the VBM on degenerate *p*-type Si and 0.55 eV above the VBM on degenerate *n*-type Si.[20]

Another important indication of the lack of filled surface states in the band gap for GaAs is the lack of any corresponding structure in the EDCs. Such structure has been identified in the EDCs measured from Si,[1,20] but no comparable structure was seen in the GaAs EDCs measured in this work. Eastman and Grobman[2] reported such states but none of our samples gave any evidence of this. Eastman and Freeouf[5,6] have apparently found no evidence for such states in their most recent work. As we will discuss in Sec. III B, we have investigated several "bad cleaves," but find no surface-state peak in the EDCs similar to that reported by Eastman and Grobman.[2]

As Fig. 2 shows, the surface Fermi-level position for the two *n*-type samples is about 0.75 eV above the VBM. As will be discussed more completely below, this Fermi-level position indicates that the bands are bent upwards on the *n*-type samples, by 0.5 eV on sample 14*n* and 0.75 on sample 18*n*. This Fermi-level pinning on *n*-type GaAs and lack of pinning on *p*-type GaAs is in good agreement with the results of Dinan, Galbraith, and Fischer[4] (DGF).

The model for the surface state distribution suggested by our results is shown in Fig. 3, and is similar to that proposed by DGF. A band of empty surface states lies in the upper half of the band gap, causing the pinning on the *n*-type samples. No surface states lie in the lower half of the band gap, so that there is no Fermi-level pinning on *p*-type GaAs, and there is no band bending. Any filled surface states lie below the VBM. However, we find no peaks in the EDCs that can be identified with surface states below the VBM, so we show the filled surface states in Fig. 3 as a dashed line, with no peaks. The UPS measurements locate the lower edge of the empty surface-state band 0.75 ± 0.05 eV above the VBM; the distribution of empty surface states is drawn to resemble the data of Eastman and Freeouf.[5] The identification of the empty surface state as Ga derived, and the filled state as As derived is consistent with several theoretical[7,21–23] and experimental[6,24,25] results.

In Fig. 2 the spacing between the Fermi level for sample 19*p*, cleave 2 and for the two *n*-type samples is 0.78 eV. A more accurate measure of the Fermi-level spacings can be obtained by averaging the Fermi-level positions for several EDCs for $h\nu = 10.2$ eV with respect to the peak 1.2 eV below the VBM. The value obtained in this way is 0.75 ± 0.03 eV for the spacing between the Fermi level for sample 19*p*, cleave 2, and the Fermi level for sample 14*n*.[26] The Fermi-level position for sample 18*n*, cleave 2, is 0.01–0.07 eV above the position for sample 14*n*, with a difference between the average Fermi level positions of 0.03 eV, i.e., the Fermi level positions for samples 14*n* and 18*n* are the same within experimental accuracy.

Since the Fermi level for sample 19*p*, cleave 2, lies at the VBM, the surface Fermi-level pinning position for both samples 14*n* and 18*n* is 0.75 eV above the valence-band maximum. The position of the Fermi level in the bulk, calculated from the carrier concentration, is 1.25 eV above the VBM for sample 14*n* and 1.5 eV for 18*n*. Thus the bands are bent upwards by 0.5 eV for sample 14*n* and 0.75 eV for sample 18*n*.

The surface-state model of Fig. 3 is in good agreement with the model of[4] DGF; however, they place the lower edge of the empty surface-state band at about 0.58 eV above the VBM, in contrast to the 0.75-eV value reported here. The photoemission results of DGF were limited to $h\nu \leq 6.2$ eV, so the EDCs consisted of only one peak, whose position could be influenced by small changes in the sample work function. Also, the low photon energy made a precise determination of the position of the VBM difficult. Thus, the discrepancy in the location of the lower edge of the empty surface-state band is not considered significant.

Eastman and Freeouf[5] have recently measured the energy distribution of the empty surface-state band using photoemission partial yield spectroscopy (PPYS). Their results are in qualitative agreement with those reported here, although their data seems to show a low-energy tail on the empty surface-state band extending 0.2 eV lower than the position we report here. Lapeyre and Anderson[27] have recently reported results that indicate an excitonic effect may be involved in the PPYS technique. An excitonic effect would be likely to lower the measured position of the empty surface-state band, so this effect may explain any discrepancy in the measured positions of the lower edge of the empty surface-state band.

As discussed above, the Fermi-level pinning on the n-type samples causes band bending of 0.5 eV for sample 14n and 0.75 eV on sample 18n. This band bending requires a negative charge in the (almost) empty surface-state band to compensate the positive space charge in the band bending region. Assuming complete carrier depletion in the band bending region, we can calculate the total amount of charge on the surface required to compensate the space charge from the equation

$$Q_{ss} = (2\epsilon_r \epsilon_0 N_d V_{bb}/q)^{1/2} \quad ,$$

where Q_{ss} is the surface charge, ϵ_r the dielectric constant of GaAs, ϵ_0 the permittivity of free space, N_d the concentration of donors, V_{bb} the band bending in electron volts, and q the electron charge. Using the band bending values we have measured, we find that the surface charge in the empty surface-state band is 6×10^{10} electrons/cm^2 for sample 14n, and 4×10^{12} electrons/cm^2 for sample 18n. If we assume that the total density of empty surface states is two for each surface Ga atom, or approximately 9×10^{14} cm^{-2}, the surface charge on sample 18n is about 0.5% of the total density of empty surface states.

The very small fraction of occupied empty surface states for sample 18n explains why no emission from the occupied portion of the empty surface states is seen in the EDCs. The surface state peak seen in Si EDCs has been estimated to represent a density of approximately 8×10^{14} electrons/cm^2.[1] A peak 0.005 as high would be very difficult to resolve.

The very low value of surface charge for sample 14n indicates that the density of empty surface states below the surface Fermi-level position for sample 14n must be $\leq 6\times10^{10}$ cm^{-2}. The fact that the surface Fermi-level position for samples 18n and 14n is the same, within experimental accuracy, indicates that the lower edge of the empty surface-state band is very abrupt. For example, if we assume the Fermi level relative to the VBM at the surface is 0.05 eV higher for sample 18n than for sample 14n, the extra surface charge for sample 18n would require that the density of empty surface states at the lower edge of the band be approximately 8×10^{13} cm^{-2} eV^{-1}. Therefore, most of the surface charge for sample 14n probably lies above the Fermi level, and the density of surface states below the Fermi level must be $\ll 6\times10^{10}$ cm^{-2}.

In one respect the empty surface states behave differently than one would expect for surface states. It is usually expected that surface states will be very sensitive to contamination on the sample surface; in fact the sensitivity to contaminants is an important criterion in the identification of surface states. For example, residual vacuum contamination[1] and oxygen adsorption[20] both greatly diminish the filled and empty surface-state density on Si; however, even very heavy oxidation does not remove the surface-state Fermi-level pinning on p-type Si, even though it reduces the density of filled surface states below the level which can be detected by UPS, i.e., by almost 10^3. Also, Eastman and Freeouf report that PPYS measurements on Ge show that the empty surface-state band is greatly diminished by a monolayer of Sb adsorbed on the surface.[5]

The available data suggest that the reaction of the GaAs empty surface state to adsorbates is more complex than that of Si or Ge surface states. Eastman and Freeouf[6] have reported that the empty surface state is insensitive to Pd and In overlayers, but Lapeyere and Anderson[27] report that a light Sb overlayer eliminates the empty surface states. Ludeke and Koma[28] report that for three reconstructions of the (100) GaAs face, the empty surface-state transition seen in low-energy electron loss spectroscopy is greatly diminished by oxygen adsorption. Our UPS results for oxygen adsorption on[19] GaAs (110) show that the Fermi-level pinning for n-type GaAs is not removed by the oxygen, suggesting that the empty surface states are not completely removed by the oxygen. New photoemission results for the oxidation of GaAs (110) have been obtained for $50 \leq h\nu \leq 300$ eV by using radiation from Stanford Synchrotron Radiation Project.[29] The EDCs from that experiment show that oxygen adsorption causes a large (~4 eV) shift in the As 3d core level, but a much smaller shift (~0.5 eV) in the Ga 3d level. This result indicates that for the (110) face the oxygen preferentially adsorbs on the surface As atoms, leaving the Ga surface atoms (and thus the empty surface states) largely unaffected. The results of Ludeke and Koma[28] indicate that oxygen exposure may affect the GaAs (100) surface differently than the (110) surface.

The resistance of the empty surface states to modification by contamination may cause one to wonder if the Fermi-level pinning on clean *n*-type GaAs could be caused by something other than intrinsic surface states, for example, by surface damage or impurities. We find that a careful consideration of all the available data shows that the intrinsic surface states provide the best explanation for the data. As will be discussed below, several different theoretical calculations are in agreement that there is an empty surface-state band in the upper half of the band gap. The Fermi-level pinning, PPYS, and low-energy electron loss results are all in agreement that there is a surface state in the upper half of the band gap. If this state were caused by surface damage or impurities, it would be expected to vary from sample to sample and cleave to cleave. However, our results are consistent for the 12 cleavage faces studied, and the results from a number of different laboratories are in good agreement.[4,5,24,27] Furthermore, as will be discussed below, we have studied several rough cleaves and find that the Fermi-level pinning position for *n*-type GaAs is affected only very slightly by the cleavage quality. Thus the presence of empty surface states in the upper half of the band gap provides the best explanation of all the results.

B. Surface states below valence-band maximum (VBM)

The discussion in Sec. III A has shown that there is a band of empty surface states in the upper half of the band gap extending down to 0.75 eV above the VBM, but there are no surface states in the band gap below this point. One would expect the same number of filled surface states as empty surface states, i.e., one empty and one filled surface state for each surface atom. Since the filled surface states do not lie within the band gap, any filled surface states must lie below the VBM. Detection of surface states below the VBM is much more difficult than states within the band gap because structure in the EDCs from the valence band masks the surface-state structure. As detailed below, we have made a careful investigation of the EDCs for evidence of surface-state structure below the VBM, but we have found no evidence of such structure.

Three tests which can be used to identify surface-state structure in[30] EDCs are: (i) band bending, as determined from Fermi-level pinning, (ii) location of structure in the EDCs which cannot be explained by the bulk band structure, and (iii) the sensitivity of structure to surface contamination. The first test is only applicable here to the location of surface states within the band gap. The first test formed the basis of most of the discussion in Sec. III A, above.

The second test involves measuring EDCs over as wide a range of $h\nu$ as possible, and comparing the behavior of structure in the EDCs with the behavior expected from the bulk band structure. In Fig. 4 we present EDCs for $6.4 \leq h\nu \leq 11.8$ eV for sample 19*p*, cleave 2. As the figure shows, there is a large number of peaks and shoulders in the GaAs EDCs. However, all the structure can be related to the bulk band structure, as Eden[14] and Spicer[31] have shown.

The structure from the EDCs of Fig. 4 is summarized in Fig. 5, where the photon energy used to measure an EDC is plotted horizontally and the energy of structure in the EDC is plotted vertically, downward from the VBM at the top of the figure. The peaks, valleys, and shoulders from the EDCs are plotted in the figure. The shoulders are indicated by error bars because it is difficult to measure the location of the shoulder. A construction similar to that of Fig. 5 was used in Refs. 14 and 31 to compare the structure in the EDCs to the structure predicted by the bulk band structure. Reasonable agreement was found between the bulk band structure and the EDCs. Since the details of the band structure vary somewhat between different calculations, the details of the comparison between the UPS results and the band structure may vary slightly for different band structure.

Our Fig. 5 is in excellent agreement with the similar plots in Refs. 14 and 31. (We have plotted the data with respect to initial-state energy, whereas Refs. 14 and 31 plotted the data with respect to final-state energy.) Figure 5 shows all the valleys, while Refs. 14 and 31 show only the more important valleys. The only significant difference in the plots is that several shoulders in Refs. 14 and 31 are resolved as peaks here. This is because the EDCs from sample 19*p*, cleave 2, were unusually sharp, apparently the result of an unusually good quality cleave. The sharpness of the data for this cleave will be discussed more completely below.

It is not our purpose to discuss the detailed identification of peaks in the EDCs with features in the band structure; the interested reader is referred to Refs. 14 and 31 for a discussion of the band structure. The general features of Fig. 5 are relevant to a discussion of surface states, however. Note that in Fig. 5 the energy of the peaks moves as the photon energy is changed, and the peaks do not move parallel to each other. Note also that peaks abruptly appear and disappear with changes in photon energy. This behavior can be explained on the basis of direct, $\vec{k}$-conserving, transitions in the bulk GaAs band structure.

Conservation of $\vec{k}$ has not been found, to date,

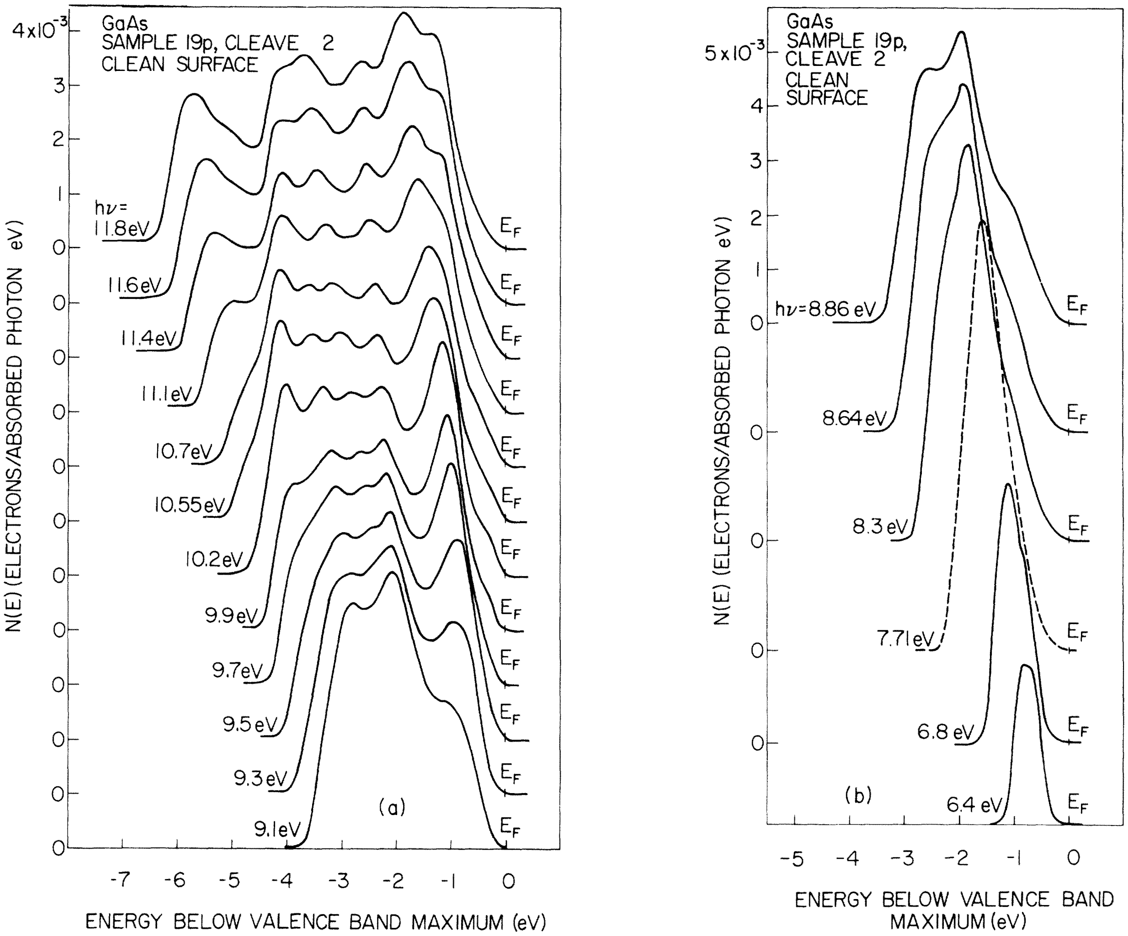


FIG. 4. EDCs for sample 19*p*, cleave 2 for $6.4 \leq h\nu \leq 11.8$ eV. Note that the position of structure in the EDCs changes with changes in $h\nu$, and that structure appears and disappears with changes in $h\nu$. The EDC for $h\nu = 7.71$ eV is shown dashed to avoid confusion where it crosses the other EDCs.

to be important in transitions from surface states. In the case of silicon, the surface-state peak remains at a constant energy relative to the VBM independent of $h\nu$, although the peaks from the bulk Si move in energy due to direct transitions. The Si surface-state peak remains visible in the EDCs for $8.6 \leq h\nu \leq 11.8$ eV.[1,30] (For $h\nu < 9.6$ eV a bulk peak moves to the same location as the surface-state peak; thus, one sees a peak due to the superposition of the bulk and surface peaks.) The Si surface-state peak appears identical for $h\nu \approx 25$ eV.[3] It should be noted that, for $h\nu < 11.8$ eV, angularly integrated EDCs are used whereas for $h\nu \approx 25$ eV the energy analyzer accepted a more restricted angular sample.

By analogy with Si, then, we would expect a surface-state peak to remain at a fixed energy with respect to the VBM independent of changes in $h\nu$. Such a peak would appear as a horizontal line in Fig. 5. As the figure shows, most peaks do not lie on a horizontal line. The two main features which do move approximately horizontally in Fig. 5 are a peak located at -4 eV, and a series of shoulders at about -1 eV. The peak at -4 eV can be ruled out by the results of O_2 exposures.[19] An oxide peak builds up under the peak at -4 eV, for oxygen exposures above 10^5 Langmuirs (1 Langmuirs $= 10^{-6}$ Torr sec), but the peak at -4 eV is still clearly present in the EDCs. Figure 6 shows EDCs for increasing O_2 exposures for sample 17*p*, cleave 1, for $h\nu = 11.6$ eV. Note that the peak at -4 eV is clearly present for even the largest exposures. Another fact making the peak at -4 eV an unlikely candidate for a surface state can be seen in Fig. 5 for $h\nu = 11.8$ for clean GaAs, where it appears that the peak at -4 eV will disappear for $h\nu > 11.8$ eV.

The oxidation behavior of the shoulder at -1 eV also appears to rule it out as a surface state. Figure 7 shows EDCs for the same sample as Fig.

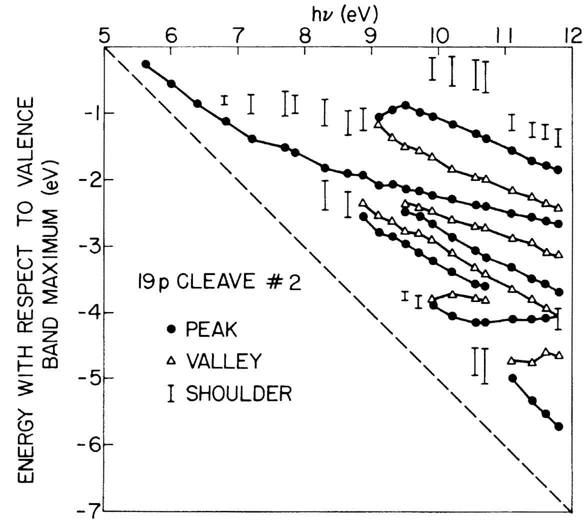


FIG. 5. Structure plot for the EDCs of Fig. 4. The photon energy is plotted horizontally and the energy of peaks, valleys, and shoulders with respect to initial states referenced to VBM from the EDCs is plotted vertically. The irregular movement of the structure can be explained on the basis of direct, $\vec{k}$-conserving bulk transitions. No structure which can be assigned to surface states is observed.

4, but with a heavy O_2 exposure. The shoulder at -1 eV is present in the EDCs, although it is not as well resolved. However, all of the structure in the EDCs is somewhat less well resolved for the heavy O_2 exposure. Recent UPS studies of GaAs at the Stanford Synchrotron Radiation Project for $10 \le h\nu \le 200$ eV show even stronger effects of oxidation of the bulk peaks for $h\nu$ near 25 eV. To be more specific, all of the peaks in the valence band portion of the EDC disappear on oxidation, leaving only a single broad peak.[29] Apparently the escape depth in this photon energy range is less than the thickness of the oxide that forms. This loss of structure is apparently reflected in a weakening of structure for $h\nu = 11.8$ eV.

As the EDCs of Fig. 7 show, the exposure did not preferentially remove any structure from the EDCs. Large oxygen exposures on samples 19*p*, 17*p*, and 14*n* produced similar results.[19] Only small O_2 exposures were made on sample 18*n*.

As will be discussed below, several calculations of surface states for GaAs (110) find a strong filled surface state within 0.5 eV of the VBM.[21–23,32] However, as Fig. 5 shows, we do not find any structure in the EDC between 0.5 eV below the VBM and the VBM, except for the weak shoulder that is seen only for $9.9 \le h\nu \le 10.7$ eV. As will be discussed below, the weak shoulder can be related to a bulk transition. The fact that the weak shoulder is present only for a narrow photon energy range would rule it out for consideration as a surface state in any case. Furthermore, the shoulder is still present as a break in slope of the leading edge of the EDCs after a heavy oxygen exposure. Thus, the UPS results show no evidence for the calculated filled surface state within 0.5 eV of the VBM.

Taken together, the movement of structure in the clean GaAs EDCs with $h\nu$ and the lack of preferential disappearance of structure in the EDCs with O_2 exposures indicate that any surface states below the VBM produce no strong structure in the EDCs. The surface states below the VBM may be spread throughout the energy range of the valence band, or they may be strongly mixed with valence-band states.

One other feature of the structure plot in Fig. 5 is the shoulder just below the valence-band maximum for $9.9 \le h\nu \le 10.7$ eV. This shoulder has been identified as arising from the Γ_{15} to Γ_{12} transition.[14,31] A recent electroreflectance study[33] has

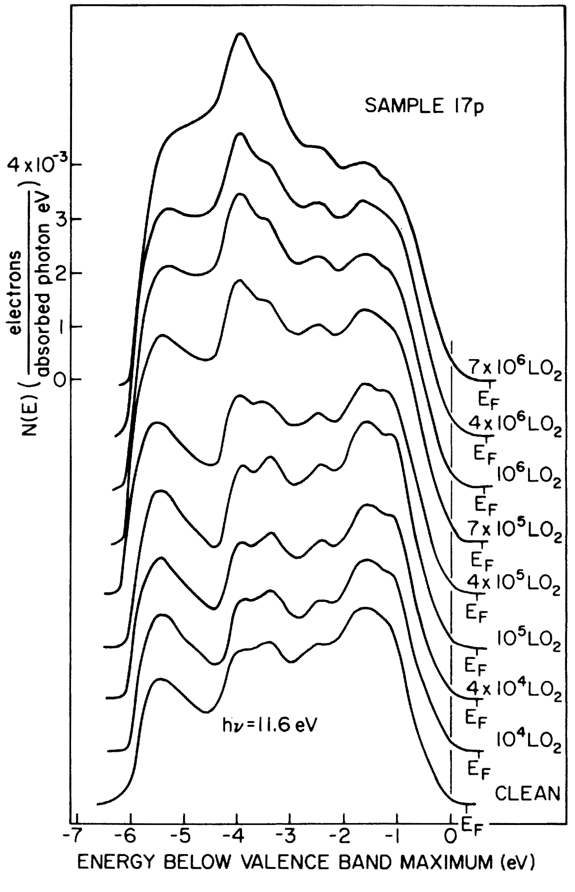


FIG. 6. EDCs as a function of O_2 exposure for sample 17*p*, cleave 1, for $h\nu = 11.6$ eV. Notice that there is no preferential disappearance of structure, as would be expected for surface states.

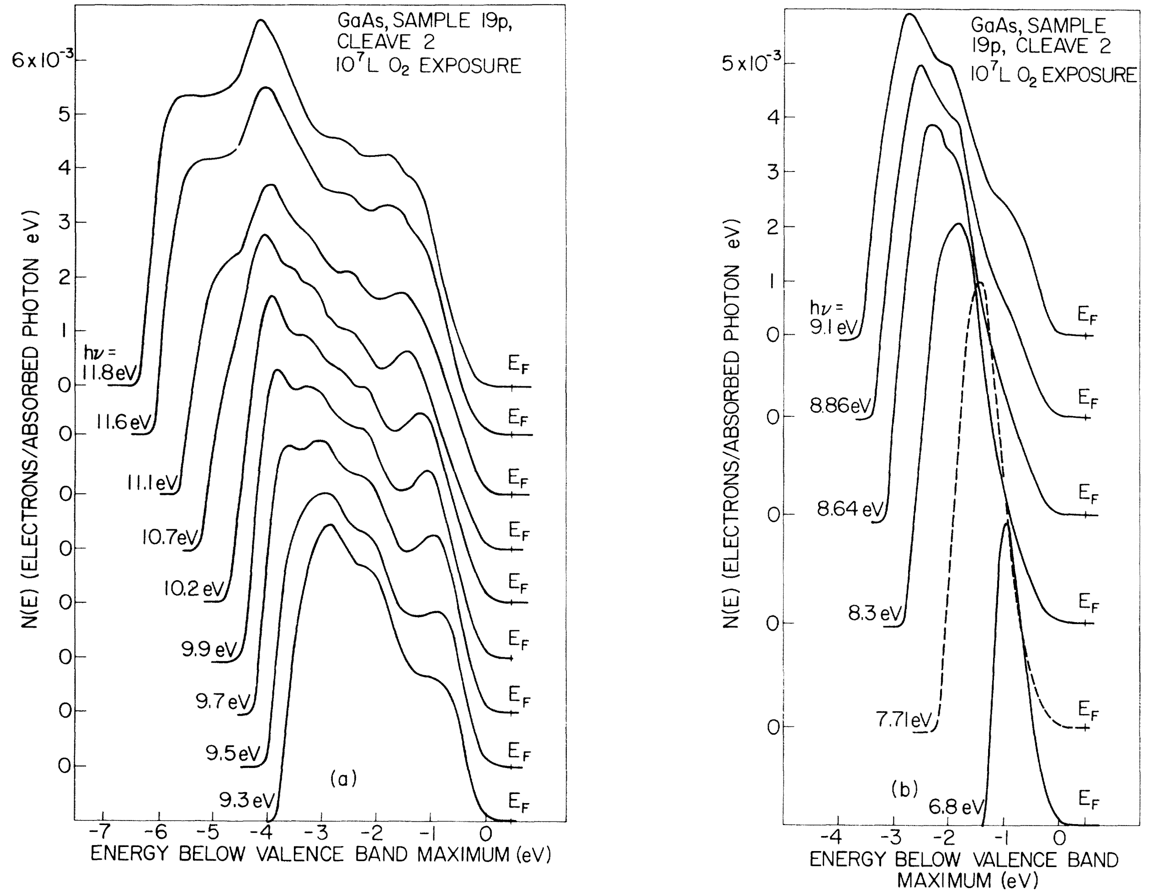


FIG. 7. EDCs for the same sample as Fig. 4, after a 10^7-Largmuirs O_2 exposure. Notice that the same features are visible in the EDCs of Figs. 4 and 7, except that the structure of the EDCs in Fig. 7 is somewhat less sharp than that in Fig. 4.

identified the Γ_{15} to Γ_{12} spacing as being 10.53 eV, in fair agreement with the photon energy range for which the structure is seen in the EDCs. The fact that we see evidence for this transition 0.6 eV lower in energy than is seen in the electroreflectance is somewhat puzzling; perhaps the details of the shape of the band structure can explain this fact. This identification is important because Γ_{15} is at the VBM; therefore, the high-energy shoulder seen in the EDCs for $9.9 \le h\nu \le 10.7$ eV represents emission from the VBM. Thus the high-energy edge of the EDCs for $h\nu = 10.2$ eV provides an accurate location of the valence-band maximum.[34]

As we have shown, there are no intrinsic surface states in the lower half of the band gap to pin the Fermi level on *p*-type GaAs. This means that the surface position of the Fermi level on *p*-type GaAs can be influenced by extrinsic factors. For example, previous studies have shown that band bending can be induced on *p*-type GaAs by the adsorption of oxygen[19] and Cs.[18] Another factor which can apparently affect the surface Fermi-level position is the quality of the cleave. Figure 8 compares EDCs for two cleaves of sample 19*p*. As the figure shows, the Fermi-level position for cleave 1 is 0.15 eV higher than for cleave 2. It is also apparent from the figure that the structure in the EDC for cleave 2 is sharper than for cleave 1. In fact, the EDCs from cleave 2 were sharper than those from any other GaAs cleave we have studied. A subjective impression obtained from making cleave 2 on sample 19*p* is that this cleave required considerably less force on the cleavage blade than for any other cleave we have made. Reinforcing this impression is the fact that the cleavage chip dropped from the sample rather than flying off with considerable speed, as is usually the case. These facts suggest that the face of sample 19*p*, cleave 2 may have been less strained than the usual cleavage face, and that the strain may have a small influence on the surface Fermi-level position. Similarly, the measured Fermi-level position for the sample 17*p* cleaves was 0.1–

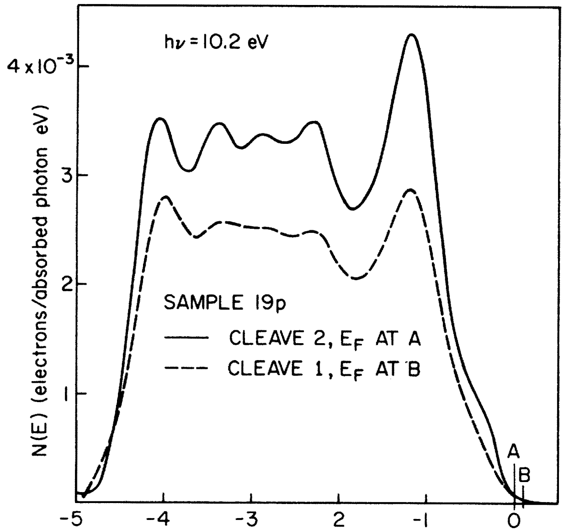


FIG. 8. EDCs for sample 19*p*, cleaves 1 and 2, for $h\nu = 10.2$ eV. The peaks in the EDC for cleave 2 are sharper than the peaks for cleave 1, and the Fermi-level position is 0.1 eV lower for cleave 2.

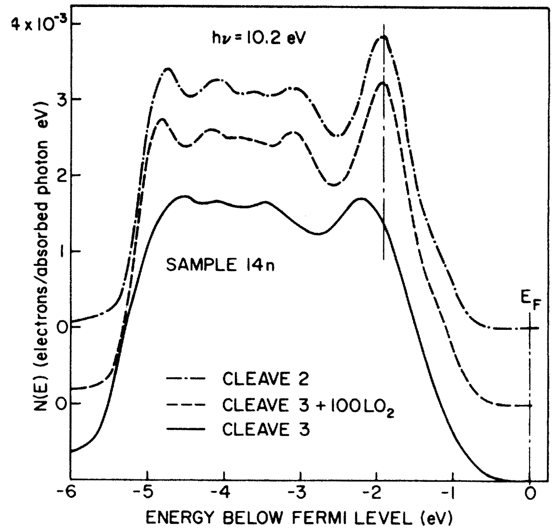


FIG. 10. EDCs for sample 14*n*, cleaves 2 and 3. Cleave 3 was a deliberate "bad cleave" (see text), and the EDC is greatly distorted from a normal EDC. An exposure of 100 Longmuirs of O_2 removed the distortion, possibly by relieving surface strain. Cleave 2 was a normal cleave.

0.2 eV higher than would be expected from the bulk Fermi-level position. Sample 17*p* was somewhat difficult to cleave, in two cases shattering rather than cleaving. Perhaps the cleave quality influenced the surface Fermi-level position for sample 17*p*, also.

The data from two rough cleaves on *n*-type samples indicates that the shape of the EDCs is affected by the cleave quality, but the Fermi-level position is not greatly affected. Sample 18*n*, cleave 1, cleaved in a series of macroscopic steps in such a way that the cleavage crack intersected the surface, leaving a 2–3 mm by 1 cm area of uncleaved, air exposed, surface on the sample. By placing a mask over half of the LiF window it was possible to measure EDCs from the cleaved part of the crystal face. The part from which EDCs was measured had a much larger number of macroscopic steps and tear marks than a normal cleave would have. An EDC from 18*n*, cleave 1 is compared to an EDC from 18*n*, cleave 2 (a normal cleave) in Fig. 9. As the figure shows, the EDC from the rough cleave has weaker, broader structure than the EDC from the normal cleave, but the Fermi levels are within 0.05 eV of the same position.

A larger distortion in the EDCs resulted from an intentional "bad cleave," sample 14*n*, cleave 3. The sample was notched before cleaving, and the notches were slightly offset. A hard ceramic rod was forced into one notch by the cleaving anvil, and the cleaving blade was forced into the other notch. The resulting cleave did not appear to be appreciably different from a normal cleave, but the EDCs were greatly distorted. Figure 10 shows an EDC from the bad cleave, an EDC from the bad cleave after it was exposed to 100 Langmuirs of O_2, and an EDC from cleave 2, a normal cleave. For some reason not completely understood, the O_2 exposure changed the shape of the EDC from the bad cleave to the shape of the EDC from the normal cleave, perhaps by re-

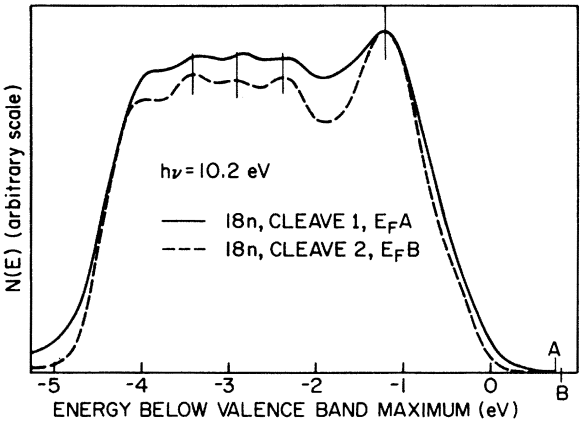


FIG. 9. EDCs for 18*n*, cleaves 1 and 2. Cleave 1 was a rough cleave, but cleave 2 was normal. The structure in the EDC for cleave 1 is weaker and broader than for cleave 2, but the Fermi-level positions are almost identical. The vertical scale is arbitrary because the light spot for cleave 1 only covered half of the sample face, so the absolute yield could not be measured.

lieving surface strain. As Fig. 10 shows, the EDC from the bad cleave has one less peak than the normal EDCs, and the peaks are spaced differently. The EDCs in Fig. 10 are plotted relative to the Fermi level because the distortion of the EDC from the bad cleave makes any other alignment hard to justify. If the high-energy peaks are aligned, the Fermi levels are 0.15 eV out of alignment, and none of the other peaks are in alignment. With the Fermi levels aligned, the leading edges of the EDCs are in fair alignment. Thus, no statement can be made as to a shift in Fermi-level pinning position for the bad cleave with respect to the normal cleaves, except that any shift must be 0.25 eV or less.

The point of Figs. 9 and 10 is that any damage to the crystal surface from the cleavage process that is serious enough to cause a significant change in the Fermi-level pinning position for *n*-type GaAs also causes a significant distortion in the EDCs. Such distortion was only seen in the EDCs from the two rough cleaves discussed above.

It has been suggested that the filled GaAs surface states originally reported by Eastman and Grobman[2] were caused by a high density of cleavage steps.[5,7] However, as Figs. 9 and 10 show, the EDCs from the rough cleaves we have studied show no structure comparable to the surface-state peak reported by Eastman and Grobman.[2]

Huijser and Van Laar[35] suggest that the Fermi-level pinning on *n*-type GaAs is caused by poor cleave quality, and that there is no pinning on a good cleave. However, Fig. 9 indicates that the pinning position is about the same for a rough cleave and a good cleave. The results of Fig. 10 indicate that the band bending is the same or less on the bad cleave than it is on the good cleave, contrary to the suggestion of Huijser and Van Laar.[35]

IV. COMPARISON WITH OTHER WORK

A. Theoretical results

We have previously compared our UPS results to calculations of the surface-state energies[7] using the bond-orbital model of Harrison and Ciraci.[36] The results of the bond-orbital calculation are in good qualitative agreement with our experimental results; the bond-orbital calculations predict a filled surface state below the VBM and an empty surface state in the upper part of the band gap. The bond-orbital results made the identification of the empty surface states as being primarily Ga derived and the filled surface states as primarily As derived,[7] as indicated in Fig. 3.

The bond-orbital model is based on a type of tight-binding calculation, and is not specific to the (110) face. Several calculations specific to the GaAs (110) surface have appeared recently. In a tight-binding calculation on two atomic layers, Lannoc[37] has obtained a (110) GaAs surface-state distribution in which a filled surface-state band lies just above the VBM and an empty band lies just above the conduction-band minimum. The results of this calculation are in poor agreement with the UPS measurements. He believes that incorporating the overlap integrals would lower both surface-state bands and might bring the calculations into qualitative agreements with the UPS results.

Calandra and Santoro have made another tight-binding calculation for the GaAs (110) surface.[21] They find an empty, Ga derived, surface-state band with a lower edge 1 eV above the VBM, and a filled, As derived surface-state band extending 0.1–0.35 eV below the VBM. The empty surface-state band is 0.25 eV wide, and the filled surface-state band has about the same width. Their results are in qualitative agreement with the UPS results in the band-gap region, but the very narrow filled surface-state band below the VBM appears to be inconsistent with the lack of surface-state structure in the EDCs.

Calandra and Santoro have improved their original calculation by including a second-neighbor interaction.[32] This improvement widened and lowered the empty surface-state band, with the result that the lower edge of the empty surface-state band lies 0.7 above the VBM, in good quantitative agreement with the UPS results. The position and width of the filled surface state is only slightly changed in the new calculation, however.

Another tight-binding calculation is that of Joannopoulos and Conen[22] for a GaAs slab 12 layers thick. They have calculated the local density of states for the three layers nearest the surface. They find a total of five surface states, one high in the conduction band (B_2'), one in the upper part of the band gap (B_1'), one at the VBM (B_1), one near the bottom of the upper valence band (B_2), and one in the lower valence band, just below the heteropolar energy gap (B_3). They find that the charge localized on the Ga or As atoms changes from layer to layer, but at the surface layer the B_1' state is formed from a Ga dangling bond and an As bond along the surface, while the B_1 state is formed from an As dangling bond. The band gap for this calculation is too wide, so a quantitative comparison cannot be made with it. Qualitatively, the position of the empty surface state is in agreement with the UPS results. However, the state B_1 extends from 0.1 eV above the VBM to 0.1 eV below the VBM. A surface state this narrow should produce a strong peak in corresponding to this calculated surface state. The state B_2 is not accessible to us, and the state B_3 (and possibly B_2)

is too far below the VBM to detect for $h\nu \leq 11.8$ eV.

There have been several pseudopotential calculations of surface states on GaAs (110). The calculations of Jones[38] predicted an energy gap in the surface-state distribution on III-V semiconductors. Ball and Morgan[39] calculated the surface states at the center of the surface Brillouin zone, using an abrupt transition between the GaAs and the vacuum potential. Their results depended on the location of the potential change, giving either an empty surface state, a filled surface state, or both in the energy gap.

More recently Chelikowski and Cohen[23] have performed a self-consistent pseudopotential calculation of the surface states on a periodic array of GaAs slabs. They find surface states centered at −9, −5.75, −0.5, and 1 eV relative to the VBM. The states at −9 and −5.75 eV are near strong features in the bulk density of states, and would be difficult to distinguish from bulk states. The state at −0.5 eV is 0.5 eV wide, extending up to the VBM, is As derived and is *p*-like. The state at 1 eV is *s*-like and Ga derived. The calculations in the band-gap region are in good agreement with the UPS results. Since the empty state is centered at 1 eV above the VBM, broadening of this state would put the lower edge in good agreement with the position found with UPS. As with the other calculations, the surface state at −0.5 eV appears to be too narrow, strong and close to VBM to be consistent with the UPS results.

Most of the calculations discussed above agree that there is a surface state in the upper part of the band gap and a filled surface state at or slightly below the VBM. The results within the band gap are in good agreement with the UPS results, as noted above. The calculations seem to agree that the filled surface state at or below the VBM is narrow and strong. Such a state should appear in the EDCs, but no evidence for it has been found. The UPS results suggest that the filled surface state band is much broader and weaker than the calculations indicate. Harrison[40] has suggested that a surface reconstriction in which the As surface atoms move out and the Ga surface atoms move in could lower the filled surface state by several eV, giving better agreement with the UPS results. Another possibility is that the filled surface states are much less localized than the calculations suggest, mixing with the bulk valence-band states so much as to be virtually indistinguishable from bulk states.

The calculations, and several experiments (see below) agree that the empty surface state is primarily Ga derived and the filled surface state is primarily As derived, in agreement with the Gregory, Spicer, Ciraci, Harrison (GSCH) model.[7–9]

B. Experimental results

We have already discussed the good agreement between the UPS results, the PPYS results,[5] and the results of DGF.[4] Low-energy electron-loss spectroscopy (LEELS) has also been used to investigate surface states on GaAs in the measurements of Ludeke and Esaki,[24] and Ludeke and Koma.[28,25] They have found evidence for the empty surface state on GaAs (110), (100), (111), and $(\bar{1}\bar{1}\bar{1})$ surfaces, including several different reconstructions on some of the surfaces. The location of the empty surface-state band varies somewhat from surface to surface, but is in the upper half of the band gap for all the surfaces, in good agreement with the UPS results. The LEELS results indicate that the empty state is Ga derived[24,25,28] and has *s*-like character.[25] Ludeke and Esaki found evidence for filled surface states above the VBM on a $(\bar{1}\bar{1}\bar{1})$-2 As-rich surface, but not for the (110) surface.[24,28] Eastman and Freeouf report that UPS studies show no filled surface states between the VBM and the Fermi level for GaAs (110) and several other III-V semiconductors.[6]

One experimental study is not in agreement with our results. Van Laar and Scheer,[41] and more recently Huijeer and van Laar[35] have reported Kelvin probe measurements on *n*- and *p*-type GaAs (110) surfaces which they interpret as indicating no Fermi-level pinning on either type, and therefore, no surface states at all in the band gap, in disagreement with our UPS results. Their Kelvin probe results are also in disagreement with the Kelvin probe studies of DGF[4] and Gobeli and Allen.[42] Both of these groups combined Kelvin probe studies with photoemission and both detected Fermi-level pinning on *n*-type GaAs.

V. CONCLUSION

We have presented the results of an extensive UPS study of the GaAs (110) surface. The results are summarized in Fig. 3. An empty surface-state band extends down to about the middle of the band gap, but there are no intrinsic surface states in the lower half of the bandgap. This surface-state distribution causes the Fermi level to be pinned at the middle of the energy gap on *n*-type GaAs, but there is no pinning on *p*-type GaAs.

Figure 3 presents the GSCH model.[7–9] It indicates that the empty surface states are Ga derived and any filled surface states are As derived. This identification is supported by theoretical[7,21–23] and experimental[6,24,25,28] work. In Fig. 3 the filled surface states are shown because it is generally believed that filled surface states should be present in a density comparable to the empty surface-state density. The UPS results show that there are no intrinsic filled surface states above the VBM. We have looked for, but cannot find, evidence of filled surface states below the VBM. Therefore, the distribution of filled surface states indicated in Fig. 3 is intended only to suggest that any filled surface states (i) must lie below the VBM, and (ii) must not have any strong structure. The indicated distribution of empty surface states is drawn to suggest the PPYS results of Eastman and Freeouf.[5]

APPENDIX: ESTIMATE FOR LIMIT OF DETECTABILITY FOR FILLED SURFACE STATES

We can estimate the limits of detectability for any filled surface states below the VBM by two methods: comparison with UPS studies of Si surface states[1] (where filled surface states were observed), and by calculating the relative number of bulk and surface states within the probing depth of UPS. If we assume one filled surface state per surface atom, the limits on detectability provide an estimate of the width of the filled surface-state band. The detectability limit is set by our ability to distinguish a surface-state peak from the bulk structure in the EDC.

The filled surface-state peak in the Si EDCs represented about one surface state per surface atom.[1] The Si-filled surface state distribution is a bell-shaped curve with a full width at half-maximum (FWHM) of 0.9 eV. At $h\nu = 11.8$ eV, the surface-state peak height is about 60% of the highest bulk peak in the EDC. The Si surface-state peak lies near the VBM, where the bulk emission is weak, but it would have been easily detectable even superimposed on the strongest bulk emission in the EDC. To estimate the limits on detectability we have added several possible surface-state distributions to the bulk Si EDC. The limiting case appears to be a surface-state distribution half as high and twice as wide as the actual Si surface state, peaked in the middle of the bulk Si EDC. This surface-state distribution appears to be at the limit of detectability. The most serious limit on detectability for this case is the width of the distribution, which approaches that of the total EDC, and acts largely as an overall increase in the magnitude of the EDC. A narrower peak of the same height would be much easier to detect. Thus, a peak half as high as the observed Si-filled surface state, with FWHM of almost 2 eV could be detected deep in the valence band. (This distribution would be more easily detected if it peaked near the VBM.)

Using the other approach to estimate the limits of detectability, we compare the bulk density of states accessible to UPS to the surface density of states. GaAs has 8.8×10^{22} valence electrons cm^{-3}, with an energy spread of about 8 eV. If we are probing a slab 20 Å deep with UPS, the average bulk density of states contributing to the UPS data is 2.2×10^{15} states $\text{cm}^{-2}\,\text{eV}^{-1}$. Two filled surface states per surface As atom gives 8.9×10^{14} states cm^{-2}. If we take the width of the filled surface-state distribution to be 0.30 eV, after Calandra and Santoro,[21,32] we get 3.0×10^{15} states $\text{cm}^{-2}\,\text{eV}^{-1}$ for the filled surface states. Assuming the same matrix elements for photoemission from the bulk and surface states, this density of filled surface states would be a very prominent feature in the EDCs. The above calculations also indicate that the narrow (0.4–0.5 eV wide) filled surface state in the work of Joannopoulos and Cohen[22] would have been observed in the EDCs. Both theoretical calculations[21,22,32] place the filled surface-state peak within a region 0.5 eV below the VBM. The bulk emission in the EDC is lower than average in this region, so a surface-state peak would be easier to detect there than it would be if it were deeper in the valence band. A 1-eV wide surface-state peak would have a density of states of 8.9×10^{14} states $\text{cm}^{-2}\,\text{eV}^{-1}$, comparable to the average bulk density of states, and easily detectable.

Thus, both estimates indicate that we should be able to detect structure from a filled surface-state band 1–2 eV wide. The fact that we do not see structure from filled surface-states in the EDCs means that the filled surface-state band must have a FWHM greater than 1 or 2 eV, in contrast to the total width of 0.3 or 0.5 eV, predicted by theory.[21,22,32]

---

[*] Research supported by the Advanced Research Projects Agency of the Department of Defense and monitored by Night Vision Laboratory, USAECOM under Contract No. DAAK 02-74-C-0069.

[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] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974).

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

[5] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974).

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

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

[8] P. Gregory and W. E. Spicer, Bull. Am. Phys. Soc. 19, 213 (1974); S. Ciraci, W. A. Harrison, P. Gregory, W. E. Spicer, and L. F. Wagner, *ibid.* 19, 214 (1974).

[9] W. E. Spicer and P. E. Gregory, Crit. Rev. Solid State Sci. 5, 231 (1975).

[10] D. E. Eastman and J. J. Donelon, Rev. Sci. Instrum. 41, 1648 (1970).

[11] R. C. Eden, Rev. Sci. Instrum. 41, 252 (1970).

[12] G. B. Fisher, W. E. Spicer, P. C. McKernan, V. F. Pereskok, and S. J. Wanner, Appl. Opt. 12, 799 (1973).

[13] H. R. Phillip and H. Ehrenreich, Phys. Rev. 129, 1550 (1963).

[14] R. C. Eden, Ph.D. dissertation (Stanford University, 1967) (unpublished).

[15] G. F. Derbenwick, D. T. Pierce, and W. E. Spicer, *Methods of Experimental Physics* (Academic, New York, 1974), Vol. 11, pp. 89–92.

[16] L. F. Wagner and W. E. Spicer, Surf. Sci. 46, 301 (1974); L. F. Wagner, W. E. Spicer, and S. Doniach, Solid State Commun. 15, 669 (1974).

[17] I. Lindau and W. E. Spicer, J. Electron. Spectrosc. 3, 409 (1974).

[18] P. E. Gregory and W. E. Spicer, Phys. Rev. B 6, 2370 (1975).

[19] P. E. Gregory and W. E. Spicer, Surf. Sci. (to be published).

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

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

[22] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974).

[23] J. R. Chelikowski and M. L. Cohen (unpublished).

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

[25] R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 817 (1975).

[26] As will be discussed below, sample 18*n*, cleave 1 and 14*n*, cleave 3 were "bad" cleaves, i.e., the surface was stepped or strained. The Fermi-level position for these cleaves was not included in the average of Fermi-level positions.

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

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

[29] P. Pianetta, I. Lindau, C. Garner, and W. E. Spicer Phys. Rev. Lett. 35, 1356 (1975), and (unpublished).

[30] W. E. Spicer, J. Phys. (Paris) 34, C6-19 (1973).

[31] W. E. Spicer and R. C. Eden, in *Proceedings of the Ninth International Conference on the Properties of Semiconductors* (Nauka, Leningrad, 1968), Vol. 1, p. 65.

[32] C. Calandra and G. Santoro (private communication).

[33] D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975).

[34] J. L. Shay, W. E. Spicer, and F. Herman, Phys. Rev. Lett. 18, 649 (1967).

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

[36] W. A. Harrison, Phys. Rev. B 8, 4487 (1973); W. A. Harrison and S. Ciraci, *ibid.* 10, 1516 (1974).

[37] M. Lannoc (unpublished).

[38] R. O. Jones, Phys. Rev. Lett. 20, 992 (1968).

[39] G. Ball and D. J. Morgan, Phys. Status Solidi B 50, 199 (1972).

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

[41] J. van Laar and J. J. Scheer, Surf. Sci. 8, 342 (1967).

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