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Photoemission studies of the GaAs-Cs interface*

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Photoemission has been used to study changes in the electronic structure of the surface of GaAs as submonolayer quantities of Cs were added to the surface. The observed behavior has implications for the theory of the formation of Schottky barriers. As the Cs coverage was increased the Fermi-level pinning position of *p*-type GaAs was seen to rise to above midgap and then to move downward by about 0.2 eV. Also, as the Cs coverage was increased, states were seen to move up into the gap from the valence-band maximum. The results indicate that the empty surface states on the clean GaAs surface play a large role in determining the Fermi-level pinning position, but that other mechanisms also play a part.

INTRODUCTION

Although metal-semiconductor contacts have been studied extensively, no generally accepted model for the formation of Schottky barriers has emerged. Historically, the most commonly used model asserts that the Fermi level is pinned at the metal-semiconductor interface by surface states on the semiconductor.[1,2] However, Heine[3] has suggested that the semiconductor surface states cannot really exist in contact with a metal. He has proposed a model in which the Fermi-level pinning is caused by electron wave functions from the metal tailing into the semiconductor band gap. In addition to Ref. 3, Inkson,[4] Phillips,[5] and others have suggested various interactions between the semiconductor and metal. The Fermi-level pinning is the result of these interactions rather than being primarily due to the effect of the intrinsic surface states of the clean semiconductor.

The usual studies made of metal-semiconductor contacts consist of measurements made on a diode consisting of a semiconductor and a thick metal film evaporated onto it. These measurements yield values of the Schottky-barrier height,[2] but are not able to determine details of the energy structure at the interface, and they are not able to measure the surface-state distribution on the clean semiconductor surface. Thus the usual type of Schottky-barrier study is not able to distinguish among the various proposed models for Schottky-barrier formation, and is not able to make correlations between the barrier height and the distribution of surface states on the clean semiconductor.

Ultraviolet photoemission spectroscopy, however, is able to make measurements from the interface region directly by studying metal-semiconductor contacts where the metal film is at most several monolayers thick. By studying the energy spectrum of electrons emitted into vacuum from the metal-semiconductor interface as a function of the thickness of the metallic layer, a large amount of information about the formation of Schottky barriers can be obtained. Furthermore, it is possible to study the energy distribution of surface states on the clean semiconductor surface using this technique. Thus it is possible to make correlations between the barrier height and the density of surface states on the clean semiconductor surface.

The work presented here on Cs-GaAs contacts shows that the Fermi-level pinning position changes as a function of the metal thickness in a complicated way. Also, as the Cs coverage increases, the valence-band edge of the GaAs broadens and tails into the energy gap. Although the pinning position of the Fermi level seems to be correlated with the surface-state distribution measured by photoemission on the clean GaAs surface, the details of the behavior cannot be explained solely by the presence of the surface states. An explanation of the results seems to require elements of several of the different proposed theoretical models. Although much more experimental and theoretical work will be necessary to obtain a definitive picture of the metal-semiconductor contact, we believe the present work gives considerable new insight into the problem.

EXPERIMENTAL DETAILS

The experiment was carried out on the (110) face of a single crystal of GaAs which had been cleaved in ultrahigh vacuum by squeezing the crystal between a tungsten carbide blade and an annealed oxygen-free high-conductivity copper anvil. Four different GaAs single crystals were studied and are described in Table I. The most detailed work was done on sample 17*p*. The samples were 1×1 cm in cross section.

The experiment was contained in a stainless-steel ion-pumped chamber with a base pressure of about 1×10^{-10} Torr as measured on a Redhead gauge. Cs or Na was applied in small doses to the sample from vapor generated by conventional Cs- or Na-chromate channels. The Cs and Na channels were not in direct line of sight of the GaAs crystal, in order to reduce contamination by impurities from

TABLE I. Samples studied.

Sample name	Doping (cm^{-3})	Type
14*n*	6×10^{14}	*n*
18*n*	1.7×10^{18}	*n*
17*p*	1.5×10^{17}	*p*
19*p*	3×10^{19}	*p*

the channels. During Cs or Na evaporation, the pressure rose to at most 6×10^{-9} Torr except for the experiments on sample 14*n* where the pressure rose to a maximum of 2×10^{-8} Torr.

It is not possible to measure coverage of Cs or Na directly when Cs or Na channels are used as a source because the Cs or Na which is evolved is normally in the form of neutral atoms. Therefore, a qualitative measure of the progress of Cs or Na coverage was made during the evaporation of Cs or Na by monitoring the photoyield at a photon energy of 6 eV for low coverages, and monitoring the white-light photoyield for larger cesium coverages. Using this technique, it was possible to stop the cesiation after only small amounts of cesium were applied. Since it was not possible to measure cesium coverage directly with our experimental apparatus, we have used yield data to estimate the cesium coverage. Madey and Yates[6] have presented data relating the change in work function to measured values of cesium coverage of *p*-type GaAs(110), and Clemens and Mönch[7] give similar data for Cs on *n*-type GaAs(110). For each Cs exposure the Cs coverage was estimated by obtaining an estimate of yield threshold from measured yield curves [or from the width of the energy distribution curves (EDCs) in a few cases]. The yield threshold was converted to a work function by correcting for the position of the Fermi level at the surface. Work function changes were then converted into cesium coverage from the data of Madey and Yates[6] for samples 17*p* and 19*p*, and from the data of Clemens and Mönch[7] for samples 14*n* and 18*n*. Madey and Yates present their data as ions deposited per cm^2. We have converted this to coverage in monolayers by allowing for their estimated 20% neutral Cs atoms, and taking a monolayer to be 8.85×10^{14} cm^{-2}, consistent with Clemens and Mönch.[7] The values of Cs coverage thus obtained are used throughout this paper.[8]

After each exposure of Cs or Na, photoemitted EDCs were measured for several photon energies, and the yield was measured for photon energies from threshold to 11.6 eV. The yield was measured relative to a Cs_3Sb photodiode which has a calibration traceable to the U.S. Bureau of Standards.[9] The yield was corrected for the reflectivity of GaAs from the data of Phillip and Ehrenreich[10] as tabulated by Eden.[11] Unless otherwise stated, EDCs presented in this paper are normalized so that the area under the EDC is proportional to the yield at the photon energy at which the EDC was measured.

EDCs were measured using the standard ac-modulated retarding potential technique with a hemispherical energy analyzer.[12] The light source was a McPherson 225 vacuum monochromator with a hydrogen-discharge lamp having a hot filament. Light entered the sample chamber through a LiF window having a high-energy cutoff of 11.8 eV.

A copper emitter could be substituted for the GaAs crystal. EDCs measured from the copper emitter were used to calibrate the system so that the position of the Fermi level on the GaAs EDCs could be determined.[13] Copper EDCs were measured frequently, and especially after each Cs or Na exposure, to correct for any changes in the collector work function caused by contamination, or Cs or Na adsorption.

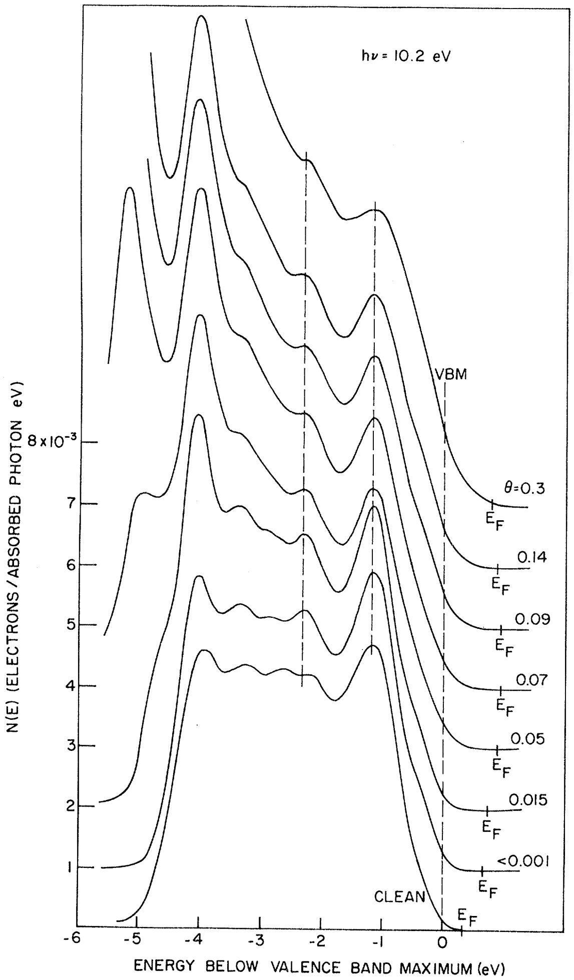


FIG. 1. EDCs for sample 17*p* at a photon energy of 10.2 eV as a function of cesium coverage, θ.

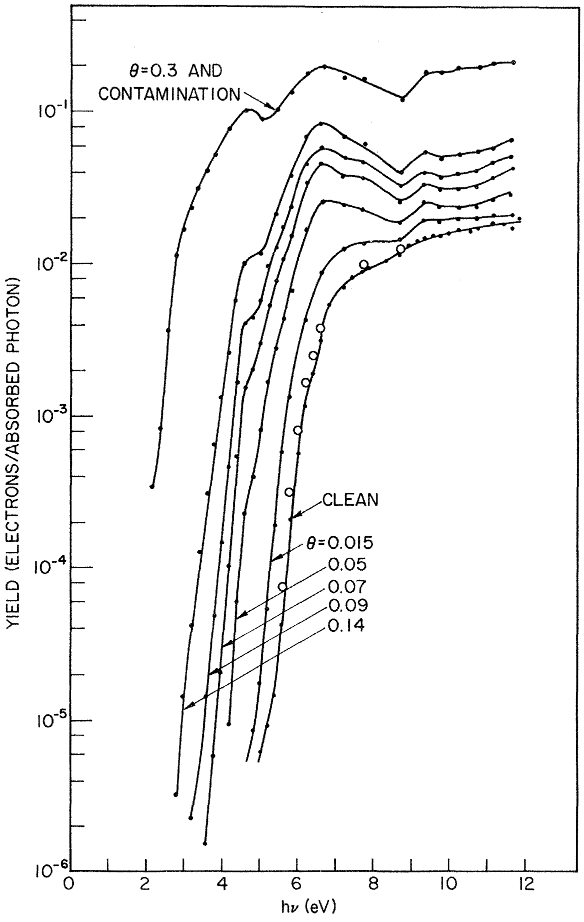


FIG. 2. Spectral yield curves for sample 17*p* as a function of cesium coverage, θ. The open circles are data points for the cesium coverage of < 0.001 monolayer.

Knowledge of escape depth and band bending are necessary to interpret ultraviolet-photoemission-spectroscopy (UPS) data. The escape depth of electrons emitted from the GaAs at the photon energies involved in the measurement of EDCs ($7.7 \lesssim h\nu \lesssim 11.8$ eV) has not been determined, but available data for other materials[14] suggests that it is 20 Å or less. For sample 17*p* the band bending length, calculated using the depletion approximation, is over 600 Å for 0.5 eV band bending. Thus for sample 17*p*, the position of structure in the EDCs with respect to the Fermi level is representative of the position of the bands at the GaAs surface. On the other hand, for sample 19*p* the band bending length is comparable to the probable escape depth. It will be shown later in this paper that for sample 19*p* the short band bending length may cause the measured difference between the Fermi level and the valence-band maximum to be somewhat less than the actual value at the surface.

RESULTS

Cesium was applied to all four GaAs samples shown in Table I and sodium was applied to a second cleave of sample 17*p*. The most detailed study of Cs on GaAs was made on sample 17*p*. Small amounts of Cs were applied to the surface of the first cleave of sample 17*p* in seven separate doses. EDCs for sample 17*p* at a photon energy of 10.2 eV are shown in Fig. 1, photoemitted yield curves are shown in Fig. 2, and a summary of the data for sample 17*p* is given in Table II. In Fig. 1, an EDC for clean GaAs is shown at the bottom; EDCs for successively larger Cs coverages are shown vertically. The EDCs are placed so that the first peaks are aligned. The Fermi-level position determined from the copper reference is indicated for each EDC. The great increase in yield and the threshold lowering caused by the Cs coverage, force us to show only the high-energy portion of the EDCs for the higher Cs coverages.

Note that throughout this paper we have defined a monolayer in terms of the GaAs (110) surface; that is, one monolayer of Cs by this definition would correspond to one Cs atom for each surface Ga and As atom. By this definition, a saturation coverage of Cs occurs at a coverage less than one monolayer. This definition may be somewhat artificial, but since the exact Cs saturation coverage is not known, the use of the GaAs surface as a reference is necessary in order to have a fixed reference point.

There are two features of Fig. 1 which are important for a study of Schottky barriers; the movement of the Fermi level with Cs coverage, and movement of states into the forbidden gap. The upward movement of the Fermi level with respect to the valence-band maximum is evident in Fig. 1, and indicates downward bending of the valence band. A very small Cs exposure cause the bands to bend down by 0.3 eV. Additional Cs causes more band bending, to a maximum of about 0.6 eV; still more Cs causes the band bending to decrease somewhat.

The movement of states into the forbidden gap is more clearly seen in Fig. 3, where the first peak in each EDC has been normalized to the same

TABLE II. Cesium exposure data for sample 17*p*.

Cesiation	Approximate threshold (eV)	Coverage [GaAs (110) monolayers]	Change in Fermi-level position from clear sample (eV)
#0	5.4	0	0
#1	5.4	< 0.001	0.3
#2	5	0.015	0.4
#3	4.3	0.05	0.6
#4	3.9	0.07	0.6
#5	3.6	0.09	0.6
#6	3	0.14	0.55
#7		~0.3	0.4

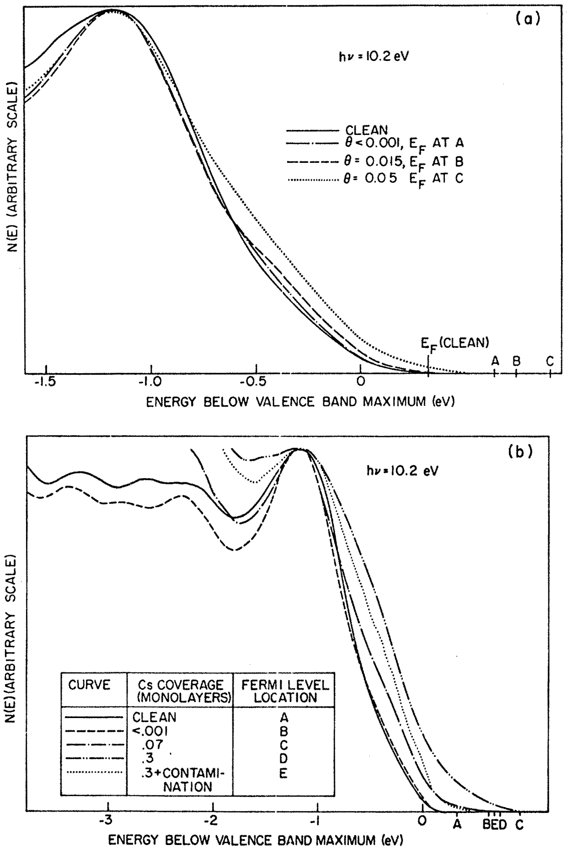


FIG. 3. High-energy portion of EDCs at a photon energy of 10.2 eV showing the upward movement of states into the energy gap as Cs coverage is increased. Part a shows the lowest Cs coverages on an expanded scale, while part b shows the effect up to the highest coverages. Letters *A*, *B*, etc., give the Fermi-level location as given in the key for each part of the figure.

height. Independent of the normalization, a straight-line extrapolation of the upper edge shows that the upper edge of the EDC moves to higher energies, with respect to the peaks of the EDCs, as the Cs coverage is increased.

Figure 3(a) shows that even at the lowest coverages there is a small buildup of emission near the base of the peak, even though the upper part of the peak has become slightly narrowed by the Cs exposure. By a coverage of 0.05 monolayers, the broadening of the first peak has become quite noticeable. Figure 3(b) shows the larger Cs coverages. By a Cs coverage of 0.3 monolayers, the broadening is quite substantial. Also note that for coverages beyond 0.05 monolayers a high-energy tail begins to develop, and by 0.3 monolayers the tail is quite large and extends up to the Fermi level.

The curve marked 0.3 monolayers + contamination in Fig. 3(b) shows the result of exposing the surface having 0.3 monolayers of Cs coverage to contamination produced by the outgassing of a hot filament which had not previously been heated in the course of the experiment. The broadening and the high-energy tail were greatly reduced by the contamination, and the Fermi-level position was lowered. Similar effects were achieved by exposure to oxygen.

Sample 19*p* was given a total of three cesium exposures. EDCs for a photon energy of 10.2 eV are shown in Fig. 4 for sample 19*p*. The band-bending behavior of sample 19*p* is similar to that of sample 17*p*, as is the movement of states into the forbidden gap. One difference in behavior is the appearance of a shoulder (*A* in Fig. 4) and a peak (*B*) on the cesiated sample 19*p*. Structures *A* and *B* are not seen in the clean GaAs EDCs and are not clearly present in the EDCs for cesiated sample 17*p*, although the shoulder *A* is in a similar position to the high-energy tail on sample 17*p* for the larger Cs coverages. The reason for this dis-

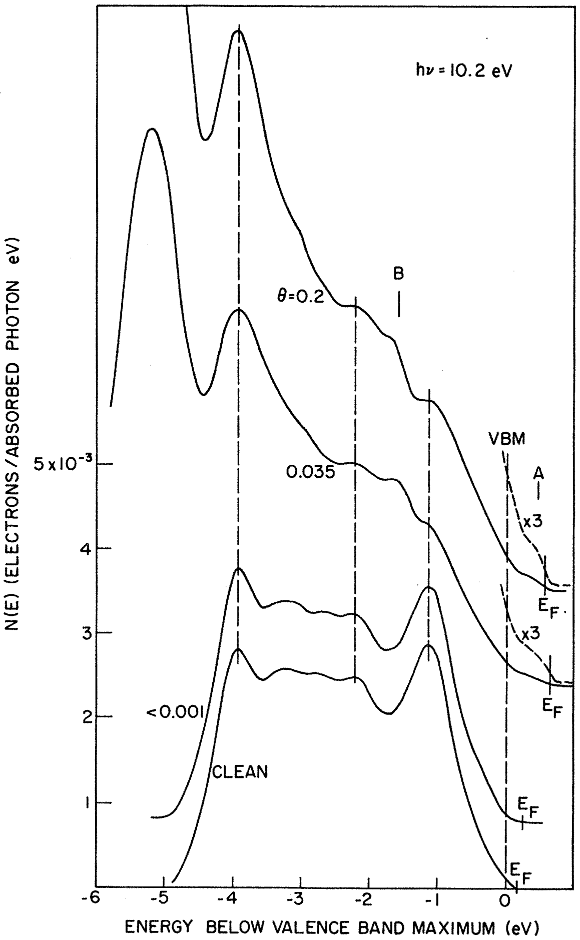


FIG. 4. EDCs for sample 19*p* at a photon energy of 10.2 eV as a function of cesium coverage, θ. *A* and *B* refer to structure not seen in EDCs from Cs covered sample 17*p*.

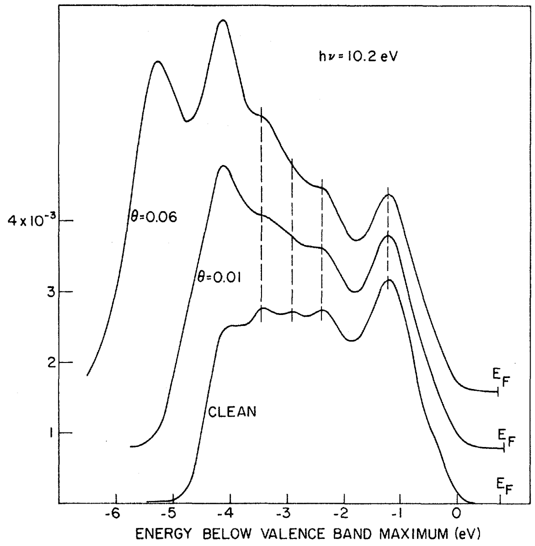


FIG. 5. EDCs for sample 18*n* at a photon energy of 10.2 eV as a function of cesium coverage θ.

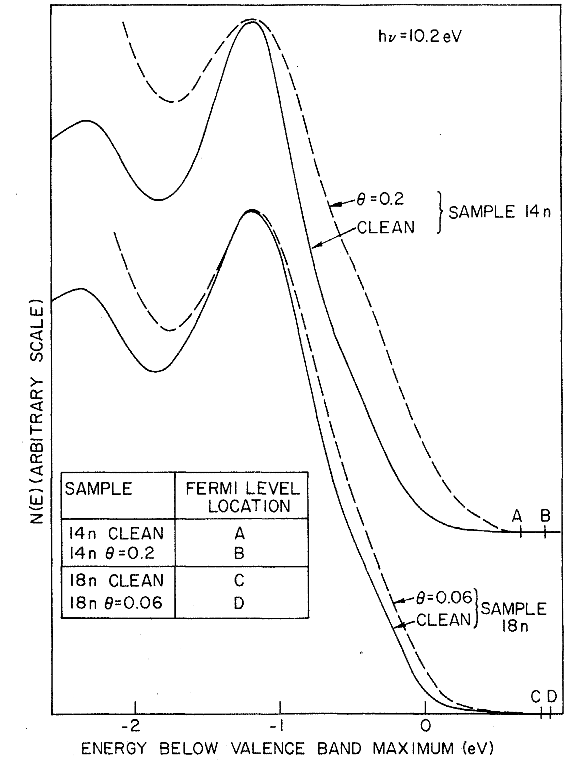
crepancy is not clear. The extra structure present in the 19*p* EDCs was visible in EDCs taken at different photon energies and was visible in the two heaviest cesiations, although the structure is less sharply defined in the heaviest cesiation. As can be seen by comparison of Figs. 1 and 3, for the heaviest Cs coverage on sample 17*p*, there is extra emission at approximately the same energy as peaks *A* and *B* in sample 19*p*, although no distinct peaks evolve. As is shown in Fig. 3, when sample 17*p* was contaminated after the last cesiation (caused by outgassing of a hot filament), this extra emission was greatly reduced. These facts lead us to believe that the extra structure in the EDCs from sample 19*p* was not caused by contamination. The origin of the extra structure, however, is not clear.

The band-bending behavior of the two *n*-type samples with Cs was different from that of the two *p*-type samples. On clean *p*-type GaAs, the bands are flat to within experimental error, while on clean *n*-type GaAs the Fermi level is pinned at about midgap, resulting in about 0.5 eV band bending for sample 14*n*, and about 0.7 eV for sample 18*n*.[15] Application of Cs to the *p*-type samples caused large changes in the Fermi-level pinning position, while it left the pinning on the *n*-type samples relatively unchanged.

Figure 5 shows EDCs for sample 18*n* clean and with Cs for hν = 10.2 eV. It can be seen that the Fermi-level position changes a small amount, less than 0.1 eV, as Cs is applied. Prior to deposition of the Cs, sample 18*n* had been exposed to 10^3 langmuir ($1 \mathrm{L} = 10^{-6}$ Torr sec) of oxygen. The O_2 produced no changes in the EDCs, and the sticking coefficient for O_2,on GaAs(110) is about 10^{-5}.[16] Thus we believe that the behavior of sample 18*n* is approximately the same as it would have been if it had not been exposed to the oxygen.

The movement of states into the forbidden gap and broadening of the first peak with Cs coverage were also seen for the two *n*-type samples and are shown in Fig. 6, where sample 14*n* is shown at the top, and 18*n* at the bottom. The amount of broadening seen on the *n*-type samples is about the same as that seen on the *p*-type samples at comparable Cs coverages. Note that for sample 14*n*, with Cs on the surface, there is a high-energy tail extending nearly to the Fermi level.

Figure 7 summarizes our data for the pinning position of the Fermi level by Cs at the surface for the four GaAs samples studied here. Two different cleaves of sample 17*p* are shown. The one having only three data points was first exposed to sodium, and as will be discussed later, the Cs exposure was made after the Na was removed. Note in Fig. 7, that the two *p*-type samples show large changes in their Fermi-level pinning position,[17] and for both samples the band bending is greater at intermediate coverages than it is for the larger coverages. The



SAMPLE	FERMI LEVEL LOCATION
14n CLEAN	A
14n θ=0.2	B
18n CLEAN	C
18n θ=0.06	D

FIG. 6. High-energy portion of EDCs at a photon energy of 10.2 eV for samples 14*n* (upper) and 18*n* (lower) showing the upward movement of states into the energy gap as Cs coverage is increased.

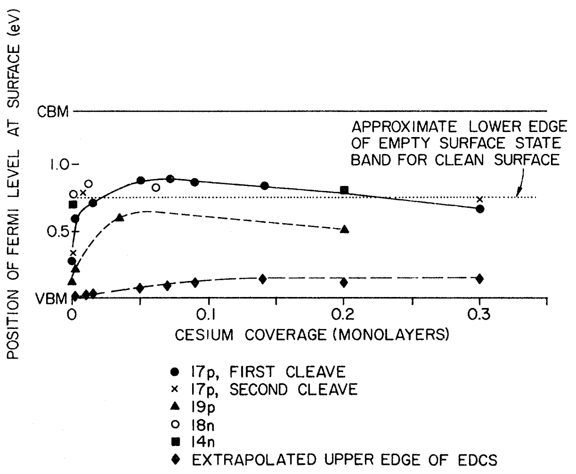


FIG. 7. Position of the Fermi level at the surface relative to the valence-band maximum (VBM) and conduction-band minimum (CBM) as a function of cesium coverage for the samples studied here. The positions of the VBM and CBM are shown for clean GaAs. The movement of states upward into the energy gap is indicated by the extrapolated upper edge of the EDCs.

limited data for the two n-type samples indicates that the pinning position on the cesium covered surface is slightly higher than on the clean surface.

The line of Fig. 7 marked VBM is the position of the valence-band maximum for the clean surface. The dotted line rising up from the VBM line is the extrapolated upper edge of the EDC, with Cs coverage. The extrapolated upper edge was determined by making a straight-line extrapolation that cuts off the high-energy tail. Thus at the higher coverages there is a considerable amount of emission above this edge, extending up to the Fermi level for the highest Cs coverages.

The application of sodium to sample 17*p* produced the rather unexpected result that although Na will stick temporarily to GaAs, under vacuum it evaporates over a period of hours. Figure 8 shows EDCs at a photon energy of 10.2 eV for Na on sample 17*p*. The bottom curve is for the clean GaAs. The top curve was taken within 15 minutes of the end of the Na deposition. The curves in between show the changes in the EDCs as the Na reevaporates. After about 3 days the Na had almost completely evaporated. Mild heating to approximately 100 °C was sufficient to remove the remaining traces of Na. This very weak binding of Na to GaAs is in contrast to the very tight binding of Cs on GaAs. Flash desorption studies[18] have shown that heating to almost 700 °C is necessary to remove all traces of Cs from the surface.

To show that the lack of band bending with the Na was not due to any peculiarities of the cleave, or due to contamination, cesium was applied to the same cleave after the Na was removed by mild heating of the sample. Subsequent application of Cs caused the bands to bend downwards in approximately the same manner as on the first cleave, to which only Cs had been applied. The band-bending behavior for the second cleave which had been exposed to Na before the Cs is shown in Fig. 7, as the points labeled "17*p* second cleave."

Figure 8 also shows another large difference in the behavior of Na on GaAs compared to that of Cs on GaAs: the Fermi-level pinning position is changed by only a slight amount at the heaviest Na coverages, and in fact, the Fermi-level pinning position is slightly lowered, rather than raised, by the Na on the surface. The Na does lower the threshold for photoemission and raise the yield, however.

In an effort to get more Na to stick to the GaAs, Na was evaporated with the GaAs held at liquid-nitrogen temperature. Immediately after evaporation, EDCs showed only a structureless scattering peak. After several hours and warming to 130 °K, an EDC with characteristic GaAs peaks was obtained. It showed a threshold about 0.5 eV lower than that of the highest curve in Fig. 8, a larger yield, and no change in Fermi-level pinning posi-

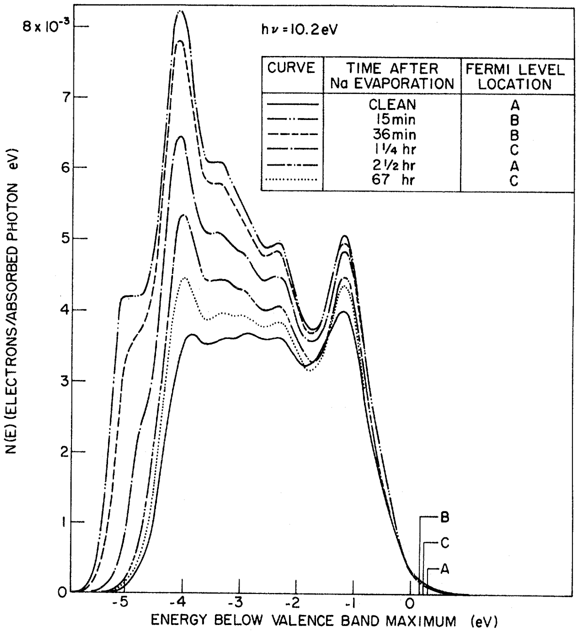


FIG. 8. EDCs for sample 17*p* showing the effect of sodium on the GaAs surface. The highest curve shows an EDC taken 15 min after the Na evaporation. The intermediate EDCs show changes with time as the Na leaves the surface, approaching the shape of the bottom EDC for the clean GaAs before Na was applied to the surface. The EDCs were taken at room temperature and at a photon energy of 10.2 eV.

tion. Further changes in the sample temperature caused only as much as ± 0.1-eV shift in the Fermi-level pinning position, but since it was not possible to separate effects due only to the cooling of the sample from effects caused by changes in the Na coverage caused by evaporation, the measurements on the cooled sample were not pursued further. Warming removed all of the Na.

There was a negligible movement of states into the forbidden gap for Na covered GaAs at room temperature, but a small measurable upward movement of states for the liquid-nitrogen cooled Na covered GaAs.

As far as we know, no data relating Na coverage on GaAs to the change in the work function are available in the literature. However, measurements of coverage versus work function for Na on sputter-cleaned Ge(111) and Si(111) have been published.[19] Although the materials, surface, and cleaning technique are different from that of this paper, and the Na did not evaporate from the Ge or Si, the values of work function change from Ref. 19 can be used to give a crude estimate of our Na coverage on GaAs. At room temperature, the greatest change in work function we saw for Na on GaAs was about 0.5 eV. From the data of Ref. 19, this would correspond to a coverage of 0.05–0.1 monolayers. For the coverage with the sample at liquid-nitrogen temperature, there was a work function drop of about 1 eV. Assuming that the larger shift is due to increased coverage and is not caused by the lower temperature, the data of Ref. 19 would correspond to a coverage of 0.2 to 0.25 monolayers.

DISCUSSION

Figure 9 shows a model for the density of surface states on the clean GaAs (110) surface, derived from photoemission measurements[15,20] and theoretical studies.[15,21] The bottom-half of the band gap is free of surface states; any filled surface states lie below the valence-band maximum. Empty acceptor-type surface states lie in the upper-half of the band gap. The approximate edge of the empty surface-state band is indicated in Fig. 7.

When the surface-state model shown in Fig. 9 is compared with the Fermi-level pinning positions for metal-GaAs Schottky barriers from previous studies,[2] an interesting problem becomes evident. Although experimental measurements of Schottky-barrier heights are usually explained in terms of pinning of the Fermi level by surface states, the pinning positions reported for most metals on 2 GaAs fall in the lower-half of the band gap, about 0.1–0.3 eV below the position we find for the lower edge of the empty surface-state band on the clean GaAs. Freeouf and Eastman[22] have found that the Schottky-barrier pinning position is well correlated with the position of the empty surface-state band for a number of III-V materials, but the Schottky-barrier pinning position for Au on these materials, determined from previous studies,[2] falls below the lower edge of the empty surface-state band. It is possible that the empty surface-state distribution seen by Freeouf and Eastman has been distorted by matrix element effects or by excitonic effects.[23] Such a distortion may sharpen and lower the measured distribution (our Fermi-level pinning measurements determine the lower edge of the distribution, as discussed below). Such effects are not likely to change the observed correlation between the position of the empty surface state band and the Schottky-barrier pinning position.

It may be asked if the lower pinning position for Schottky-barriers on GaAs could be caused by a tail of empty surface states extending below the empty surface-state edge shown in Fig. 7. Our data from the clean GaAs samples allow us to set an upper limit on the number of states in any such tail. Using the measured band bending of about 0.5 eV in the case of sample 14*n*, a calculation using the depletion approximation shows that the surface charge required to produce this band bending is about 6 $\times 10^{10}$ electrons/cm^2. This is the total number of filled surface states for sample 14*n*. Averaging the Fermi-level positions from our available EDCs at 10.2 eV for clean samples 14*n* and 18*n* shows

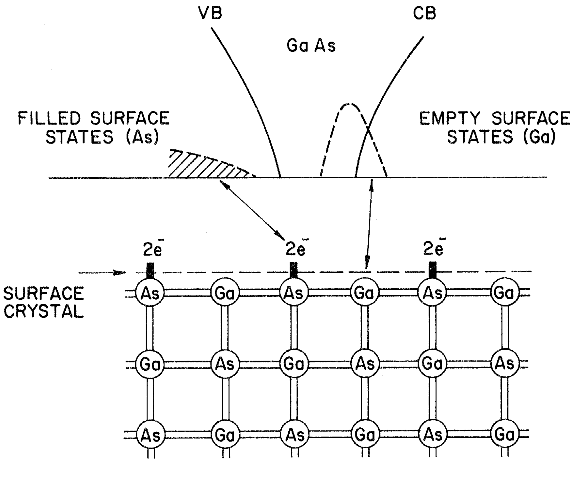


FIG. 9. Model for the clean GaAs (110) surface derived from photoemission studies and theoretical work (Refs. 15 and 20). The upper part shows the energy location of the surface states: empty surface states fill the upper-half of the energy gap, while filled surface states (which have not been detected) lie below the valence-band maximum. The lower part of the figure shows the spatial location of the surface states: the empty surface states are primarily associated with surface Ga atoms, while the filled surface states are primarily associated with surface As atoms.

that the Fermi level on sample 18*n* is about 0.02 eV higher on sample 18*n* than on 14*n*. This very small change in pinning position with a large change in doping shows that the Fermi level for sample 14*n* is at the edge of a large density of surface states. Since the thermal broadening of the Fermi function at room temperature gives a significant probability of occupation up to 0.1 eV above the Fermi level, the electrons on the surface of sample 14*n* must be mostly located above the Fermi level in the high density of empty surface states, rather than in a tail extending below the empty surface-state band. Any such tail must contain much less than 6×10^{10} states/cm^2, and it is doubtful if such a low density of states could be the cause of Fermi-level pinning in Schottky barriers.

As will be discussed below, we believe our data indicate that the empty surface-state band represents a first approximation to the Fermi-level pinning position for Schottky barriers, but the presence of the metal on the surface causes the electronic structure of the surface to be modified in such a way as to cause the actual pinning position to differ from the position of the empty surface-state band on the clean GaAs.

Figure 7 shows the pinning position of the Fermi level at the surface as a function of cesium coverage for the four GaAs samples studied. The data for Fig. 7 was measured from EDCs made at a photon energy of 10.2 eV. This photon energy was used because it is believed that at 10.2 eV the upper edge of the EDC for clean GaAs represents the valence-band maximum. Since direct transitions dominate the EDCs of GaAs,[11,24] the upper edge of the EDC does not necessarily represent emission from the valence-band maximum. However, two features of the EDCs at 10.2 eV lead one to believe that the upper edge of the EDCs at 10.2 eV does represent emission from the valence-band maximum: (a) by plotting the position of the upper edge of the EDC relative to the position of the Fermi level for clean GaAs, it is found that the upper edge is at the highest energy in the photon energy range of 10–11 eV, and (b) there is a small shoulder on the upper edge of the EDCs in a small range of photon energies around 10.2 eV which has the characteristics of a transition at Γ in the Brillouin zone, the location of the valence-band maximum in k space.[25]

The Fermi-level points in Fig. 7 were measured using the first peak in the EDCs as a reference point because the peak is sharp and easily located.[26] As can be seen in Figs. 1, 4, and 5, alignment of the first peak of the EDCs for various Cs coverages brings the other peaks into close alignment. The line marked VBM, for valence-band maximum, in Fig. 7 is taken from the extrapolated upper edge of the EDC for clean GaAs. The upper edge of the EDC for clean GaAs, measured from the first peak, comes to within 0.05 eV of the same energy for the four samples studied. States moved into the forbidden gap and the first peak broadened with cesium exposure in a similar manner on all four samples (see Figs. 3 and 6 for the broadening of sample 17*p*). The extrapolated upper edge of the EDC moves to higher energies as the Cs coverage is increased. This movement of the upper edge is also shown in Fig. 7. By extrapolating the upper edge of the EDC, the high-energy tail was cut off, so for the larger Cs coverages there is appreciable emission from above the extrapolated upper edge. This effect will be discussed more completely below.

From Fig. 7 it can be seen that the movement of the Fermi level at the surface is similar for samples 19*p* and 17*p*, but that the Fermi level remains about 0.2 eV closer to the valence-band maximum for sample 19*p* than it does for sample 17*p*. A likely explanation for the lower Fermi-level pinning position for sample 19*p* is that the heavy doping of sample 19*p* produces very sharp band bending. For both *p*-type samples the bands bend down, but for sample 19*p* the band bending length is comparable to the electron escape depth. Thus for sample 19*p* the highest-energy electrons escaping from deepest in the GaAs originate far enough below the surface that the valence band is closer to the Fermi level than it is at the surface. The depletion approximation is probably not very accurate for a sample doped as heavily as 19*p*, but it allows us to make a rough calculation to see if the above explanation is reasonable. The depletion approximation gives a total band-bending length of 50 Å for sample 19*p*, and 630 Å for sample 17*p*, assuming a band bending of 0.5 eV at the surface. Calculating the band bending 10 Å below the surface, we find a difference between the position of the valence-band maximum at the surface, and 10 Å below the surface, of 0.2 eV for sample 19*p*, and 0.02 eV for sample 17*p*. The 10 Å depth is reasonable in view of the expected electron escape depth, and the calculated 0.2 eV difference in band bending at that depth is about what is seen in Fig. 7. This simple calculation gives us confidence that the difference shown in Fig. 7, is at least partly due to the difference in band bending lengths.

It is important to learn what role the empty surface states that reside in the upper-half of the band gap on clean GaAs play in the formation of Schottky barriers. The data shown in Fig. 7 suggest that the empty surface states may play an important part in the determination of the Fermi-level pinning position, but that it is not simply a matter of filling these states with electrons from the metal.

One might be tempted to assume that the Fermi-level pinning is due to simple filling of the empty surface states and/or bulk acceptor states with electrons from the metal. However, it is easy to show that this cannot be reconciled with the existing data. For example, if this were the case the Fermi level should not drop with increasing coverage as it does (see Fig. 7) for coverage above about 0.05 monolayers. Thus it is important to realize that there may be interactions between the surface states and the metal which also play a role in determining the pinning position.

These might, for example, include some degree of mixing of surface state and metal wave functions,[3] dielectric effects,[4,5,27] or some combination of these effects. Other work suggests this also, for example, the slight dependence of the pinning position on electronegativity of the metal.[2]

Once all of this has been said, it is important to note that the final pinning position is within tenths of an eV from the bottom of the empty surface states. Thus a strong correlation exists between the pinning position and the bottom of the empty surface states, and deviations of the pinning position from this energy due to metal-surface state interactions are only on the scale of tenths of an eV.

Riach and Peria[19] studied Cs on *p*-type Ge and obtained a curve showing the position of the Fermi level at the surface that is similar to our Fig. 7, in that the Fermi level rises sharply for small coverages of Cs and then falls with larger exposures. The drop with larger exposures is much steeper and drops farther than on GaAs, however. Their explanation for their data is similar to our explanation for the Cs-GaAs data: the behavior at low coverages can be explained as the Cs acting as a donor level, but for larger coverages it is necessary to assume that the surface state distribution is changed by the presence of the Cs on the surface.

Uebbing and Bell[28] have studied Cs-GaAs Schottky barriers with about 900 Å of Cs "frozen" onto a GaAs surface at liquid-nitrogen temperature. The GaAs was cleaved and the Cs was evaporated under ultrahigh vacuum. They found a barrier height of 0.63 eV, a result which is in agreement with the Fermi-level pinning position we find here for the larger Cs coverages. When plotted versus electronegativity, the Cs-GaAs Schottky-barrier height fits the trend of the data of Mead[2] for Schottky-barrier heights from other metals on GaAs. This fact shows that Cs-GaAs Schottky barriers are similar to Schottky barriers formed with other metals. Thus any explanation of the Cs-GaAs Schottky-barrier height should apply to Schottky barriers on GaAs formed with other metals.

Scheer and VanLaar[17] have also reported the pinning of the Fermi level on GaAs caused by Cs. They based their conclusions on an interpretation of yield data. The pinning position they report (0.44 eV above the valence-band maximum) is about 0.2 eV below the position reported here. However, it is likely that in their experiment the Cs also caused the upward movement of states into the energy gap as seen in our study. In that case their measurement should be compared to the distance between the Fermi level and the extrapolated upper edge of the EDCs as shown in Fig. 7. Making that comparison, the value of Fermi-level pinning position found by Scheer and VanLaar[17] is in good agreement with the position at highest coverage reported here.

It is interesting to note that from the electronegativity of Na extrapolating the trend of the data of Mead,[2] we would expect a Na-GaAs Schottky barrier to have a pinning point 0.6 eV above the valence-band maximum. Our data, however, shows no pinning caused by Na on GaAs. We do not know of any Schottky-barrier studies made on a thick Na film on GaAs, but it would be quite surprising if Na on GaAs did not form a Schottky barrier. It is possible that if a thicker layer of Na could be applied to the GaAs that pinning of the Fermi level would occur.

It should be noted that the ionization potential of Na (5.15 eV) is considerably larger than that of Cs (3.9 eV), so that the Na is less likely to form a positive ion at the GaAs surface. If Cs forms an ionic bond with the surface and Na does not, the fact that Cs causes band bending and sticks tightly while Na does not would be explained. It appears that there may be an activation energy for transfer of an electron from the Na to GaAs.

The broadening of the first peak and high-energy tailing caused by Cs coverage, shown in Figs. 3 and 6, is probably evidence of an interaction between the Cs and the GaAs. Before discussing the possible interactions, we will first discuss several possible experimental artifacts which might be cited as a cause for the broadening, and will show that the artifacts cannot explain the observed broadening. Possible artifacts are: (a) reduction of the resolution of the energy analyzer caused by uneven deposition of Cs on the collector surface, (b) contamination of the cesiated surface, and (c) uneven deposition of Cs on the GaAs surface.

The resolution of the energy analyzer can be checked by measuring the broadening of the Fermi edge of the copper sample used to determine the position of the GaAs Fermi level. Measurement of the width of the Fermi edge of the Cu EDCs taken at a photon energy of 7.7 eV showed that for sample 17*p*, for all seven Cs coverages, the width for 10% to 90% of the edge height was 0.2 to 0.27 eV, with the sharpest Fermi edge for the 0.001 monolayer coverage, and the broadest Fermi edge for the 0.09 and 0.3 monolayer coverages. Thus any changes in analyzer resolution are much too small to account for the observed broadening of the first peak.

Contamination as a source of broadening can be ruled out. Although there may have been a small amount of contamination of the Cs film during the course of the experiment, there were no changes with time in the EDCs that could be attributed to contamination. The seventh cesiation of sample 17*p* was heavily contaminated, however, by the outgassing of a filament which had not been heated previously during the course of the cesiations. The result is shown in Fig. 3(b) as the curve for 0.3 monolayers + contamination. As can be seen in the figure, the broadening is greatly *reduced* by the contamination. Thus contamination reduced the broadening instead of causing it. Exposure of the contaminated 0.3 monolayer cesiation to 24 L of oxygen caused an additional small decrease in the broadening.

Uneven coverage of Cs on the GaAs would have two effects; a variation in work function over the surface, and a variation in band bending over the surface. A variation in work function would cause a broadening of the low-energy edge of the EDC, but not the high-energy edge. Figure 7 shows that the band bending changes by only a small amount over a wide span of Cs coverages, so that band-bending variations over the surface could not be sufficiently large to cause the observed behavior. Furthermore, one would expect that with additional Cs coverage, nonuniformities in coverage would tend to disappear. In fact, the broadening increases with coverage.

Having shown that experimental artifacts are not the cause of the broadening, it remains to decide what is the cause. The broadening was also seen by Eden[11] for Cs on GaAs on a heavily doped *p*-type sample comparable to sample 19*p*. Eden explained the broadening as being caused by emission from within the band-bending region. If electrons were excited from a range of depths within the band-bending region which corresponded to a large variation in the amount of band bending, peaks in the EDCs would be broadened. However, sample 17*p* shows the same sort of broadening as sample 19*p*, and for sample 17*p* the band-bending length, calculated from the depletion approximation, is much greater than the electron escape depth. For the bands to bend sharply enough to cause the effect seen here, there would have to be some source of band bending besides the unscreened acceptors in the depletion region.

One such source of band bending is the interaction described by Inkson.[4] He has developed a model of Schottky barriers in which the image potential associated with the metal layer causes the valence band of the semiconductor to rise, and the conduction band to drop, causing the semiconductor energy gap to shrink to zero at the interface. Although the movement of the band edge seen here is not as extreme as suggested by Inkson, it may be due to the mechanism suggested by him. The Fermi-level pinning appears to be largely caused by the empty surface state band, and the conventional depletion-region band bending seems to be present. If we add to this picture an upward band bending of the valence band, similar to that proposed by Inkson,[4] we can explain the observed data. The combined picture for the valence band bending would be a downward band bending extending from 600 Å into the GaAs for sample 17*p*, and about 50 Å for sample 19*p*, followed by a short upward band bending starting ~ 5 Å from the Cs-GaAs interface. The upward band bending would bring the tail of the valence-band edge up to the Fermi level. In this picture the peaks in the EDCs would come from electrons excited from behind the 5 Å up-bent region. Electrons excited from the sharply upbent region would contribute to the broadening and tailing of the first peak, the sharpness of the bending smearing out any structure from the last 5 Å.

While the above reasoning shows that grafting Inkson's model onto a more conventional Schottky-barrier model can explain the observed data, it is clear that more theoretical work is necessary to see if such a combination of models can, in fact, be made, and what effect the empty surface state band would have on Inkson's model.

Another possible explanation for the broadening of the first peak is emission from electrons in states caused by the presence of the Cs on the surface. This emission could have two origins: emission from metallic Cs, or emission from electron wave functions tailing into the GaAs band gap from the Cs in resonance states, such as those suggested by Heine.[3] However, the possibility of emission from metallic Cs seems unlikely to us. The broadening and tailing seen does not look at all like the sum of a GaAs EDC and a bulk Cs EDC.[29,30]

Emission from Cs resonance states seems like a possible explanation for the broadening; however, there are some possible objections to this explanation. The lack of any structure in the broadened and tailing region is one such objection. Intuitively one would feel more comfortable attributing structure in the EDC to a Cs-induced level, rather than a broadening of structure already present. Perhaps a more important objection is the fact that Heine's model was developed to account for pinning in the absence of true surface states, on the assumption that the intrinsic surface states would join onto Bloch waves in the metal and would thus be removed.[3] However, our data indicate that the empty surface state band remains in the presence of the Cs, although it may be modified somewhat by the Cs. Furthermore, Freeouf and Eastman have reported that the empty surface state band remains when several monolayers of Pd are evaporated onto the GaAs surface.[22] Apparently the empty surface states are so well localized on the surface Ga atoms that they do not strongly interact with the metal.

Whatever the detailed explanation for it, the broadening and tailing of the first peak seems to indicate some type of interaction of the Cs with the GaAs beyond simply filling the existing surface states. Comparison of Figs. 3 and 7 shows that the downward movement of the Fermi-level pinning position occurs at about the same Cs coverage as appreciable broadening of the first peak, that is, at about 0.07 monolayers. Thus both the broadening and the downward movement of the Fermi-level pinning position probably are the result of the same mechanism.

CONCLUSIONS

The use of photoemission has allowed us to study the interface between a metal and a semiconductor for metal coverages below a monolayer. For even very low Cs coverages the Fermi-level pinning and band-bending characteristic of a Schottky barrier are evident. However, as the Cs coverage is increased the Fermi-level pinning position changes in a complicated way which cannot be explained in terms of the surface state distribution present on the clean surface.

At the lowest coverages of Cs, the Fermi-level pinning behavior can be explained by assuming that the Cs gives up an electron to the GaAs, and the net positive surface charge caused by the Cs$^+$ ion causes downward band bending which is limited by the empty surface state band. At higher coverages, however, two effects are seen which cannot be explained in terms of the surface state distribution on the clean surface: the Fermi-level pinning position moves downward somewhat, and the leading peak of the EDC becomes broadened. A narrowing of the band gap caused by image forces, as proposed by Inkson,[4] seems to explain our data qualitatively if it is assumed that the narrowing occurs over a very short distance (approximately 5 Å), and if the narrowing is superimposed on conventional band bending picture in which surface states are present. Theoretical work on a model incorporating the above features would be very useful.

Other proposed interactions[3,5,27] between the Cs and GaAs may also explain the observed behavior if they can be reconciled with the presence of surface states which apparently persist in the presence of metal on the surface.

The data presented in this paper give strong evidence that pinning by intrinsic surface states is not sufficient in itself to explain the formation of Schottky barriers, and indicates that some of the features of more sophisticated models[3,4,5,27] may be present. However, much more experimental and theoretical work will be necessary to determine the complete picture.

APPENDIX

We can examine the Fermi-level movement up to the point when it starts to move back down, for sample 17*p* on the basis of a simple model of the empty surface-state band. We will base our model on a combination of our work and that of Freeouf and Eastman.[22] For the empty surface-state distribution we will take a triangular distribution starting 0.7 eV above the VBM, peaked at 0.9 eV above VBM and falling to zero again at 1.4 eV above VBM. The total number of states will take as one per surface atom (two states per surface Ga atom), or 9×10^{14} cm^{-2}. Our purpose here is to give the reader some indication of what may be happening. The details of the model should not be taken seriously.

For the first cesiation with coverage estimated below 0.001 monolayers, the surface states play no part. The observed 0.3-eV band-bending change requires a surface charge of about 7×10^{-11} carriers/cm^2, or 8×10^{-4} monolayers. If the cesium is completely ionized, this calculated value is in good agreement with the estimated coverage.

For the third cesiation, with estimated coverage of 0.05 monolayers, the Fermi level has penetrated about 0.2 eV into the empty surface-state band. Approximating the Fermi function by a step function, this would give a surface charge of about

TABLE III. Cesium coverage calculated from surface dipole model.

Cesiation	Threshold drop	Estimated coverage (monolayers)	ρ (ions/cm^2)	ρ (monolayers)	Percent of ionization of surface Cs atoms
#1	0	< 0.001	...	...	...
#2	0.4	0.015	4.42×10^{12}	0.005	33%
#3	1.1	0.05	1.22×10^{13}	0.0137	27.5%
#4	1.5	0.07	1.66×10^{13}	0.0187	26.8%
#5	1.8	0.09	1.99×10^{13}	0.0225	25%
#6	2.4	0.14	2.65×10^{13}	0.03	21%
#7	4	0.3	4.42×10^{13}	0.05	16%

2.6×10^{13} electrons/cm^2, and incidentally would put the Fermi level right at the peak of the distribution. This compares to a cesium coverage of (0.05 monolayers) $(8.85\times10^{14}\ \text{cm}^{-2}) = 4.43\times10^{13}$ Cs atoms/cm^2. Again it appears that, assuming this model, most of the Cs is ionized.

If we assume that the work-function drop is caused by a dipole caused by the Cs donating electrons to the GaAs an remaining on the surface as an ion, we can use the measured drop in threshold to get an estimate of the Cs ion density of the surface.

The formula for the potential drop in going through an infinite (in two dimensions) dipole sheet is $V = a\rho/\epsilon$, where a is the spacing, and ρ the surface charge density. If we take $a = 5$ Å and $\epsilon = 8.84\times10^{-12}$ F/m (the value of the dielectric constant for free space), we can generate Table III. Considering the many approximations and simplifications involved, the two values calculated for the surface charge density for Cs # 3, 1.22 and 2.6×10^{13} cm^{-2}, are very close.

Beyond the third cesiation the Fermi-level pinning drops. Either the empty surface-state band has become modified, or it is emptying out. As can be seen from Table III, the surface charge for the dipole to reduce the work function must continue to increase, however. Thus one cannot explain the data in terms of simple filling of existing states.

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