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Surface and interface states of GaSb: A photoemission study*

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Photoemission experiments at $h\nu < 11.8$ eV indicate that there are no filled or empty surface states in the bandgap of GaSb. Small amounts of oxygen or alkali metals pin the Fermi level (E_F) on n-type samples and move it down to near the valence band maximum, showing that Schottky barrier pinning is possible without intrinsic surface states in the band gap. When GaSb is cesiated to give maximum "white light" yield, the cesium coverage is unstable and partially desorbs. The electronic structure as seen in photoemission also appears to be different at this stage of cesiation. These and other results provide a new insight on the GaSb surface.

I. INTRODUCTION

During the last few years, numerous studies on semiconductor surfaces and interfaces have been made by many different groups. These studies led to some general agreements. One particularly important and well accepted result is the association of the filled surface states with the nonmetallic (column V) surface atoms and the empty surface states with the metallic (column III) surface atoms in the group-III-V semiconductors, with the two kinds of surface states separated in energy by a band gap of several electron volts[1] (the Gregory-Spicer-Ciraci-Harrison model). Other results, such as the pinning of the Fermi level (E_F) at midgap in GaAs by *intrinsic* empty surface states[2-5] and the apparent correlation between the bottom of the empty-surface-state band and the Schottky-barrier pinning position,[5,6] have now been rejected in light of very recent experimental evidence. In order to put the present work in better perspective, we shall briefly review the most striking recent results.

Chye *et al.*[7] showed directly for the first time that on n-type GaSb(110), where E_F is unpinned on the clean surface, it is possible to have Schottky-barrier pinning well below the conduction-band minimum (CBM). Van Laar and Scheer[8] and Huijser and Van Laar[9] have shown previously that on clean, cleaved GaAs(110) the pinning position is close to the CBM instead of at midgap as reported by others, although later on a "very irregular surface," obtained when a crystal snapped during cleaving, pinning near midgap was observed.[10] Recent measurements by Gudat *et al.*[11] indicate no unoccupied surface states in the band gap of GaAs(110). At the Stanford Synchrotron Radiation Project (SSRP), experiments show that E_F is pinned near midgap on some cleaves of GaAs while on others no pinning is present.[12] Photoelectron partial yield spectra show little change up to 10^5 langmuirs ($1L = 10^{-6}$ Torr sec) of oxygen exposure while the E_F pinning positions vary a good deal. This shows that the pinning is due to extrinsic states and that the empty surface states are located in the conduction band. Gudat and Eastman[13] also came to the same conclusion recently. Earlier, Rowe *et al.*[14] concluded that on the (111) and (100) faces of group-IV and -III-V semiconductors, extrinsic states cause the Schottky-barrier pinning, but that the (110) face is anomalous.

The above experiments demonstrate clearly that the earlier association of the Schottky-barrier pinning with the bottom of the empty intrinsic surface-state band is incorrect. One important fact to bear in mind while studying E_F pinning is that E_F may be pinned by as few as $< 10^{12}$ states/cm^2, and numerous factors (surface strain, surface defects, impurities, residual gases whose effects may be much accentuated when a hot-filament gauge is present) may produce enough states to pin E_F. Thus, one must be extremely careful in associating pinning on a cleaved surface with intrinsic surface states without further experimentation, although when no pinning is observed on either n- or p-type samples one can safely conclude that surface states are absent from the band gap. In this paper, we report photoemission work at $h\nu < 11.8$ eV on n- and p-doped GaSb(110) surfaces. The behavior of GaSb will be compared with other group-III-V semiconductors such as GaAs so that important differences in surface chemistry between these materials may be identified and their significance examined.

II. EXPERIMENTAL DETAILS

The experimental setup has been described previously.[5] The ion-pumped stainless-steel experimental chamber has an ultimate base pressure of better than 10^{-11} Torr. Preparation of clean (110) surfaces is by cleaving *in situ*. A Varian leak valve is used to make gas exposures. The research purity (99.99% pure) gases are obtained from Matheson Gas Products in glass flasks. At low exposures (10^4 L or less), a Redhead (cold cathode) gauge is used to make the exposure while at higher exposures a mTorr gauge (emission current 7 μA) is employed. The Redhead gauge has the nice feature in that no hot filament is needed. Recent experiments at[15] SSRP demonstrate that a hot-filament Bayard Alpert ultrahigh-vacuum gauge, by exciting the oxygen gas molecules, can dramatically alter the oxidation rate and, in some cases, introduce new oxidation states. It is not clear at the moment whether a hot filament alone is sufficient to excite the oxygen without the voltage applied to the gauge. These effects were found to be very pronounced for GaAs but less important for GaSb. The mTorr gauge has a hot filament, but its emission current is much smaller than that of a Bayard Alpert ultrahigh-vacuum gauge (4 mA) and, therefore, will not affect the oxidation process as much. Exact agreement between other oxidation experiments employing hot-filament gauges and the present work is therefore not expected. All of the data presented in this paper are taken without the use of a Bayard-Alpert ultrahigh-vacuum gauge.

Schottky barriers are formed by deposition of controlled amounts of alkali metal from Cs or K channels. During photoyield measurements on cesiated surfaces, the Redhead gauge is turned off since it occasionally affects the photoyield near threshold. Normal incidence light with $h\nu \leq 11.8$ eV is used, with the upper limit in photon energy determined by the cutoff of the LiF window used to isolate the good vacuum of the experimental chamber from the poor vacuum of the monochromator. Photoelectron energy distribution curves (EDCs) are measured using the ac modulated-retarding-potential method. Fresh Cu was evaporated onto the collector surface from three oxygen-free high-conductivity Cu beads inside the collector can. By substituting a metal emitter (Cu or Au) for the semiconductor, E_F locations may be determined to within ±0.1 eV.[16] Metal EDCs were taken periodically both to locate E_F and to check the collector resolution by examining the broadening of the metal Fermi edge. There is no accurate means of measuring the alkali-metal coverage, but a very rough estimate may be made from the amount of photothreshold lowering, in the following manner. There exist accurate curves of work function versus Cs coverage for[17] GaAs; by plotting a similarly shaped curve for GaSb, we can determine roughly the coverage corresponding to a particular change in threshold. We assume, as in GaAs,[18] that the coverage which maximized "white light" photoelectric yield is a third of a monolayer, with a monolayer corresponding to one alkali-metal atom for every surface atom. As we shall show later, we now have strong indication that the thickness of Cs is greater on GaSb than GaAs under this criterion. Therefore, there may be some tendency to underestimate the coverage here. Unless noted otherwise, the EDCs here are normalized according to yield.

III. RESULTS AND DISCUSSIONS

Figures 1 and 2 show, respectively, the EDCs from clean, cleaved n-type (sample 18n, Te doped, carrier concentration 1.1×10^{18} cm^{-3}) and p-type (sample 17p, undoped, carrier concentration 1.6×10^{17} cm^{-3}) GaSb. Both samples were obtained from Asarco Intermetallics Corp. These EDCs are not particularly rich in structure, and when they are presented with the valence-band maximum (VBM) aligned (as in Figs. 1 and 2) one can readily see that the structure moves with photon energy, in the same manner as structure due to the bulk direct transitions. In particular, note the region within 0.7 eV of the VBM. This region is completely devoid of structure which may be attributed to surface states. The fairly broad high-energy tail seen in the n-type GaSb EDCs is not believed to be due to emission from filled

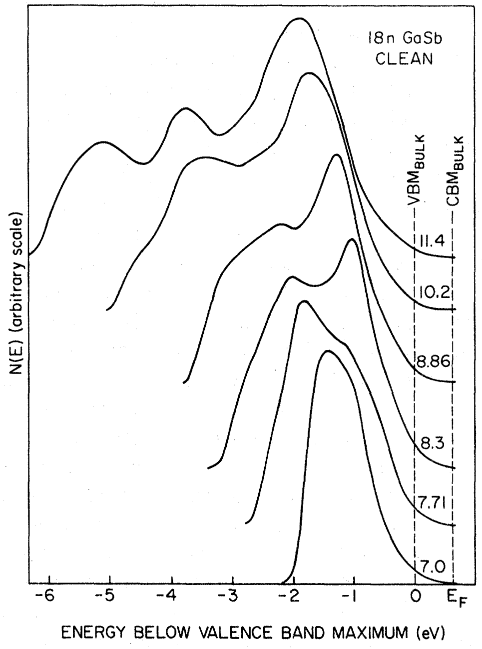

FIG. 1. EDCs of clean, cleaved n-type GaSb as a function of photon energy. Note the absence of strong emission from surface states.

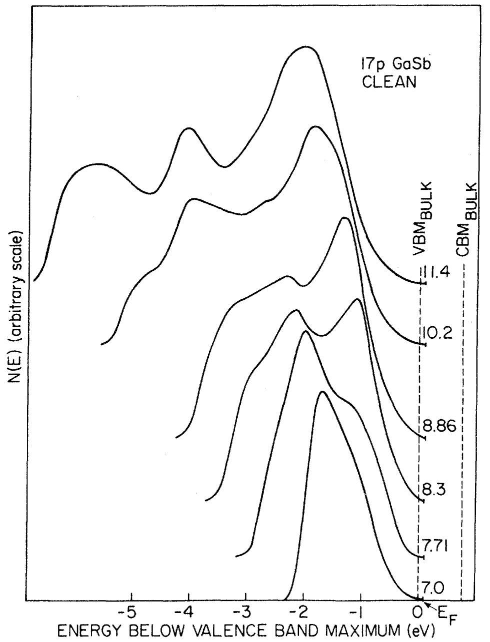

FIG. 2. EDCs of clean, cleaved p-type GaSb as a function of photon energy.

surface states and will be discussed below. This absence of filled-surface-state emission near the VBM is interesting in that a number of calculations[19–21] for GaAs have placed a narrow band of filled surface states within 0.5 eV of the VBM. Although these calculations are for GaAs(110), the qualitative features would be expected to apply to GaSb(110) as well and would have placed the filled surface states near the VBM. The present experimental results suggest that such states, if existent, form a broad band several electron volts below the VBM. The above calculations have not considered surface relaxation; however, recent detailed analysis of low-energy electron diffraction (LEED) data by Lubinsky *et al.*[22] shows that the GaAs(110) face has rearrangement within the unit mesh, even though the surface is not reconstructed (that is, the LEED pattern is 1×1). Although it has long been known from early LEED work of MacRae and Gobeli[23] that a number of III-V semiconductors including GaAs and GaSb have rearrangements within their (110) surface unit mesh despite their 1×1 LEED patterns, a successful intensity analysis of the LEED spots to reveal the type of rearrangement has not been carried out until now. A surface rearrangement can lower the surface-state band and lead to its broadening, producing the disagreement between theory and experiment.

In order to decide whether E_F is pinned or not, one needs to determine its location in energy relative to the VBM. In GaAs or InP location of the VBM is easy because the transition from the VBM—the Γ transition—is visible as a small shoulder on the leading edge of EDCs at photon energies near 10 eV. In GaSb such a transition is not visible in the $h\nu$ range used here, so other methods must be used. By aligning the structure on the EDCs of the n- and p-type crystals, the difference in energy of the E_F locations may be determined. This is shown in Fig. 3. The energy difference, 0.55 ± 0.1 eV, is close to the band gap, suggesting strongly that E_F is close to the bulk position on both type samples. A second method is the following: the back edge of an EDC represents the vacuum level cutoff; the difference in energy between this and E_F, subtracted from the photon energy, yields the work function ϕ which is the difference in energy between the vacuum level and E_F. Photoelectric threshold measurements give one the energy difference between the vacuum level and the VBM. For these two values (ϕ and threshold energy) E_F may be located relative to the VBM. This method is not very accurate due to errors in determining the vacuum cutoff, the photoemission threshold energy, and E_F. Application of this method indicates, however, that E_F is at the bulk positions on both n- and p-type samples. Moreover, as reported below, E_F on n-type samples moves down towards the VBM by nearly the full band gap upon absorption of oxygen or alkali metals, which indicates that

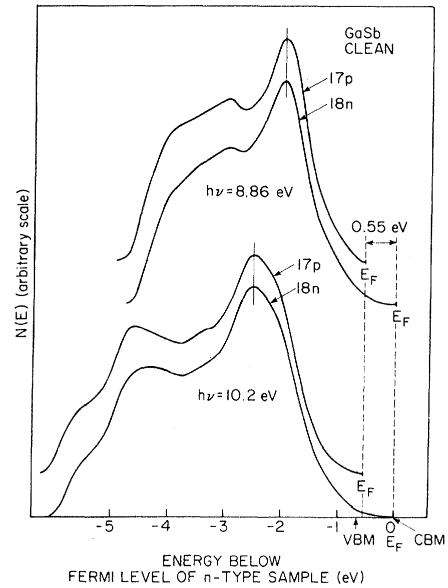

FIG. 3. EDCs of clean, cleaved n- and p-type GaSb at two photon energies. By aligning the structure in the EDCs, the energy difference between the Fermi levels may be determined. This energy difference is almost the full band gap (0.67 eV).

it is at or very close to the bulk position immediately after cleaving. Thus, the bandgap is free of pinning states, intrinsic or extrinsic. Recent work by Huijser *et al.*[10] also confirms that E_F is unpinned on *n*-type GaSb.

Previously, Eastman and Freeouf[5] have found E_F to be below midgap on *n*-type GaSb. Viljoen *et al.*[24] have found that E_F varied by 0.6 eV across the surface of cleaved *n*-type GaSb, and after several days in vacuum E_F stabilized near the VBM. It is appropriate to point out here that the high-energy "tail" of the EDCs from *n*-type GaSb presented in Fig. 1 may be due to emission from a small fraction of the surface where E_F is pinned. That is, since E_F is constant throughout the crystal, in regions where E_F is pinned the valence band emission will be at higher energy than emission from unpinned regions. It also may be due to the imperfect analyzer resolution.

A. Adsorption of oxygen

The behavior of *n*- and *p*-type GaSb under oxidation is shown in Figs. 4 and 5. There is an absence of oxygen-sensitive structure in the EDCs, supporting the earlier observation that filled surface states with a sharp density of states seem to be absent, particularly near the VBM. The *p*-type sample oxidizes faster than the *n* type. The reason for this behavior is not understood. A very striking phenomenon is the movement of E_F with oxidation. By aligning the structure in the EDCs, as in Figs. 4 and 5, the E_F movement may be determined, and this is shown in Fig. 6. A very small amount of O_2 (10 L) produces a shift in E_F and by 10^5 L, E_F has moved through the band gap and lies at approximately 0.1 eV above the VBM. With further oxidation, a small (0.1 eV) upward movement of E_F is seen. Deposition of Cs and K caused the same downward movement of E_F to 0.1 eV above the VBM, but no upward movement was seen. These results will be presented later.

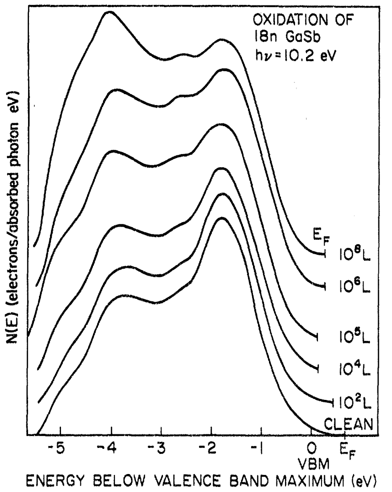

FIG. 4. EDCs of *n*-type GaSb at $h\nu = 10.2$ eV as a function of oxygen exposure. Note the large downward movement of E_F with oxidation.

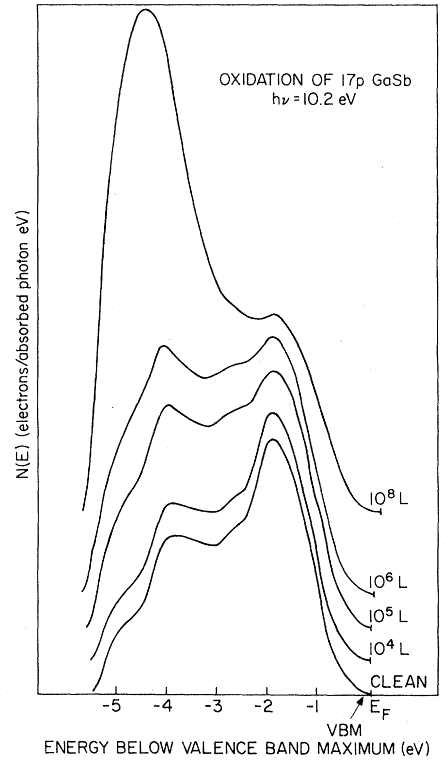

FIG. 5. EDCs of *p*-type GaSb at $h\nu = 10.2$ eV as a function of oxygen exposure.

The *p*-type sample exhibits a stable E_F up to 10^5 L O_2; then E_F starts moving upward in energy and at 10^8 L O_2 has risen by nearly 0.15 eV. The final pinning position appears to approach that of the *n* type, as might be expected. It is interesting to note that at around 10^5 L exposure the electron affinity—obtained from the width of the EDC—decreases, suggesting a long-range interaction

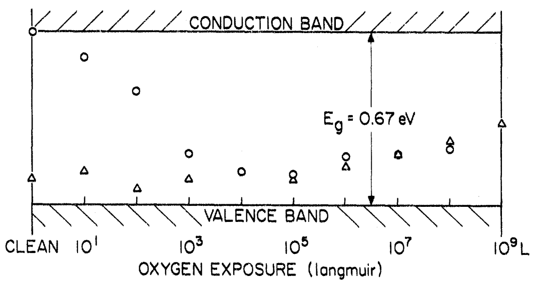

FIG. 6. Positions of the surface Fermi level as a function of oxygen exposure.

with the oxygen going beneath the surface as oxygen ions sitting on the surface would provide a negative dipole and thus increase, rather than decrease, the electron affinity.

The results obtained here on GaSb are different from earlier results on GaAs obtained by Gregory and Spicer[25] using the same equipment. They observed a pinning of E_F at midgap on all n-type samples, and this pinning remains with oxidation. E_F is unpinned on p-type GaAs and oxygen up to 10^5 L does not affect E_F, but with further oxidation E_F moves upward towards midgap. It should be noted that the quality of cleave, that is, the roughness of the surface, may affect the location of E_F. For example, Gregory and Spicer's[25] results are different from recent results of Spicer *et al.*[12] at SSRP using different equipment and smaller samples.

Spicer *et al.*[12] and Pianetta *et al.*[15] concluded from studies of the chemical shifts of core levels in GaAs and GaSb upon exposure to both "nonexcited" and "excited" oxygen that on GaAs the oxygen binds only to the As even at 10^{12}-L exposure unless the oxygen is "excited" by a hot-filament gauge, in which case it is able to break Ga = As bonds and bond with the Ga atoms. However, even "nonexcited" oxygen is able to break Ga = Sb bonds and the "excited" oxygen merely increases the oxidation rate of GaSb. Since they reproduced these results on numerous cleaves of varying quality, it is unlikely that surface "steps" or roughness is responsible for this difference, and the dissimilarity between the GaAs and the GaSb surfaces is apparently real.

The role of Ga during the initial stage of oxidation is still controversial, however. Ludeke and Koma[26] concluded from energy-loss experiments on (100) surfaces of GaAs that oxygen initially bonds on to the Ga atoms. This controversy will be discussed in detail in a future paper.

It is interesting to consider what the pinning mechanism is on n-type GaSb during the adsorption of oxygen or alkali metals. Since 10^{12} states/cm^2 is sufficient to pin E_F, a strong possibility is the pinning by extrinsic states. A second possibility is pinning by relaxed intrinsic empty surface states. If small amounts of adsorbed foreign atoms can cause rotation of surface atoms as in GaAs,[22,27] the empty surface states (Ga) may be lowered in energy to pin E_F, and the pinning position will not be strongly dependent on the adsorbed species. However, when foreign atoms start bonding on to the Ga atoms to form extrinsic states, the pinning position is expected to depend on the adsorbed species. In the adsorption of oxygen, an upward movement of E_F is observed around 10^5 L on both n- and p-type samples, and the final pinning position of the n-type sample at very large exposures approaches that on the p type. No such upward movement is observed with alkali-metal adsorption. These results, of course, merely suggest rather than prove conclusively that surface relaxation provides the initial pinning of E_F with adsorption. More research has to be conducted to show which, or neither, of the above two possibilities is correct.

B. Adsorption of CO

A quite welcome property of the cleaved GaSb surface is its extreme insensitivity to CO, since CO is a common contaminant in ultrahigh-vacuum systems. From Fig. 7, one can see that 10^9 L of CO is necessary to bring about a change in the EDCs. The maximum exposure during a typical ultrahigh-vacuum experiment is 10 L. This change is time stable. E_F is stable to within 0.05 eV up to 10^7-L exposure; then at 10^9-L exposure, it moves upward in energy by about 0.2 eV. The electron affinity, estimated from the EDC width, remains almost constant with small differences which are probably due to the increased uniformity of the collector can work function with gas adsorption.

C. Alkali-metal Schottky barriers

The behavior of cesiated n-type GaSb is shown in Fig. 8. The EDCs are plotted with the leading peaks aligned, except for the $\theta = 0.3$ EDC, so that the large movement of E_F downward with increas-

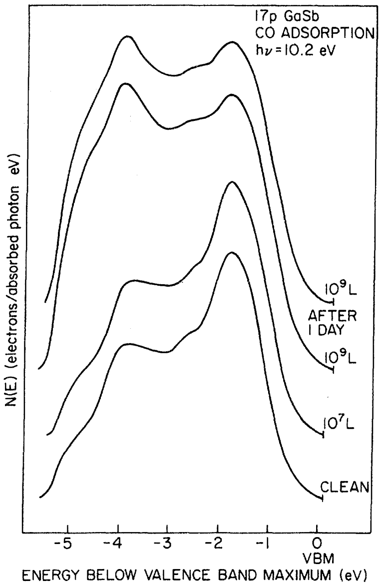

FIG. 7. EDCs of p-type CaSb at $h\nu = 10.2$ eV as a function of CO exposure and time.

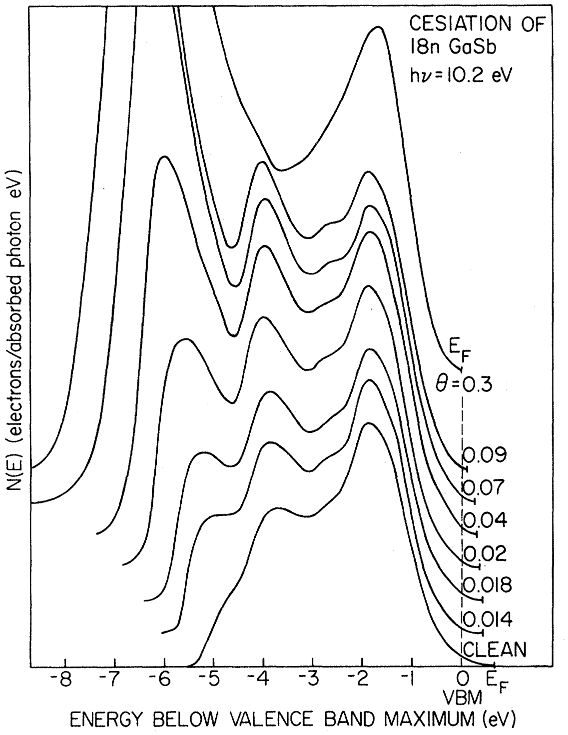

FIG. 8. EDCs of n-type GaSb at $h\nu = 10.2$ eV as a function of cesium exposure. The curves are labeled with the cesium coverage θ in fractions of a monolayer.

ing Cs coverage can be clearly seen. For reasons to be discussed later, the $\theta = 0.3$ EDC is plotted with E_F arbitrarily aligned with the VBM. This movement was reproduced on a second cesiated cleave. Figure 9 shows the E_F movement with Cs deposition. The high-energy portions of some EDCs in Fig. 8 are shown in Fig. 10 with the leading peaks aligned. The leading edge shows little upward movement in energy even at a Cs coverage of 0.09. At this coverage on GaAs and InP,[6] large upward movements were seen. (The reader is reminded that the coverages here tend to be underestimated.) At higher coverage ($\theta = 0.17$) on a second cleave, a small upward movement of the leading edge was observed. However, the resolution for that particular run was very poor at higher coverages, as evidenced by a very broad Fermi edge on the Cu EDCs, so it is not clear whether that data should be taken seriously. In any case, the upward movement of the valence-band edge in GaSb is smaller than those observed in GaAs and InP at comparable coverages.

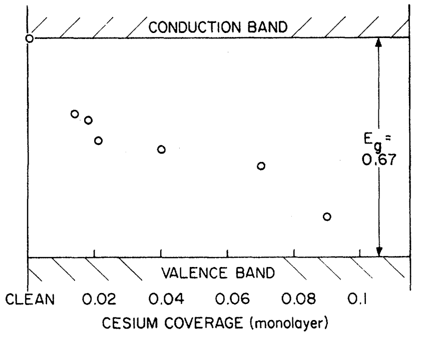

FIG. 9. Position of the surface Fermi level as a function of cesium coverage.

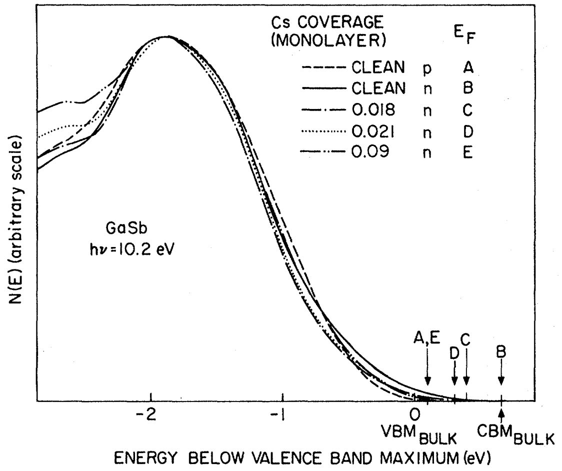

FIG. 10. High-energy portions of some EDCs of cesiated GaSb at $h\nu = 10.2$ eV.

When GaSb is cesiated to maximize "white light" yield ($\theta = 0.3$), the leading peak in the EDC changes shape, as can be seen in Fig. 8. The leading edge shows a sharper rise, and most of the structure in the EDC is gone. This is also seen on a second cleave. However, on GaAs, the structure remains at this coverage. The leading edge is believed to be different in nature from the leading peaks in the EDCs at lower coverages, both because of the steeper leading edge and because if one aligns this peak with the peaks at lower coverages, then E_F falls about 0.2 eV below the VBM. This is why this particular EDC is plotted with E_F aligned with the VBM in Fig. 8. The other interesting thing about optimally cesiated GaSb is that the Cs is unstable and some leaves the surface almost immediately when Cs deposition is terminated. This has also been observed by others.[28] When the optimally cesiated surface is oxidized with 30 L O_2, Cs-oxide-like structure appears immediately in the EDCs, for both n- and p-type samples. This is shown in Fig. 11. The origin on the horizontal axis is placed arbitrarily as E_F could not be determined. Gregory and Spicer[29] did not observe similar structure on GaAs until after 19 cycles of cesiation followed by oxidation.

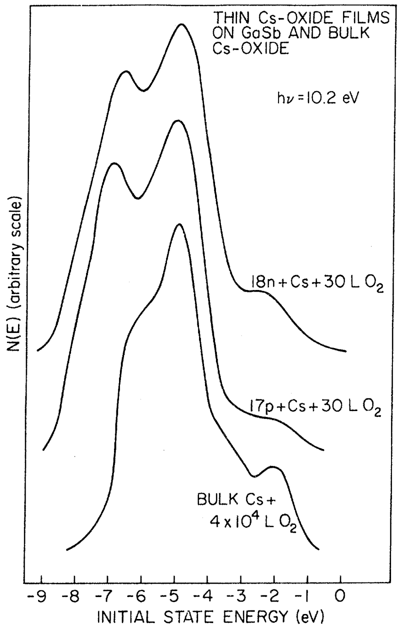

FIG. 11. EDCs of thin Cs-oxide on GaSb and bulk Cs-oxide.

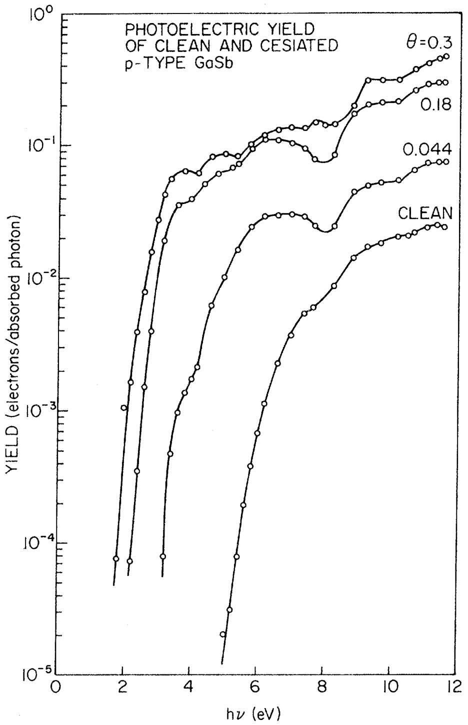

FIG. 12. Photoelectric spectral yield curves for *p*-type GaSb as a function of cesium coverage θ.

There is a lot of similarity between the *n*- and *p*-type EDCs. Exact resemblance is not expected between the Cs oxide on GaSb and the oxidized bulk Cs because of the many possible types of Cs oxides which are fairly sensitive to the proportions of Cs and O_2 present during preparation. Gregory *et al.*[30] studied the oxidation of thick, "frozen on" Cs films at temperatures below −100 °C. They found a large number of different EDCs as the oxide compositions were changed, corresponding to different mixtures of the different compounds. The Cs-oxide film on the GaSb is much thinner and is prepared at room temperature. It is, therefore, not surprising that EDCs taken from bulk Cs-oxide at low temperatures at discrete stages of oxidation do not match up exactly with the EDCs from much thinner Cs-oxide on GaSb at room temperature. A bulk Cs-oxide EDC from Gregory *et al.*[30] that is close in appearance to EDCs of Cs-oxide on GaSb is presented in the same figure.

The above data then suggest strongly that the optimal Cs coverage on GaSb is thicker than on GaAs. The interaction between the metal and the semiconductor is also not as strong, as some Cs leaves the surface and the leading edges of the EDCs do not show as large an upward movement at the same coverage. It is also demonstrated directly that Schottky barrier pinning is not produced by intrinsic surface states characteristic of the clean surface on a III-V material, as the Cs-Schottky-barrier pinning position is much below the bottom of the empty-surface-state band. Rather, this is due to extrinsic states induced by the metal. Earlier theories associating the Schottky-barrier pinning with the bottom of the empty-surface-state band now clearly need modification.

The photoelectric yield curves of clean and cesiated *p*-type GaSb is shown in Fig. 12. The region near 8 eV is interesting in that a peak is seen at $\theta = 0.3$ where there are valleys at lower coverages. The estimated threshold for photoemission of optimally cesiated *p*-GaSb is 1.6 ± 0.1 eV.

Deposition of K produced the same qualitative results as deposition of Cs. From Fig. 13, where the high-energy positions of EDCs from K-covered *n*-type GaSb is shown, it can be seen that E_F moves downward through the bandgap with increasing K coverage. A small movement upward in energy of the leading edge of the EDCs is also seen at higher coverages, and the final Schottky-barrier pinning position is about the same as the Cs-Schottky-barrier pinning position.

From these data, it is apparent that the surface chemistry of GaSb is very different from the most widely studied III-V semiconductor, GaAs. We shall conclude this section with a brief comparison of these two semiconductors. The most striking

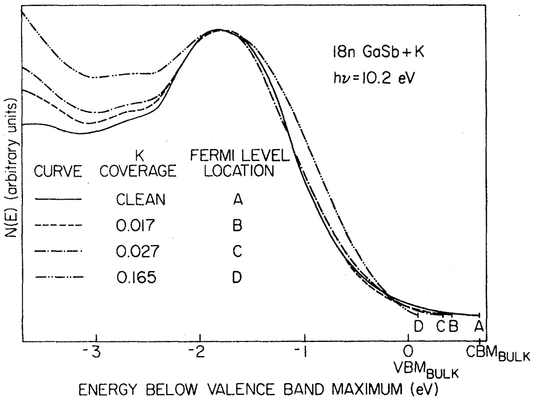

FIG. 13. High-energy portions of some EDCs of K-covered GaSb at $h\nu = 10.2$ eV. Note the downward movement of E_F.

difference is their behavior under oxidation. Oxygen is able to break bonds and combine with the Ga atoms on GaSb; excited oxygen is required to do this in GaAs. This may be because the cohesive energy of GaSb is much lower than that of GaAs. Neither semiconductor is very reactive with CO; however, CO will stick permanently on GaSb after very high exposures while it desorbs from GaAs within a matter of minutes.[26] When both samples are cesiated to give optimal photoelectric yield, the Cs will stick on GaAs,[29] while it is unstable on GaSb. The cesium layer also appears to be thicker on GaSb, when both have been cesiated to give optimal yield. At this Cs coverage, the EDCs of GaAs,[29] and InP,[31] show a large upward movement in energy of the leading (high energy) edge while the leading edge of the EDCs of GaSb is quite different, as discussed above. One cycle of Cs-O_2 treatment is sufficient to yield bulk Cs-oxide-like structure in the EDCs of GaSb while numerous cycles are necessary to produce the same structure on GaAs. These differences demonstrate the importance of studying each individual semiconductor carefully as each may have certain properties that depart from the general trend.

IV. CONCLUSIONS

Careful studies of *n*- and *p*-type GaSb show that E_F is unpinned on the clean (110) surface. Thus, the surface state density within the bandgap must be less than about $10^{12}/\text{cm}^2$. There is no obvious structure in the EDCs of the clean, cleaved surface which may be attributed to emission from filled surface states. Thus, there is no filled-surface-state structure strong enough to be seen against the background of bulk emission[15,32] (note that such structure is easily seen in Si). At certain photon energies, e.g., 7 and 11.4 eV, there is little emission from within about 1 eV below the VBM; thus, there is little possibility of appreciable filled-surface-state resonances lying in this region. This does not rule out the existence of a broad band of filled surface states several electron volts below the VBM. The lack of surface-state structure near the band edge is probably due to strong rearrangements of the atoms within the unit mesh as is the case with GaAs.

With oxidation, E_F on *n*-type GaSb moves downward through almost the entire band gap with exposures of about 10^4 L (oxygen coverages of much less than 1%); then at exposures $> 10^5$ L it shows a small upward movement of about 0.1 eV. On *p*-type GaSb, E_F begins to move upward from the bulk position near the VBM at exposures $> 10^5$ L O_2 (approximately 1% coverage) and approaches the pinning position of the *n*-type sample at large exposures. Cs and K pin E_F at about 0.1 eV above the VBM at fractions of a monolayer coverage and form thicker layers on GaSb than on GaAs or InP when optimal photoelectric yield is reached. This thicker layer is unstable and partially desorbs with time after the Cs vapor was removed. Other evidence that GaSb interacts less strongly with Cs than GaAs or InP is the upward movement of the leading edge of the EDCs with increasing Cs coverage which is less pronounced in GaSb than the other materials and is only seen at heavy coverages.

This study of the Cs-GaSb and K-GaSb Schottky barriers demonstrate directly that Schottky-barrier pinning is possible when E_F is unpinned on the clean, cleaved surface, and that the pinning here is due to extrinsic states induced by the metal overlayer. Previous conclusions[5,6] correlating the bottom of the empty-intrinsic-surface-state band and the Schottky-barrier pinning position have to be modified.

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