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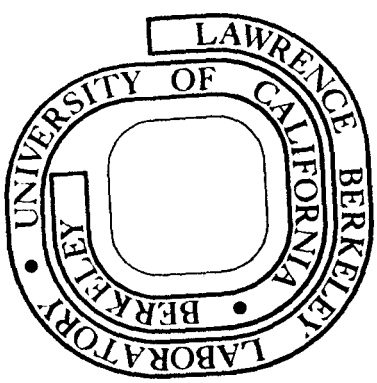

DISCLAIMER

ELECTRONIC STRUCTURE IN GaAs/Ge THROUGH ANGLE-RESOLVED PHOTOEMISSION

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ABSTRACT

We present preliminary results of experiments detailing the changes in the valence band electronic structure of GaAs upon the submonolayer evaporative deposition of Ge. Measurements for electron wavevectors along the $\bar{\Gamma}\bar{X}$ and $\bar{\Gamma}\bar{X}'$ directions in the surface Brillouin Zone show a loss of photocurrent from states in the valence band edge and the growth of sharp features. These features are found: near but within the calculated valence band edge (∿1.4 eV, $\bar{\Gamma}\bar{X}$ direction; ∿1.2 eV, $\bar{\Gamma}\bar{X}'$); midband (∿3.2 eV, $\bar{\Gamma}\bar{X}$; ∿4.2 eV, $\bar{\Gamma}\bar{X}'$); in and near the projected gap (∿4.1 eV, $\bar{\Gamma}\bar{X}$; ∿2.5 eV, $\bar{\Gamma}\bar{X}'$); and in the ionic gap (∿7.1 eV). In addition, a new deeply bound (13 eV) GaAs surface state is observed.

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The nature of the electronic structure of metal-semiconductor and semiconductor-semiconductor interfaces, and the process by which very thin films evolve toward the limit of two bulk materials joined at an interface, are of considerable scientific and technological interest. It has only been in the last few years, however, that microscopically sensitive techniques, such as angle-integrated photoemission,[1,2] partial yield spectroscopy,[3] and electron energy-loss spectroscopy[4] have been utilized for studying the growth of metal films on semiconductors. Until now, these studies have been concerned primarily with the elucidation of general interface electronic properties such as band discontinuities.

Recently, we have found that angle-resolved photoemission (ARP) is a useful technique for studying discontinuities in semiconductor-semiconductor heterojunctions.[5] We present here preliminary results of experiments which show that ARP may be used to more fully elucidate the detailed evolution of electronic structure in the initial stages of interface formation. In particular, we have found a number of features, some of which correspond to recent calculations of interface states.[6] These features follow regular trends as successively greater amounts of Ge are deposited.

The experimental apparatus has been described elsewhere.[5,7] ARP spectra were taken at 21.2 eV (He I) photon energy for an n-type GaAs(110) single crystal cleaved in situ, using a CMA with an energy resolution of 0.07 eV; the sample orientation

was fixed, following cleavage along the $\bar{\Gamma}\bar{X}'$ direction, by laser autocollimation. Successive layers of Ge were produced by evaporative deposition with the substrate held at the epitaxial growth temperature[8] of 350°C. Coverage was determined by calibrating the oven with a piezoelectric thickness monitor, with one monolayer defined[1] as 8.85×10^{14} atoms/cm^2; the base pressure in the chamber was 2×10^{-10} torr. Spectra were taken as a function of θ, the polar angle from the surface normal, for azimuths corresponding to electron wavevectors along $\bar{\Gamma}\bar{X}$ ($\phi = 0°$) and $\bar{\Gamma}\bar{X}'$ ($\phi = 90°$) in the surface Brillouin Zone (SBZ); the geometry is summarized in Fig. 1.

A detailed analysis of GaAs photoemission will be published elsewhere,[9] and we shall comment on it only briefly here, as a basis for discussing the interface states. Most of the structure is associated with bulk transitions. At normal emission, all the peaks may be accounted for by the use of existing band structures[10,11] and a direct transition model, except for the peak at ca. 13 eV. This latter feature, which is almost dispersionless with θ, was found to be cleavage-dependent, and was observed to disappear for heavy Ge coverage. It occurs in a bulk band gap for GaAs. Accordingly, we attribute it to a new, deeply bound surface state in GaAs. No such state has been predicted for $\bar{\Gamma}\bar{X}$, although Chadi[12] has predicted a state at ca. 11.2 eV between $\bar{M}$ and $\bar{X}$, and recent self-consistent calculations[13] show a surface resonance not yet split off the bulk bands at 11.5 eV.

Spectra are presented in Fig. 2 for a series of evaporations corresponding to submonolayer coverages of Ge. Here, the electrons are emitted with the parallel component of their wavevector ($k_{\parallel}$) oriented along the $\bar{\Gamma}\bar{X}$ line in the SBZ. The primary features are labelled one through four. Several phenomena are observed upon overlayer formation. The gap between the surface state 1 at 1.1 eV and the bulk peak 2 at 2.3 eV is seen to fill in; in addition, there is an apparent broadening of the latter feature and the peak 4 at 6.4 eV for evaporation 1 (E1). Apparent broadening in peak 2 also occurs, but has decreased by E2, as has that for peak 4 by E3.

These features are admittedly subtle. To better explicate them, we have calculated difference spectra, presented in Figs. 3 and 4, for the various evaporations relative to the clean substrate. These spectra clearly show a loss in strength for the most weakly bound states. Such behavior is frequently observed in ARP spectra of adsorbate-substrate systems, and is attributable to a transfer of intensity toward higher binding energy. In addition, several generally sharp features appear; they are summarized in Fig. 5. The features are found to fit one of two cases for the location of at least some of their associated (E_B, $k_{\parallel}$) paired values: (1) in a region which is calculated to be forbidden to itinerant (bulk-like) states, or (2) within or at the edge of a region in which itinerant states are allowed. The first case is necessary for the formation of a truly localized state, while the second is typical

for the occurrence of resonances.[14] In the present experiment, all features falling above 7 eV are found to persist in the region of itinerant states, regardless of whether they can be found in gaps or not. For case (1), this is shown by features C for the $\bar{\Gamma}\bar{X}$ azimuth and E, F, and G for the $\bar{\Gamma}\bar{X}'$ azimuth, all of which penetrate from a gap into the bulk-forbidden region. The features D and H are noteworthy in that they fall in the ionic gap of GaAs. The effect on the surface of the Ge deposition, in the limit of a thick overlayer, will be to partially close the gap at $\bar{X}'$, and completely close it at $\bar{X}$. This will prevent the formation of localized states, and it is therefore consistent that D (and to a degree H) is strongly damped for greater depositions; in fact, feature D has disappeared by evaporation 3. All other features are persistent, and in particular the feature C agrees with the prediction of a "Ge-As bond" state (B_1) by Pickett, et al.[6] at 3.64 eV. The feature F can correspond to either B_1 or P_1 of the above calculations, while feature E might be a resonant precursor of B_2 or P_2. Feature G does not correspond closely to any predicted states.

Features corresponding to the second case are peaks A and B for the $\bar{\Gamma}\bar{X}$ azimuth. The feature B is found at mid-band and is of uncertain origin. The nature of the feature A, on the other hand, strongly suggests that it too is a resonant precursor for the interface state B_2, analogous to feature E. One can trace the center of gravity of features A and E

through the successive evaporations (Fig. 6). In fact, evolution is found toward the main gap, with the trend being stronger for the E state.

In conclusion, these preliminary results have shown that ARP is capable of making effective measurements of the electronic structure of heterojunctions in the initial stages of interface formation. We have further found correspondence with the main features of available calculations.[6] It is apparent that the spectral evolution warrants further investigation at the supermonolayer level.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1. Experimental geometry and surface Brillouin Zone for GaAs.

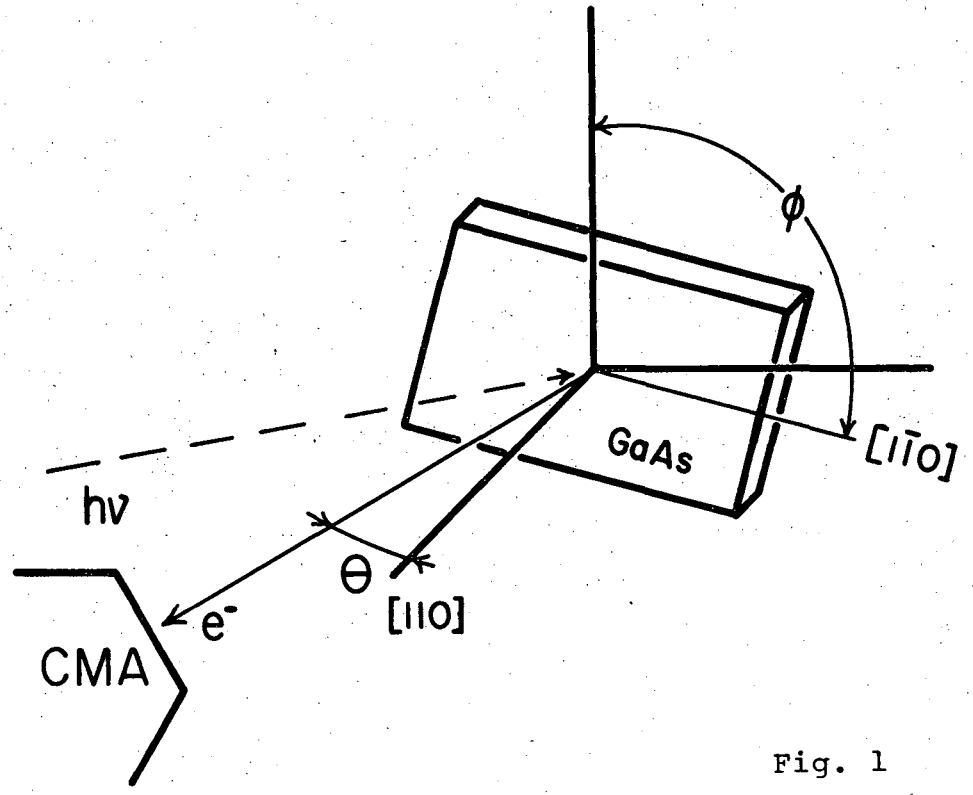
Figure 2. Selected spectra for $k_{\parallel}$ along $\bar{\Gamma}\bar{X}$ as a function of Ge coverage. Binding energies are referred to the valence band maximum at Γ.

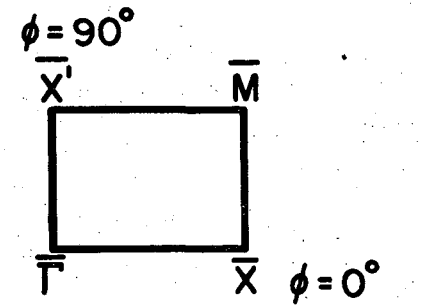
Figure 3. Selected difference spectra for the $\bar{\Gamma}\bar{X}$ direction in the SBZ.

Figure 4. Selected difference spectra for the $\bar{\Gamma}\bar{X}'$ direction in the SBZ.

Figure 5. Observed ARP features and projected surface band structure for GaAs/Ge (after Ref. 6). Cross-hatched areas are GaAs bulk-forbidden regions. Interface states are labelled with the notation of Pickett, et al., and the features in Figs. 3 and 4 are labelled as A through H. Peaks are plotted from data for all evaporations, but not all data is shown; in some cases, peak positions were identical for successive evaporations.

Figure 6. Binding energy shift for peaks A and E as a function of Ge coverage. Each point represents the mean value of the set of points common to these features for each evaporation.





Surface Brillouin Zone

Fig. 1

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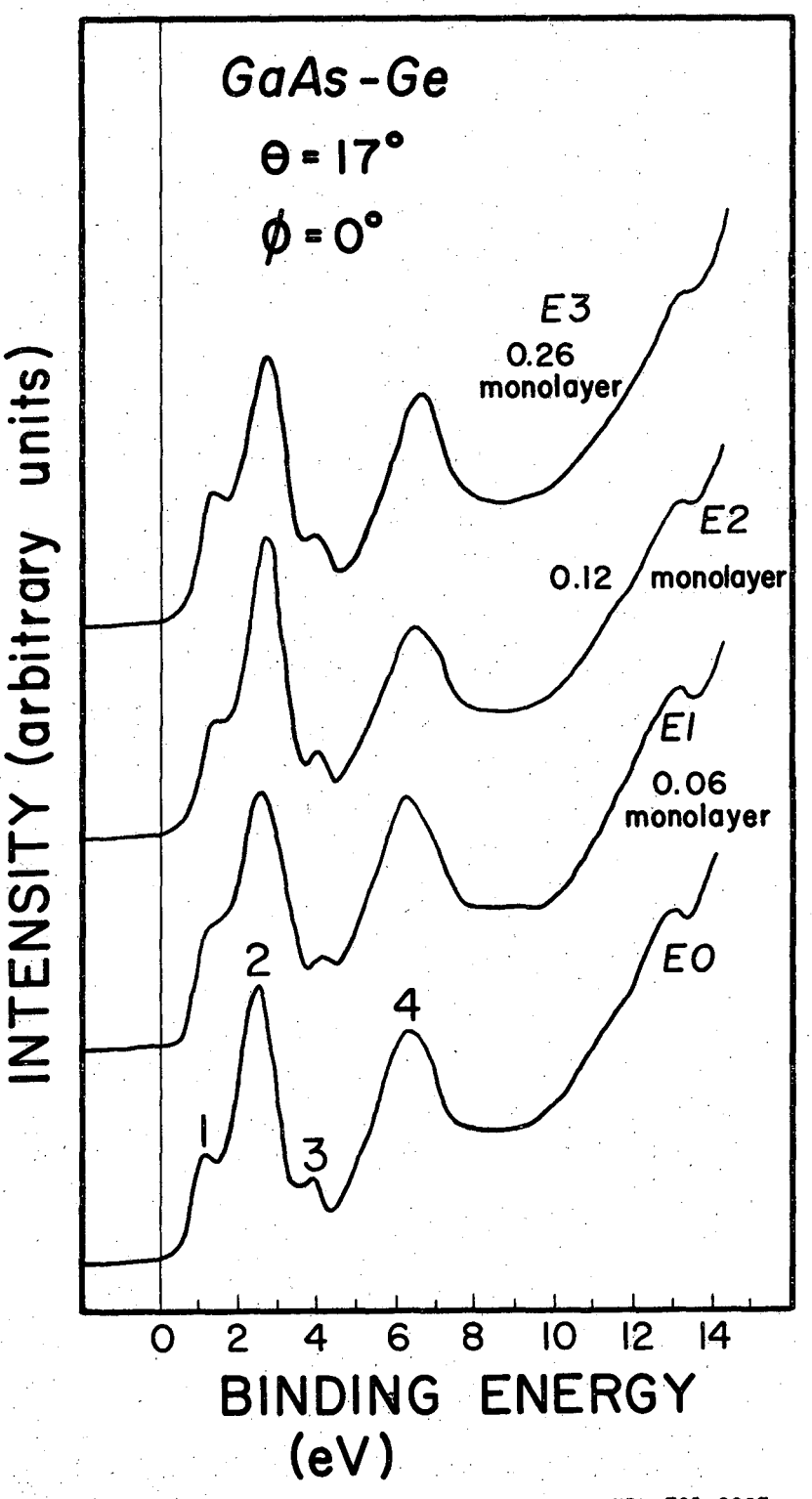

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Fig. 2

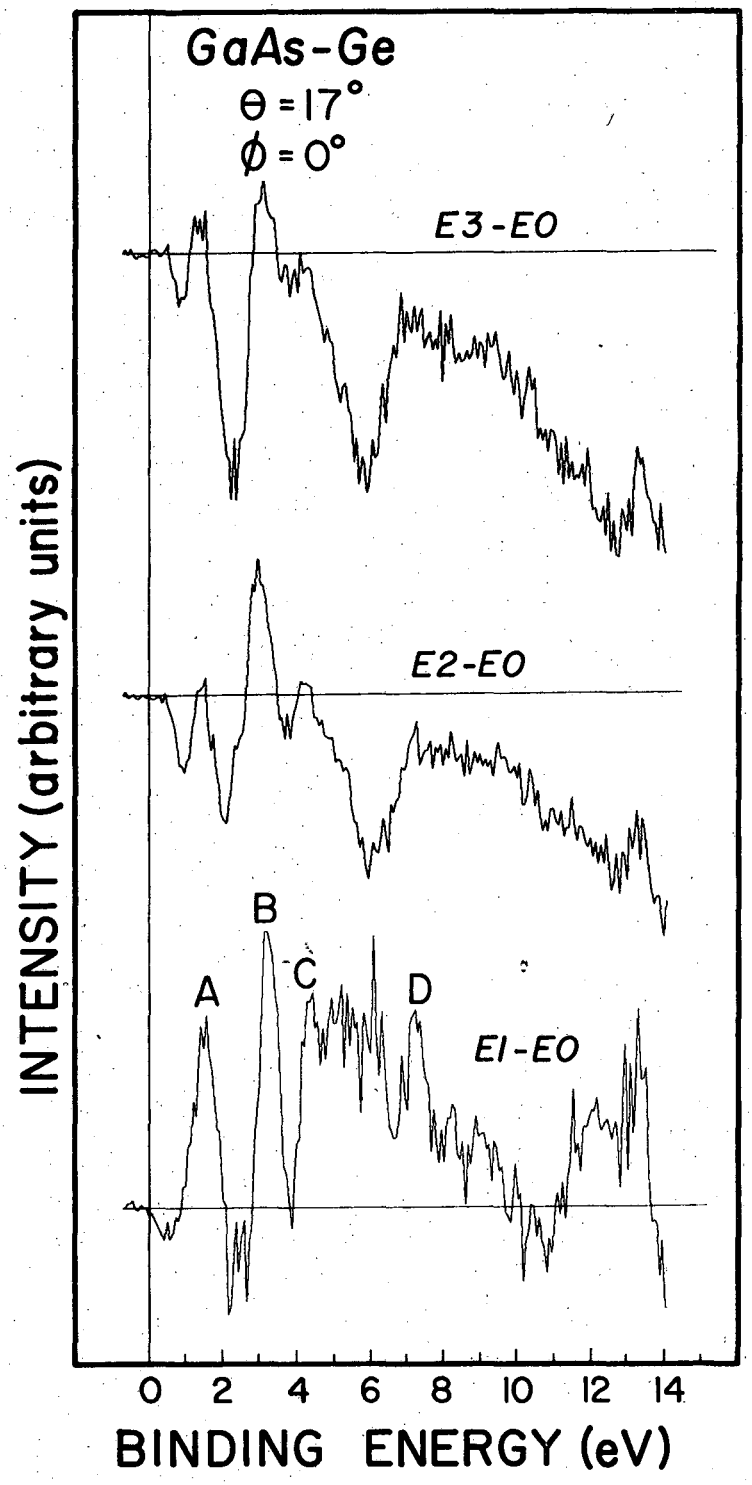
GaAs-Ge
θ = 17°
ϕ = 0°
E3-E0
E2-E0
E1-E0
A
B
C
D
INTENSITY (arbitrary units)
0
2
4
6
8
10
12
14
BINDING ENERGY (eV)
XBL 791-8088

Fig. 3

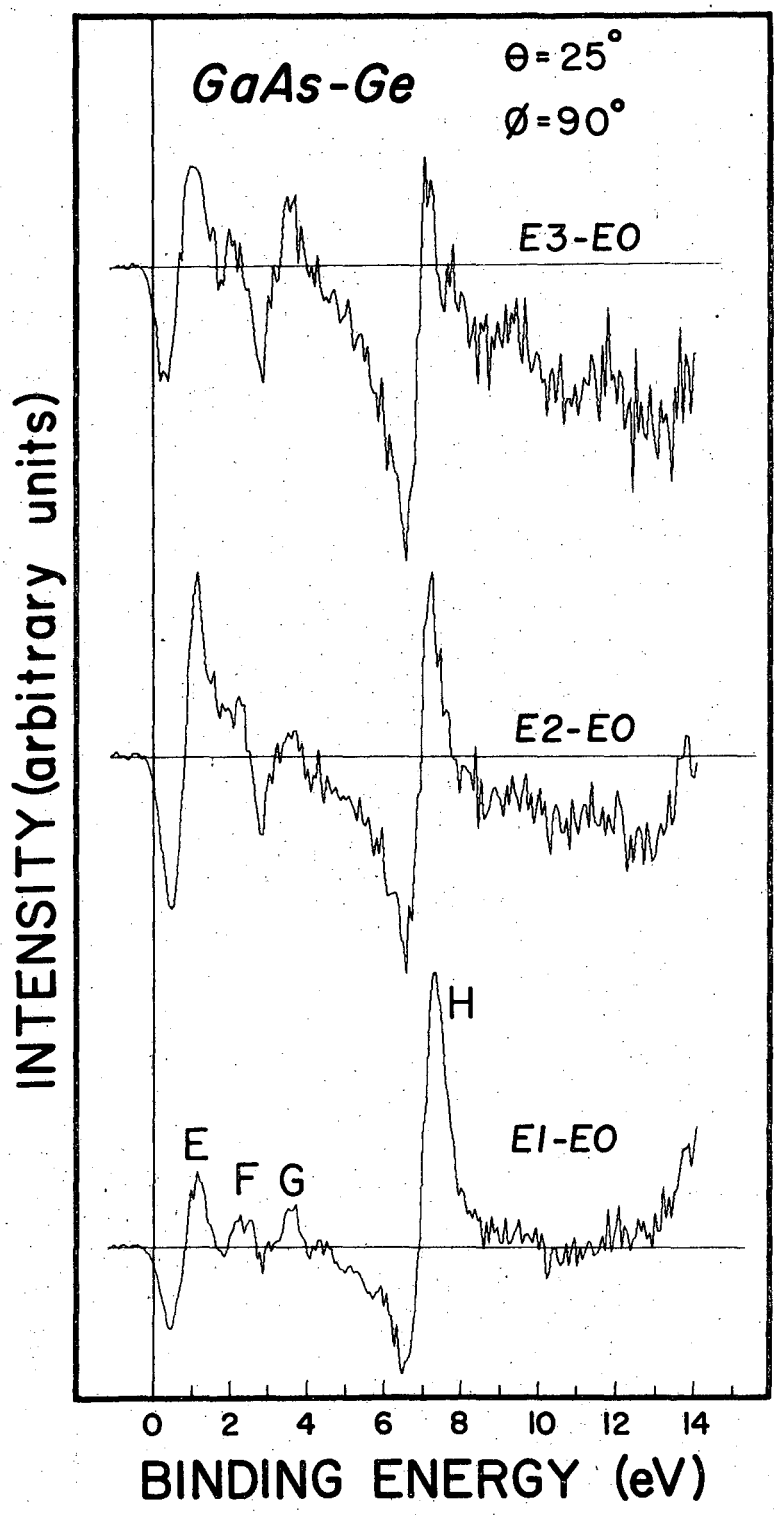

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Fig. 4

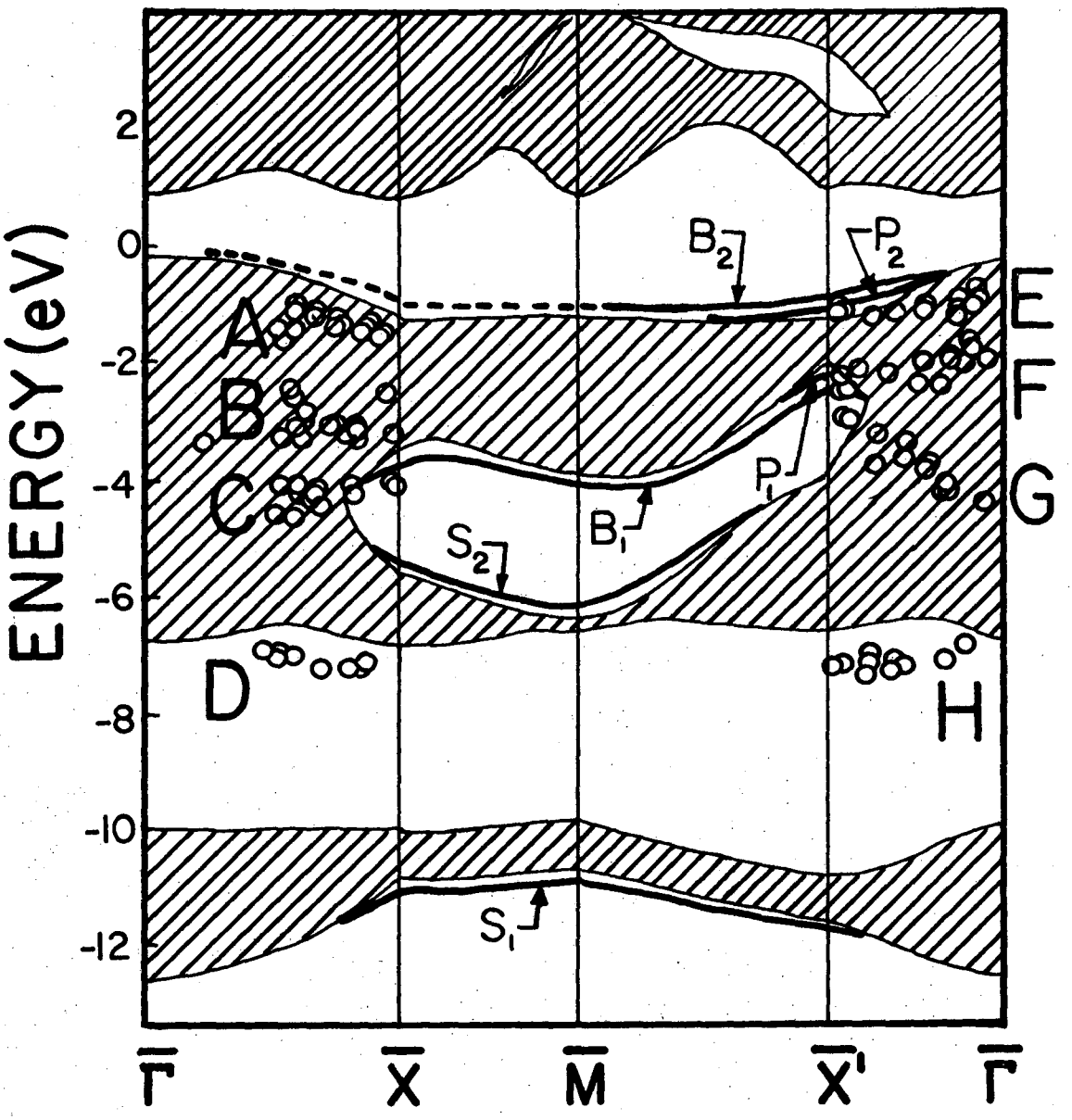

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Fig. 5

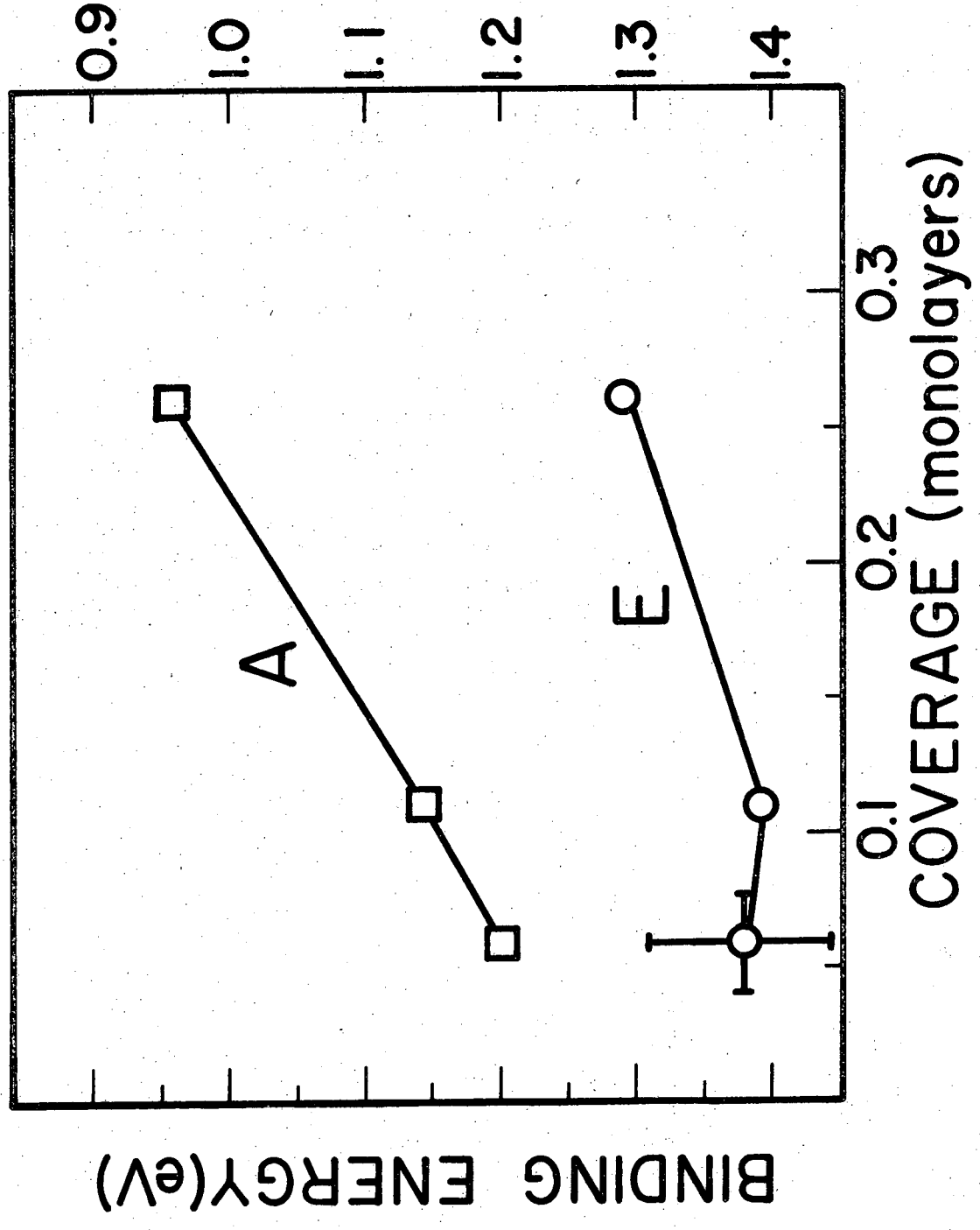

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Fig. 5

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