PHYSICAL REVIEW B VOLUME 28, NUMBER 4 15 AUGUST 1983

Microscopic study of semiconductor heterojunctions: Photoemission measurement of the valance-band discontinuity and of the potential barriers

A. D. Katnani and G. Margaritondo
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

(Received 4 January 1983)

We report on synchrotron-radiation photoemission measurements of the valence-band discontinuity and of the Fermi-level position for 25 different interfaces involving group-IV, III-V, and II-VI semiconductor substrates and Ge or Si overlayers. A comparison is made between our measured discontinuities and the predictions of current theoretical models. We find the best agreement with empirically corrected versions of the models of Harrison and of Frensley and Kroemer. However, we present a new empirical rule based on our present results and on those of other authors which yields even more accurate predictions of band discontinuities. The measured Fermi-level-pinning position of each substrate is the same for both Ge and Si overlayers. This result is discussed in terms of the "defect model" of Fermi-level pinning, originally developed for Schottky barriers.

I. INTRODUCTION

Photoemission experiments have been performed in recent years[1–5] on a limited number of prototypical semiconductor-semiconductor interfaces to test the current theoretical models for heterojunction-band discontinuities. These experiments have emphasized the need for a systematic study on a large number of heterojunctions. In fact, photoemission discontinuity measurements on a few prototypical interfaces did not provide conclusive evidence in favor or against any one theory. We report here the results of a systematic photoemission study of 25 interfaces involving Ge or Si overlayers on group-IV, III-V, and II-VI semiconductor compounds. These results were compared to the predictions of the electron-affinity rule,[6] the pseudopotential approach of Frensley and Kroemer,[7] Harrison's linear combination of atomic orbitals (LCAO) model,[8] Adam and Nussbaum's model,[9] and the Von Ross model.[10] The measured valence-band discontinuities, ΔE_v, show the best overall correlation with the predictions of empirically corrected versions of the models of Harrison and Frensley and Kroemer. However, even for those models the accuracy in predicting ΔE_v, 0.15–0.2 eV, is not sufficient for most practical applications. A somewhat more accurate, empirical approach to predict valence-band discontinuities was developed based on our present data and on those of other authors. This approach calculates ΔE_v as the difference between the valence-band-edge positions of the two semiconductors, empirically deduced from the measured discontinuities between each semiconductor and Si or Ge.

We also measured the interface Fermi-level position, E_F, relative to the substrate valence-band maximum, E_v. The most relevant result of these measurements is that we obtained the same value of E_F for a given substrate, both for Ge and for Si overlayers. This result suggests that the defect model originally proposed by Spicer and coworkers[11] for metal-semiconductor interfaces could be applicable in certain cases to heterojunction interfaces.

Figure 1 shows a schematic energy-band diagram of two semiconductors forming a heterojunction. The transport properties of all heterojunction devices strongly depend on three interface characteristics[12–14]: band discontinuities, interface states, and potential-barrier height. The change in the forbidden gap across the interface is distributed between a valence-band discontinuity, ΔE_v, and a conduction-band discontinuity, ΔE_c. These discontinuities may form barriers for the charge carriers crossing the interface and dramatically influence the operation of heterojunction devices.[12] Interface states, including defect states, also influence the heterojunction-device behavior by acting as charge traps or recombination centers.[13,14] Finally, the position of E_F at the interface determines the barrier height on the two sides of the interface, V_{D1} and V_{D2}.

Interface characteristics, such as ΔE_v, ΔE_c, and the interface states, were the subject of many theories and experiments over the past 20 years. In 1962, Anderson[6] formulated a semiempirical rule to calculate ΔE_c, based on the free-surface properties of the two semiconductors. In his model ΔE_c is given by the difference between the electron affinities of the semiconductors. The lack of reliable measurements of the band discontinuities and the spread in

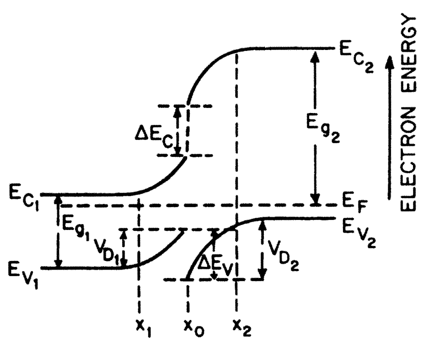

FIG. 1. Schematic energy-band diagram for a semiconductor-semiconductor interface. The two semiconductors have band gaps E_{g1} and E_{g2}. The difference between the two gaps gives rise to a conduction-band discontinuity, ΔE_c, and to a valence-band discontinuity, ΔE_v.

the experimental values of the electron affinity made it hard to test the accuracy of Anderson's model. On the other hand, this "electron-affinity rule" has been—and still is—very widely used in heterojunction-device research. The Anderson model was criticized on theoretical grounds by Kroemer[15] because it uses a free-surface parameter, the electron affinity, to describe interface properties.

Two different kinds of approaches were used in later theoretical works. The first kind of theory tried to calculate the band lineup from bulk crystal properties. The second kind of approach calculated the local electronic structure of the interface in detail, leading in particular to a direct estimate of the discontinuities. Examples of the first approach are the potential-matching model of Frensley and Kroemer,[7] the tight-binding approach of Harrison,[8] the continuous–intrinsic-Fermi-level model by Adams and Nussbaum,[9] and the continuous–conduction-band model by Von Ross.[10] Examples of the second approach are the self-consistent calculation of Baraff *et al.*[16] and Pickett *et al.*,[17] the cluster approach of Swart *et al.*,[18] and the tight-binding approach of Pollman and Pantelides.[19] In principle, some of the models of the second kind can be developed to any degree of accuracy and therefore they are ideal methods for the estimation of discontinuities. However, the practical present accuracy in estimating ΔE_v and ΔE_c is still limited. Furthermore, these approaches imply lengthy and expensive calculations. As a consequence, "general" approaches such as the electron-affinity rule and the other models mentioned above[7–10] are still very widely used in heterojunction research. In turn, it is necessary to perform more extensive tests of the accuracy of these approaches.

The validity and the limits of accuracy of the theoretical models for band discontinuities cannot be tested without direct and reliable measurements of these parameters. Transport techniques provide only indirect, "macroscopic" estimates of ΔE_v and ΔE_c. Futhermore, these measurements rely heavily on specific assumptions about the distribution of dopants at the interface and about the spacial distribution of the interface states. In 1978 the first results were reported on measurements of the valence-band discontinuity using photoemission spectroscopy.[4,20,21] At the same time, photoemission provided an insight into the microscopic electronic structure of the interface and a *local* measurement of ΔE_v. Other surface-sensitive techniques such as Auger electron spectroscopy and electron-energy-loss spectroscopy have also been used to study heterojunction interfaces.[22] However, the most extensive results were obtained using photoemission spectroscopy and in particular photoemission with synchrotron radiation. For example, studies of the interface states and in general of the evolution of the local electronic structure during the interface formation were made possible by the use of angle-resolved photoemission.[23,24]

The detailed theoretical calculations available for the GaAs-Ge interface[16–19] stimulated many experimentalists to investigate the microscopic characteristics of that interface by photoemission spectroscopy. A few other interfaces of fundamental and technological importance have also been studied with surface-sensitive techniques.[25–28] Those pioneering experiments were not sufficient to test the discontinuity models and to assess their limits. For example, the experimental values for the GaAs-Ge valence-band discontinuity ranged between 0.25 and 0.65 eV. This range of values reflects in part the experimental uncertainty—but is also a result of the dependence of ΔE_v on experimental variables such as annealing or substrate orientation. The wide range of reported values made it impossible to test the discontinuity models based on this interface only. The situation did not improve much when photoemission measurements of ΔE_v became available for a few other prototypical interfaces.[25–28] This suggested to us that the best way to test the discontinuity models was to investigate their ability to reproduce the general dependence of ΔE_v on the properties of the two semiconductors forming the heterojunction. This test required systematic, time-consuming measurements for a large number of interfaces under similar experimental conditions. We present here the results of the first systematic investigation of this kind.

The theoretical problems concerning the Fermi-level pinning and the potential-barrier formation are similar to those found for metal-semiconductor interfaces. The Schottky barrier, which is the equivalent for metal-semiconductor interfaces of the heterojunction potential barriers, has been widely studied.[11,29–31] Experimental results demonstrated that for many metal-semiconductor interfaces the Fermi-level-pinning position is obtained at small metal coverages and is independent of the metal overlayer. This observation led Spicer and co-workers[11] to propose in 1979 the "defect model" for Fermi-level pinning at III-V–semiconductor-metal interfaces, which relates this effect to native defects of the semiconductor surface created during the interface formation. Several theoretical studies recently tried to understand the nature of the Fermi-level-pinning defects. Daw *et al.*[32] identified the defects as vacancies created at the surface during the metal deposition. However, Dow *et al.*[33] argue that antisite defects are the most energetically favorable. In general, the nature of the local defects at metal-semiconductor interfaces and their role in pinning E_F remains a rather controversial issue. Recent experiments[34] suggested that the defect model could be extended to certain kinds of semiconductor-semiconductor interfaces. Our present systematic results on the Fermi-level-pinning position strengthen that conclusion.

The remainder of this article will be organized as follows. Sections II and III will discuss the experimental procedure and present the experimental results. These results will be analyzed and discussed in Sec. IV, and our conclusions will be summarized in Sec. V.

II. EXPERIMENTAL PROCEDURE

The experimental procedure consisted of taking photoemission spectra on clean, cleaved semiconductor substrates and then on the same substrates covered by Ge or Si overlayers of increasing thickness. The spectra were then analyzed to deduce the value of the valence-band discontinuity and the pinning position of the Fermi level at the interface. The experiments were performed under ultrahigh vacuum [operating pressure $(4–60)\times 10^{-11}$ Torr, including evaporation]. The substrates were cleaved *in situ*. Table I lists the samples we studied, their source, doping, and dopant. The initial position of the Fermi lev-

TABLE I. Characteristics of the semiconducting substrates used in our experiment.

Semiconductor	Dopant	N_D, cm^{-3}	d, Å	E_g, eV	Source[a]
Si	B,n	10^{15}	2.35	1.11	ESPI
Ge	Sb,n	10^{15}	2.44	0.67	GTI
GaAs	Te,n	$10^{17}-10^{18}$	2.45	1.40	CLC
GaP	S,n	$10^{17}-10^{18}$	2.36	2.25	CI
GaSb	Te,n	$10^{17}-10^{18}$	2.65	0.67	MS
InAs	S,n	$10^{17}-10^{18}$	2.61	0.36	MS
InP	Sn,n	$10^{17}-10^{18}$	2.54	1.34	CC
InSb	S,n	$10^{17}-10^{18}$	2.81	0.17	MS
CdS	n[b]	10^{16}	2.53	2.42	CLC
CdSe	n[b]	10^{16}	2.63	1.70	CLC
CdTe	n[b]	10^{16}	2.81	1.44	JW
ZnSe	n[b]	10^{16}	2.45	2.67	CLC
ZnTe	n[b]	10^{16}	2.64	2.26	CLC

[a] ESPI indicates Electronic Space Product Inc.; GTI is Glass Technology Inc.; CI is Cambridge Instruments Company; MS is Metal Specialties Company; CC is Crystal Company; CLC is Cleveland Crystal Company; JW indicates courtesy of Professor J. D. Wiley.

[b] Nominally undoped.

el E_F indicated a flat band condition, i.e., no band bending and therefore a low density of cleavage steps, except for GaP, Si, and Ge which exhibit band bending due to intrinsic states in the forbidden gap.

Ge was evaporated from a tungsten basket and Si from a homemade, miniature electron-bombardment source where electrons with 3-KeV energy were directed against a Si single crystal. The overlayers were deposited on room-temperature substrates and their thicknesses were monitored with a quartz-crystal oscillator. The evaporation rates ranged from 0.3 to 1.5 Å per minute. Photons of energy 40—200 eV were used to probe the freshly-cleaved surfaces and the overlayer-covered surfaces. The photons were emitted by the University of Wisconsin Synchrotron Radiation Center storage ring Tantalus and monochromatized by a grazing-incidence "Grasshopper" monochromator. The photoelectrons were analyzed by a double-pass cylindrical-mirror analyzer. The overall experimental resolution (analyzer and monochromator) was 0.2—0.5 eV. Data acquisition was controlled by a Tektronics 4051 minicomputer.

For each interface we measured the photoelectron energy-distribution curves (EDC's) of the valence band and of several core levels on the clean substrate and then on the overlayer-covered surface for different overlayer thicknesses. We selected the photon energy so as to minimize the photoelectron escape depth for maximum surface sensitivity. The top of the valence band was measured by a linear extrapolation of the leading edge of the valence-band EDC's. The energy position of all spectral features was referred to the Fermi level of the system, deduced from the leading EDC edge of a thick metal film, gold or aluminum.

The accuracy of our experimental measurements of E_v and E_F, which are discussed in the next section, is primarily limited by the determination of the valence-band edge from the experimental spectra. This factor is more important than other factors such as the accuracy in determining the core-level peak position and the Fermi edge. Kraut *et al.*[28] recently proposed a method to estimate E_v with very high accuracy based on the calculated density of states in the valence-band region. However, this method could not be systematically applied to all our interfaces since the required theoretical density of states is only available for a few substrates. Therefore, in our systematic study we preferred to use the most common approach to determine the valence-band edge, i.e., linear extrapolation of the leading edge of the EDC's. This method, although somewhat less accurate than that proposed by Kraut *et al.*,[28] could be consistently used for all the substrates we investigated, and therefore it was more appropriate for our systematic measurements. Repeated tests on a large number of systems indicate that ±0.05 eV is the typical estimated accuracy in determining E_v's with this approach. The corresponding accuracy of our measurements is ±0.1 eV for ΔE_v and for the Fermi-level-pinning position.

III. EXPERIMENTAL RESULTS

Measurements of the valence-band discontinuity from the EDC's were performed with two different methods. One of these methods was direct but it could only be used for a small number of interfaces. The other method was less direct, but it could be applied to all interfaces. Whenever possible, both methods were applied and their results were compared to test the reliability of the less direct method.

The large ΔE_v's at certain interfaces, e.g., ZnSe-Ge, CdS-Ge, and CdS-Si, enabled us to spectrally resolve the valence-band edges of both semiconductors, substrate and overlayer. Figure 2 shows the valence-band EDC's for a clean, cleaved CdS($10\bar{1}0$) surface (bottom curve) and for increasing Si coverages of the same surface. Notice that at intermediate coverages both valence-band leading edges are visible. A direct measurement of ΔE_v is possible in this case by linear extrapolation of the two edges, and it gives a discontinuity of 1.55±0.1 eV. The edge positions

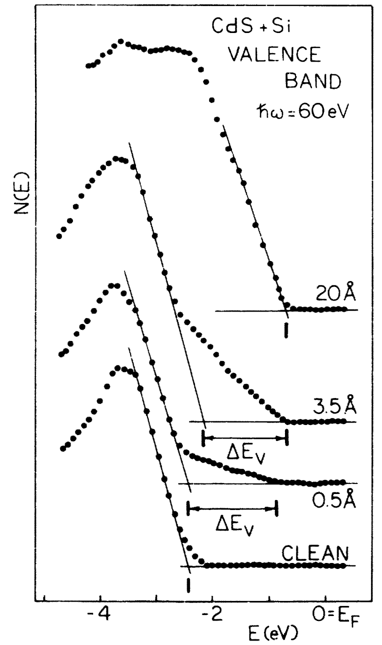

FIG. 2. EDC's of the valence band of freshly cleaved and Si-covered CdS substrate taken with 60-eV photon energy. Notice that at intermediate coverages one is able to resolve the valence-band edges of both semiconductors. This makes it possible to perform a direct measurement of ΔE_v. The two valence-band-edge positions are estimated by linear extrapolation as shown in the figure and discussed in the text. The estimated accuracy of ΔE_v is ± 0.1 eV, and its average value deduced from Si overlayers of different thicknesses on CdS is 1.55 eV.

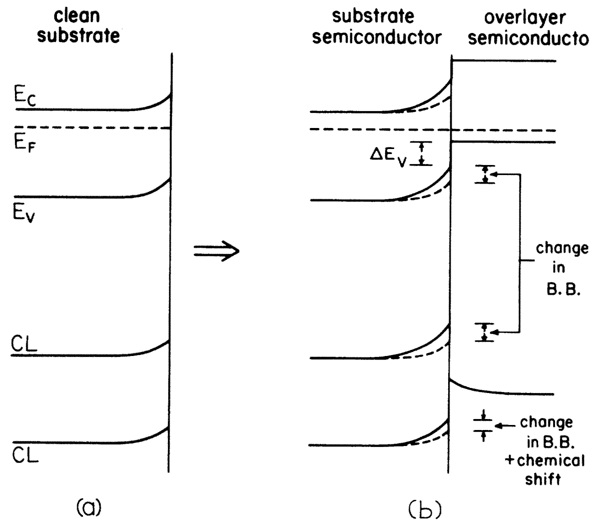

FIG. 3. Energy-band diagram for the interface between clean substrate and vacuum (a) and between clean substrate and overlayer (b). The solid lines in (b) represent the final position of the valence-band edge, of the conduction-band edge E_c, and of two different core levels, CL, while the dashed lines reproduce the same positions as in (a). The difference between the solid lines and dashed lines for E_v and E_c is due to the change in band bending (B.B.). One of the core levels is primarily affected by the band-bending changes, while the other core level is also strongly affected by changes in the chemical shift, as discussed in the text. ΔE_v is equal to the distance in energy between the *final* positions of the E_v's of the substrate and of the overlayer.

deduced by linear extrapolation were cross-checked for different systems with those deduced from the energy positions of the corresponding core levels. For Ge and Si core levels this was done by using as a reference the distance in energy between the bulk Ge 3*d* or Si 2*p* levels and features in the valence band, including the edge. For the substrate core levels the test is part of the indirect method of estimating ΔE_v discussed in the next paragraph.

The above direct method of estimating ΔE_v could not be applied to most interfaces since the two edges were too close in energy to be resolved. For those interfaces we used the more indirect approach to estimate ΔE_v. This method consisted of measuring the substrate valence-band-edge position, correcting it for band-bending changes during the interface formation, and estimating ΔE_v from the distance in energy between this corrected substrate valence-band edge and the measured valence-band edge of the overlayer. Figure 3(a) shows the energy-band diagram of the interface between a clean substrate and vacuum. Photoemission probes the surface region and enables one to measure the top of the valence band at the vacuum-substrate interface. Figure 3(b) shows the energy-band diagram for the semiconductor-semiconductor interface. As the overlayer is deposited, the top of the valence band of the substrate moves from the dashed-line position to the solid-line position. This change in position is due to the change in band bending caused by the changes in the local charge distribution. Also, notice that the substrate core-level positions change with increasing coverage. Typically, at thicknesses ≥ 5 Å one already observes the top of the valence band of the overlayer (solid line on the overlayer side). ΔE_v in Fig. 3(b) is the distance between the two solid lines representing the substrate and overlayer valence-band edges at the interface. This is equal to the distance in energy between the top of the valence band of the clean surface, corrected for the change in band bending, and the top of the valence band for the overlayer. In practice, the shift of the substrate valence-band edge due to change in band bending is obscured by the overlayer valence-band signal. However, the band-bending changes can be deduced from the shift in energy of the substrate core-level peaks with increasing coverage. In general, this shift is due to changes both in the band-bending and in the core-level chemical shift. The chemical-shift changes are due to the formation of interface chemisorption bonds. We found that the substrate *cation* core-level peaks are primarily affected by the band-bending changes during the early stages of interface formation. In fact, for all interfaces we observed at small coverages a correlation between the cation core-level shift and the substrate valence-band-edge shift. We found a similar correlation with the shift of other substrate features in the valence-band EDC's. Also, for small and intermediate (<30 Å) overlayer thicknesses the cation core-level line shape showed no broadening with increasing coverage and this again indicated a negligible change in chemical shift. For some interfaces, for example, ZnSe-Si, ZnSe-Ge, and CdS-Ge, a broadening of the cation core-level peak was observed at high coverages (≥ 30 Å). However, this broadening did not affect our estimate of the band-bending changes which occurred at much lower coverages as shown by the initial

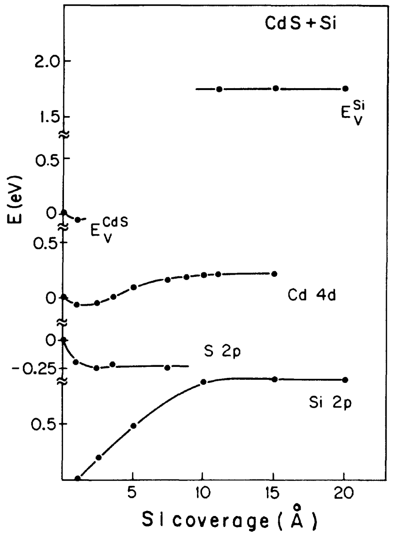

FIG. 4. Energy shift of the valence-band edge and of the Cd 4*d*, S 2*p*, and Si 2*p* core levels with increasing Si coverage on a CdS substrate. The zero for each plot is the clean surface energy positions. Notice the low-coverage correlation between E_v and Cd 4*d* shifts. This plot was used to estimate ΔE_v as explained in the text. The estimated ΔE_v is 1.60 eV, in good agreement with the direct method.

shift of the peak. In summary, the above observations enabled us to estimate the band-bending changes from the substrate cation core-level shift. In turn, we estimated ΔE_v by subtracting the shift of the cation core-level peak from the distance in energy between the leading edges of the EDC's taken before and after interface formation.

An example of the above method is the estimate of ΔE_v for the CdS-Si interface. Figure 4 shows the shift with coverage of the top of the valence band and of the core-level peaks. Notice the correlation between the Cd 4*d* shift and the shift of the top of the valence band at small coverages. Instead, the S 2*p* shift is not correlated with those of E_v and Cd 4*d*, and therefore is due to a combination of change in chemical shift and change in band bending. As discussed above, ΔE_v is estimated from the distance in energy between the initial and final valence-band edges after subtracting from it the total shift of the cation core-level peak. The ΔE_v deduced in this way from the data of Fig. 4 is 1.6 eV. This value is in agreement with the result of the direct method, 1.55 eV. The agreement demonstrates the reliability of the "indirect" method of measuring ΔE_v. Similar positive tests of the indirect method were performed for all the interfaces for which the direct method could be used. Table II summarizes our results on ΔE_v for the different interfaces.

An investigation of the interdiffusion across the interface is important for a meaningful comparison with theory because all theoretical models calculate the band discontinuity for an abrupt interface. The intensity attenuation of the substrate and of the overlayer core-level peaks during the interface formation was used to monitor possible interdiffusion process. In Fig. 5 we plot the normalized Cd 4*d* and S 2*p* intensities versus coverage for Si overlayers on CdS. The plot is consistent with an exponential attenuation of both core-level peaks with increasing coverage. The exponential attenuation length deduced from this plot, ~9 Å, is close to the escape depth for photoelectrons of this energy across the Si overlayer.[35] This indicates the formation of an abrupt interface.

The interface-pinning position of the Fermi level within the substrate gap was derived from the position of the top of the valence band in the clean-substrate EDC's after correction for the changes in band bending. The absolute position of E_F for our spectrometer was deduced from a linear interpolation of the leading spectral edge of a thick film of freshly evaporated Al or Au. The change in band bending was again estimated from the cation core-level shift. Figure 6 shows the Fermi-level shift at the interface as a function of coverage for CdS with Si and Ge over-

TABLE II. Experimental valence-band discontinuities measured from our spectra and corresponding theoretical predictions.[a]

	Experimental		EA		AN		Von Ross		Harrison		FK	
Substrate	Si	Ge	Si	Ge	Si	Ge	Si	Ge	Si	Ge	Si	Ge
Ge	−0.17		−0.31		−0.21		−0.42		−0.38		0.09	
Si		0.17		0.31		0.21		0.42		0.38		−0.09
GaAs	0.05	0.35	0.27	0.70	0.15	0.37	0.30	0.73	0.03	0.35	0.80	0.71
GaP	0.95	0.80	0.33	0.64	0.58	0.79	1.15	1.57	0.50	0.88	0.96	0.87
GaSb	0.05	0.20	−0.37	−0.07	−0.21	0.00	−0.42	0.00	−0.81	−0.31	0.73	0.64
InAs	0.15	0.33	0.15	0.46	−0.37	−0.16	−0.74	−0.31	−0.29	0.09	1.22	1.13
InP	0.57	0.64	0.55	0.85	0.12	0.34	0.24	0.67	0.14	0.64	1.42	1.33
InSb	0.00	0.00	−0.34	−0.03	−0.47	−0.25	−0.93	−0.50	−1.09	−0.71		
CdS	1.55	1.75	1.30	1.61	0.66	0.88	1.32	1.75	1.62	2.00	2.26	2.17
CdSe	1.20	1.30	0.49	0.80	0.30	0.52	0.60	1.03	0.85	1.23	2.13	2.04
CdTe	0.75	0.85	0.64	0.94	0.17	0.39	0.34	0.77	−0.18	0.20	1.74	1.69
ZnSe	1.25	1.40	1.68	1.99	0.79	1.00	1.57	2.00	1.08	1.46	1.91	1.82
ZnTe	0.85	0.95	0.64	0.96	0.58	0.80	1.16	1.59	0.00	0.38	1.58	1.49

[a] Values in eV, uncertainty ±0.1 eV. The theories are the following: EA indicates Anderson's electron-affinity rule (Ref. 6), AN is the Adam-Nussbaum model (Ref. 9), Von Ross's model (Ref. 10), Harrison's tight-binding model (Ref. 8), and FK is the Frensley-Kroemer model (Ref. 7). ΔE_v is taken to be positive when the overlayer valence-band edge is *above* the substrate valence-band edge.

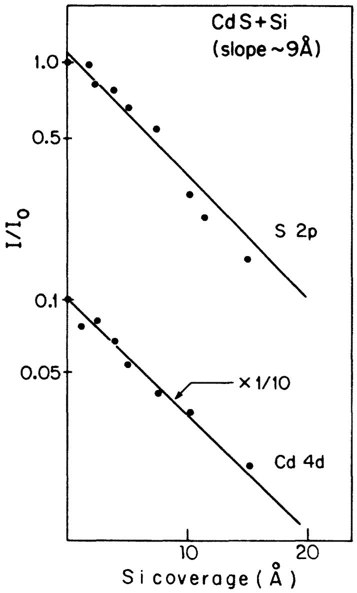

FIG. 5. Intensity attenuation of the Cd $4d$ and S $2p$ with increasing Si coverage of a CdS substrate. The exponential attenuation length estimated from this plot is 9 Å. This is close to the escape depth from Si for photoelectrons at these energies and it indicates that the interface is reasonably abrupt.

layers. Notice that the final pinning position of E_F is the same for $CdS(10\bar{1}0)$-Si, $CdS(10\bar{1}0)$-Ge, and $CdS(11\bar{2}0)$-Ge. Table III summarizes our results on the Fermi-level-pinning position for different interfaces. These results generalize the above observation—the pinning positions for a given substrate are independent, within the experimental uncertainty, of the nature of the overlayer, Ge or Si.

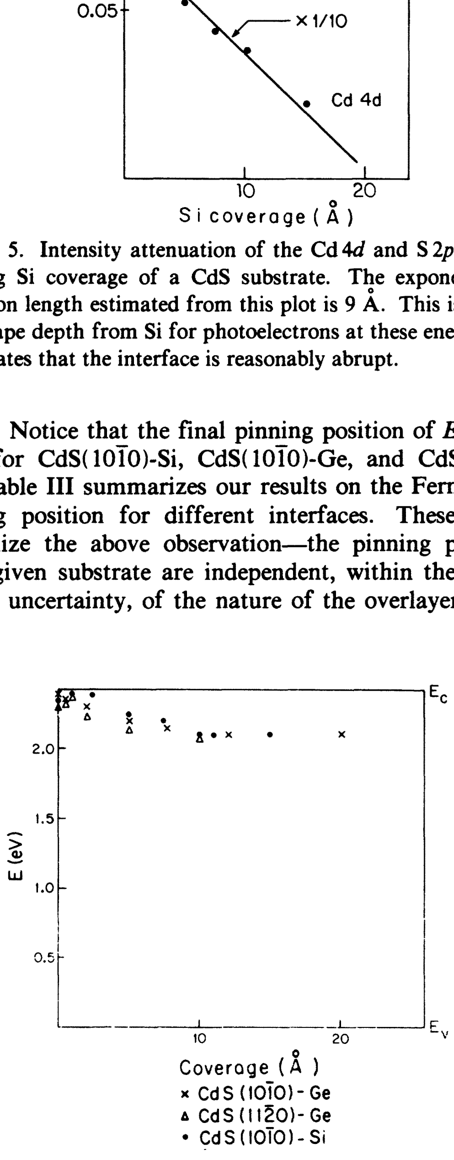

FIG. 6. Interface Fermi-level-pinning position vs the nominal thickness of the overlayer during the formation of interfaces between $CdS(10\bar{1}0)$ or $CdS(11\bar{2}0)$ and Si or Ge. The Fermi-level position in the CdS gap was estimated from the distance in energy between the substrate E_v corrected for band-bending changes and the Fermi level of the photoelectron spectrometer. In turn, the Fermi level of the spectrometer was deduced by linear interpolation of the leading spectral edge of a freshly evaporated thick film of metal. The band-bending changes were estimated from the Cd $4d$ shift.

IV. DISCUSSION

The discussion of the experimental results will be organized in Secs. IV A–IV D. First, we shall briefly present the current theoretical approaches to predict band discontinuities for all heterojunction interfaces[6–10] and discuss their characteristics. Second, we shall estimate the general theoretical accuracy limits of these approaches. The estimated accuracy limits underlying all models will then be compared with the specific accuracy limits of each model. Third, we shall describe our new empirical method to predict band discontinuities. Finally, we shall discuss our experimental results on the Fermi-level interface pinning position.

A. Theoretical discontinuity models

We have shown that the general theoretical approaches developed to calculate ΔE_v for *any* heterojunction interface include Anderson's electron-affinity rule,[6] Harrison's LCAO model,[8] the Frensley-Kroemer pseudopotential model,[7] the Adam-Nussbaum continuous—intrinsic-E_F rule,[9] and the continuous—conduction-band-edge rule by Von Ross.[10] As already mentioned, the Anderson model expresses ΔE_c as the difference between the electron affinities of the two semiconductors. Harrison used a tight-binding approach to calculate the absolute position of the valence-band maximum, while Frensley and Kroemer used a pseudopotential approach to calculate the valence-band maximum relative to an average interstitial potential. ΔE_v in both cases is simply given by the difference between the calculated valence-band maxima of the two semiconductors. In both approaches terms calculated from the bulk crystal parameters replace the electron affinities used in Anderson's model. Two other general discontinuity models were proposed in recent years. Adam and Nussbaum[9] calculated the valence-band discontinuity by aligning the intrinsic Fermi levels of the two semiconductors, while Von Ross[10] simply estimated ΔE_c to be zero, and therefore ΔE_v to be equal to the difference between the forbidden gaps.

A common characteristic of all the above models is that they express the band discontinuities as the difference between two terms characteristic of the two semiconductors. Therefore, ΔE_v and ΔE_c are linearly related to these terms (notice that the sum of the two discontinuities is equal to the difference between the forbidden gaps). This "linearity" is a powerful simplification and at the same time a limiting factor. For example, all linear models ignore the peculiar *microscopic* properties of each interface. In fact, most of them give a band discontinuity which is independent of the crystallographic faces involved in the interface and of the general interface morphology. This implies, for example, that the predicted band discontinuities must be the same for different surface orientations of a given substrate combined with a given overlayer. It also implies that the discontinuities are not different for ordered and disordered overlayers. Two other general consequences of the linearity of the above models are the commutativity and the transitivity of the predicted discontinuities. The commutativity rule implies that the valence- (or conduction-) band discontinuity for the interface between a substrate of material A and an overlayer of material B

(A-B interface) is equal in magnitude and opposite in sign with respect to that for the B-A interface. The transitivity rule implies, for example, that the sum of the valence- (or conduction-) band discontinuities for the three interfaces formed by different combinations of three given semiconductors is zero, i.e., the valence-band discontinuities for the A-B, B-C, and C-A interfaces add up to zero.

B. General accuracy limits and specific accuracy limits of the linear discontinuity models

The peculiar microscopic properties of each interface, such as the charge distribution on each side of the interface due to the formation of chemical bonds, in principle, affect the band discontinuity. A realistic band-discontinuity model should take these effects into consideration. Therefore, all the above linear models, which essentially ignore the peculiar microscopic properties of each interface, have intrinsic accuracy limits. An estimate of these general accuracy limits and of the specific accuracy of each model can be obtained from our results. The general accuracy limits for all linear models can be estimated by testing the predictions discussed in Sec. IV A. The specific accuracy of each model can be estimated by a direct comparison between our results and its predicted band discontinuities.

1. General accuracy limits

The underlying accuracy limits arising from the linearity of the models were empirically estimated by analyzing the extent to which our data and those of other authors agree with the predicted independence of substrate orientation and of overlayer ordering, with the commutativity rule and with the transitivity rule. In particular, we did find the measured ΔE_v to be independent of the surface orientation for substrates with Ge overlayers. In fact, we measured the same ΔE_v's for CdS(10$\bar{1}$0)-Ge and CdS(11$\bar{2}$0)-Ge interfaces. However, earlier experiments by Fang *et al.*[36] and by Grant *et al.*[4] revealed non-negligible substrate surface-orientation effects. For example, Grant *et al.*[4] measured discrepancies of the order of 0.2 eV between the ΔE_v's of Ge-covered GaAs substrates with different orientations.

The independence of overlayer ordering was tested for Ge overlayers on[25] Si without detecting significant changes in ΔE_v when the overlayer was ordered by annealing. A difference in ΔE_v of the order of 0.2—0.3 eV was reported for ordered and disordered Ge overlayers on[34] GaAs and on epitaxial ZnSe substrates,[27] while no difference was observed for ordered and disordered ZnSe overlayers on Ge.[27] Our preliminary tests did not show any ΔE_v difference between ordered and disordered Ge overlayers on cleaved ZnSe. Systematic data on the effects of overlayer ordering are not yet available, but from the above preliminary results they do not appear to affect the ΔE_v's by more than a few tenths of an electronvolt per interface—0.1—0.15 eV on the average. This point is relevant since in our systematic study we tried to use similar experimental conditions for all interfaces, and in particular room-temperature substrates during deposition which give disordered overlayers—while some of the discontinuity models apply to ordered systems. However, the limited-overlayer ordering effects mentioned above do not jeopardize the overall comparison between our data and those models, and do not significantly affect our tests of the models and the corresponding conclusions.

TABLE III. Interface Fermi-level-pinning position.[a]

Substrate	Si	Ge
Si		0.40
Ge	0.30	
GaAs	0.80	0.75[b]
GaP	1.05	1.05
InP	0.75	0.80
CdS	2.10	2.10
CdSe	1.30	1.40
CdTe	1.00	0.95
ZnSe	1.80	1.80
ZnTe	1.25	1.20

[a] Measured with respect to the substrate valence-band edge. Uncertainty ±0.1 eV.

[b] See Ref. 34.

The commutativity implied by all linear models was tested in three experimental measurements. One is our own present experiment and the other two are x-ray photoelectron spectroscopy (XPS) measurements by Waldrop *et al.*[5] and by Kowalczyk *et al.*[27] We have not observed a dependence of ΔE_v on the growth sequence for the Ge-Si combination. In fact, we have measured the same ΔE_v, 0.17 eV, for Ge-Si and Si-Ge interfaces. Instead, the other two experiments have measured deviations from the commutativity rule. Waldrop *et al.*[5] found a deviation of 0.25 eV for GaAs-AlAs and AlAs-GaAs and Kowalczyk *et al.*[27] found deviations of 0.32—0.54 eV for ZnSe-Ge and Ge-ZnSe.

We analyzed eleven different groups of three semiconductors each to test the transitivity rule. Each group includes Si, Ge, and a third material, X. Table IV lists the difference between ΔE_v's of X-Ge and X-Si interfaces. This difference should be equal to the valence-band

TABLE IV. Test of the transitivity rule.[a]

X (substrate)	$\Delta E_v^{X\text{-Ge}}$-$\Delta E_v^{X\text{-Si}}$
GaAs	0.20
GaP	0.32
GaSb	0.15
InAs	0.20
InP	0.07
InSb	0.00
CdS	0.20
CdSe	0.10
CdTe	0.10
ZnSe	0.15
ZnTe	0.10

[a] Reported in the table is the sum of the ΔE_v's for the two heterojunctions involving a given substrate X and Si or Ge. The transitivity rule implied by all linear models requires this sum to be equal to the discontinuity of the Si-Ge interface, 0.17 eV.

discontinuity of the Si-Ge interface, 0.17 eV, if the transitivity rule holds. In fact, the difference is equal to the measured ΔE_v of the Si-Ge interface within the combined experimental uncertainty—except for GaP, where a discrepancy of the order of 0.15 eV occurs. Previous experiments by Waldrop and Grant[3] on GaAs-Ge, CuBr-GaAs, and CuBr-Ge interfaces revealed a 0.64-eV deviation from zero of the sum of the corresponding ΔE_v's. Also, a recent XPS study[27] of ΔE_v for Ge-ZnSe and ZnSe-GaAs when combined with previous ones[3–5] for GaAs-Ge reveals a deviation of 0.20 eV from the zero sum predicted by the transitivity rule.

In conclusion, several of the above tests revealed deviations from the general predictions of all linear models beyond the combined experimental uncertainty. From the magnitude of these deviations, we conclude that the effects ignored by the linear models are not negligible, but they do not affect each band discontinuity by more than 0.25 eV. In fact, their average magnitude, corresponding to the average accuracy limit underlying all linear models, appears close to 0.15 eV.

2. *Specific accuracy limits of each theoretical model*

The above tests confirmed that the accuracy of any linear model is necessarily limited. However, the predictions of each model do not necessarily achieve even the above accuracy limits. Therefore, specific tests of the predictions of each model are necessary to select the most accurate among them. Table II lists, together with our results, the ΔE_v's predicted by the different linear models for the interfaces we studied.

The most widely used band-discontinuity model is Anderson's electron-affinity rule. Recent photoemission experiments[37] in which the two electron affinities and ΔE_v were measured in the same system demonstrated the failure of this model in predicting the band discontinuity. In fact, the discrepancy between ΔE_v and the measured difference in the electron affinities was of the order of 0.5 eV. One routine difficulty in using Anderson's model is selecting the appropriate electron affinities from the wide range of values found in the literature for each semiconductor. Table II shows that even after making a "biased" selection of the published electron affinities that best fit our data the average accuracy is not better than 0.25 eV.

To analyze the correlation between theory and experiment in the case of the Frensley and Kroemer model, a plot of our results versus the theoretical predictions is shown in Fig. 7. The solid line is the line of perfect agreement. The correlation between our results and the model is not excellent, although the model does give reasonable predictions for some interfaces, e.g., GaP-Si. The average accuracy is about 0.4 eV, i.e., worse than the experimental uncertainty and above the underlying accuracy limit of all linear models. Corrections for the interface dipoles do not improve the agreement with our results. However, the model does reproduce recent XPS measurement of ΔE_v's for[26] GaAs-InAs and ZnSe-GaAs.[27] This suggests that the discrepancy between this theory and our data primarily arises from errors in the predicted E_v's for Ge and Si. In fact, if we move the predicted valence-band-edge energy position by 0.70 eV for Si and by 0.40 eV for Ge we improve the overall accuracy of the model bringing it to ~0.20 eV. Figure 8 shows a plot similar to that of Fig. 7 after including this empirical correction, and emphasizes the better correlation between theory and experiment.

Figure 9 shows a comparison between our results and Harrison's model. The correlation between our results and the predictions of the model is reasonable. However, the overall accuracy of the model is about 0.4 eV, i.e., again worse than the experimental uncertainty. Notice that the

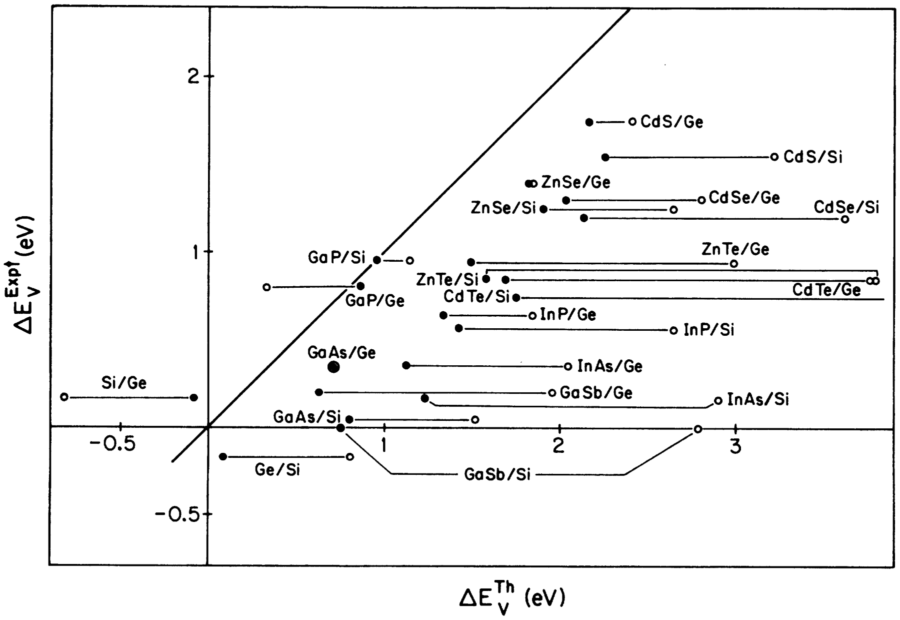

FIG. 7. Comparison between our experimental data and the predictions of the Frensley-Kroemer model (closed circles) (Ref. 7). The solid line is the line of perfect agreement. We also include in the plot a version of the model corrected for the local dipoles (open circles) (Ref. 7). In both cases there is limited correlation with our results.

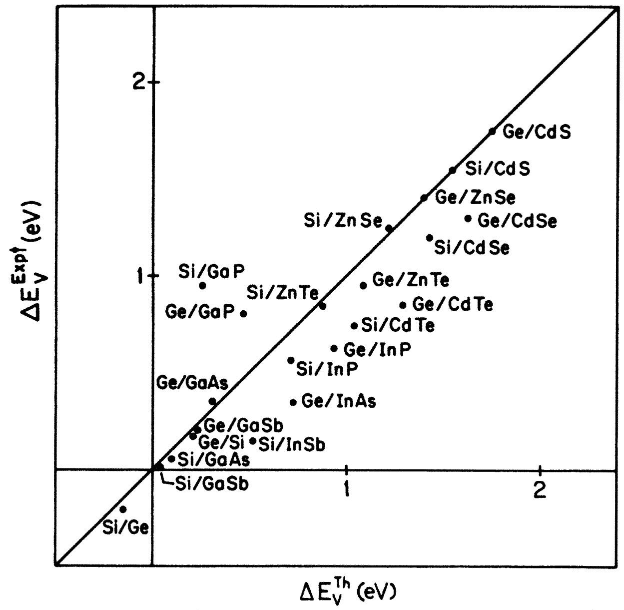

FIG. 8. Comparison between our data and an empirically corrected version of the Frensley-Kroemer model. The corrections are discussed in the text. Notice that the overall accuracy of the model is improved after the correction.

model successfully predicts the band discontinuities for lattice-matched interfaces, while it becomes much less accurate for lattice-mismatched interfaces. For example, the predicted ΔE_v's for GaAs-Ge and ZnSe-Ge, which exhibit good lattice matching, are in excellent correlation with the experimental findings. On the contrary, the predictions for InSb-Ge, GaSb-Ge, and CdTe-Ge which have very severe lattice mismatch are very far from the experimental results. This observation leads us to introduce a simple correction for interface relaxation[2] to compensate for the lattice mismatch. We assumed that the overlayer interatomic distance approaches the substrate interatomic distance, d, near the interface. As a result the calculated E_v for the overlayer changes at the interface because of the dependence of the interatomic matrix elements on the interatomic distances. This empirical correction substantially improved the accuracy of Harrison's model. In fact, similar improvements can be obtained by replacing the overlayer interatomic distance with the average of substrate and overlayer interatomic distances. Figure 10 shows a comparison between our experimental findings and the predictions of the model after substituting the overlayer interatomic distance with the substrate interatomic distance (open circles), or with the average of the overlayer and substrate interatomic distances (closed circles). The improvement with respect to Fig. 9 is evident. Notice in particular that the correction is successful in improving the model for lattice-mismatched interfaces, e.g., for InSb-Ge, GaSb-Ge, CdTe-Ge, CdTe-Si, and ZnTe-Si. The average accuracy of the model, after including either one of the above corrections, is improved to 0.15—0.2 eV.

Finally, we compared our results to the predictions of the Adam-Nussbaum model[9] and of the Von Ross model.[10] The average accuracy in reproducing our data is of the order of 0.4 eV for both models. This accuracy is comparable to the average accuracies of the Frensley-

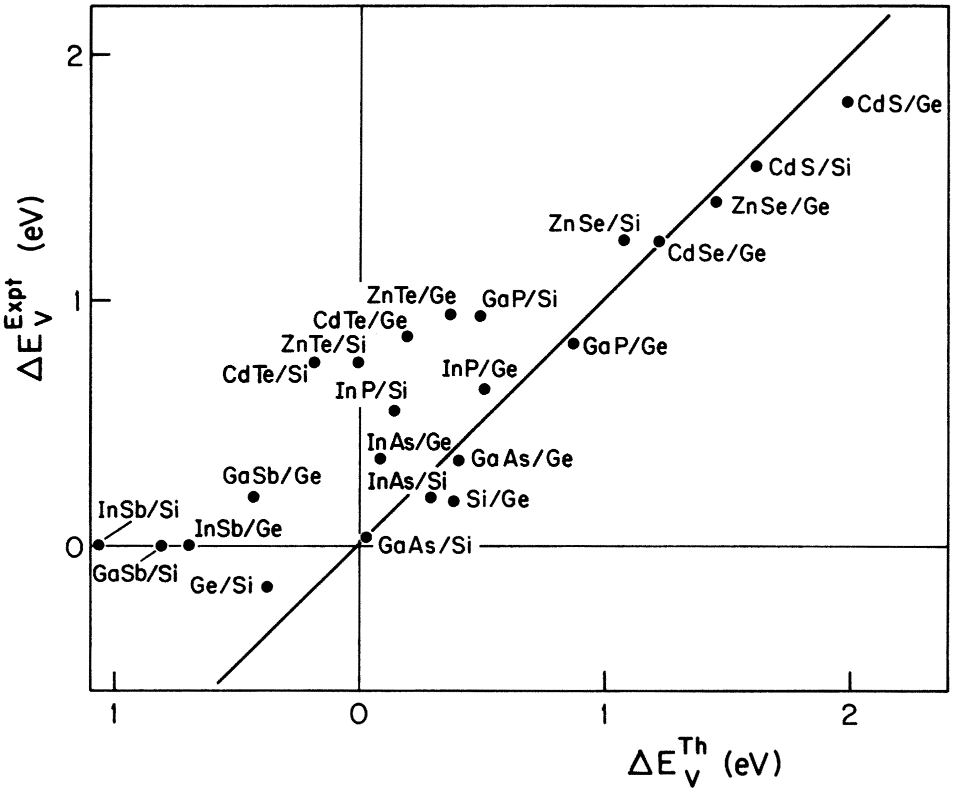

FIG. 9. Comparison between our results and the prediction of Harrison's model (Ref. 8). The average accuracy of the model is ~0.4 eV. Notice that the accuracy is better for lattice-matched interfaces, e.g., GaAs-Ge, than for lattice-mismatched interfaces, GaSb-Ge.

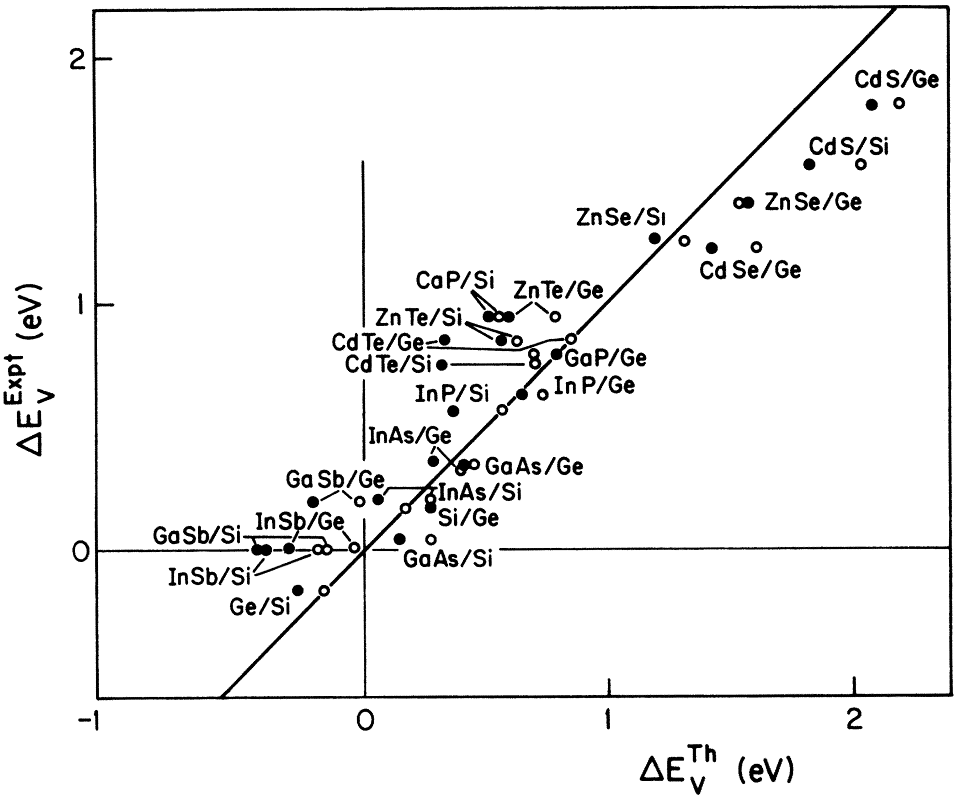

FIG. 10. Comparison between our results and empirically corrected versions of Harrison's model. The corrections are discussed in the text. Notice the improvement in accuracy for lattice-mismatched interfaces. The average accuracy of the model is close to 0.15 eV after the corrections.

Kroemer and Harrison models, but it is worse than the average accuracies of their empirically modified versions.

In summary, most current discontinuity models do not reproduce our results with an accuracy close to the empirically estimated general limits of all linear models. The best overall agreement is given by the empirically corrected versions of the models of Harrison and Frensley and Kroemer, which both reach an average accuracy of the order of 0.15—0.2 eV.

C. Empirical table to predict valence-band discontinuities

The accuracy limits estimated in the preceding section for the current discontinuity models are not sufficient for most applications in heterojunction-device research. In particular, the widely used electron-affinity rule is among the least accurate models. Even the most sophisticated theoretical calculations[16–19] do not provide the required accuracy. This led us[38,39] to develop an empirical method to estimate ΔE_v's, based on a table of experimentally deduced valence-band-edge positions of the semiconductors we studied. Table V lists empirical E_v's referred to the valence-band edge of Ge. The distance in energy between the valence-band edge of Ge and that of a given material X was estimated by taking the average of the ΔE_v of X-Ge and of the sum of the ΔE_v's of X-Si and Si-Ge. Whenever available, discontinuities measured with photoemission methods by other authors were considered, and an average

TABLE V. Empirical position in energy of the valence-band edge.[a]

Semiconductor	E_v
Ge	0.00
Si	−0.17
GaAs	−0.33[b]
GaP	−0.96
GaSb	−0.21
InAs	−0.33
InP	−0.69
InSb	−0.11
CdS	−1.73
CdSe	−1.33
CdTe	−0.88
ZnSe	−1.41[c]
ZnTe	−0.98

[a] Position in eV, referred to the valence-band edge of Ge. These positions were empirically estimated from the experimental ΔE_v's as discussed in the text (Ref. 38). The valence-band discontinuity at the interface between any two semiconductors listed in the table can be simply estimated by taking the difference of their empirical E_v's.

[b] Average value deduced from the data of Refs. 2, 20, 28, 34, and 37.

[c] Average value deduced from the data of Refs. 27 and 2.

of all the experimental ΔE_v's for each interface was used in estimating ΔE_v.[38] The value of ΔE_v for the interface between two materials listed in Table V can be simply estimated by taking the difference of their E_v's. We tested the accuracy of our empirical approach by reversing the procedure to develop the table, i.e., by using it to predict our results (notice that this is not a trivial test since the table is based on results by other authors as well as on our data). The accuracy was always better than 0.16 eV, and the average accuracy was of the order of 0.05 eV per interface. Therefore, the use of our empirical table gives a better average accuracy than all the models we tested. Attempts to use the table to predict band discontinuities between compound semiconductors[38] indicate that our empirical approach is close to the underlying average accuracy limits of all linear models as estimated above, 0.15 eV.

It should be emphasized that our approach is *not* a new theory. It is simply an optimized empirical table based on the "linearity" assumption. While it can be useful for practical uses, it does not provide an insight into the nature of the band discontinuities. This insight must be provided by theories based on physical assumptions, and the discussion in Secs. IV A–IV C clarifies to some extent what the important factors are influencing the band discontinuities. The success of the modified versions of the tight-binding and pseudopotential models, although limited, indicates that the absolute position of the bulk valence-band edges *is* an important factor in ΔE_v. The empirically determined accuracy limits which underlie all linear models indicate that "local" effects contribute to ΔE_v by no more than a few tenths of an eV. Of course, effects of this magnitude are important in a number of practical problems, and a satisfactory theory of the band discontinuities should be able to describe and predict them. Futher refinements of the "realistic" calculations of the interface electronic structure[16–19] are the only hope to solve this problem. The linear, i.e., "nonlocal" approaches—including our own empirical rule—cannot be improved beyond the estimated ~0.15-eV accuracy limit, which is not satisfactory for many applications. Further experiments are also necessary to detect the nature and magnitude of the local contributions to ΔE_v, thereby guiding the theoretical efforts to include these contributions in a satisfactory description of the band discontinuities.

D. Potential-barrier heights

The interface position of the Fermi level in the gaps of the two semiconductors determines the band bending on each side of the junction and therefore the potential-barrier height seen by carriers crossing the junction region. As already mentioned, there is a correspondence between the establishments of these barriers and the creation of the Schottky barrier at a metal-semiconductor interface.[39] Extensive experimental and theoretical work has clarified several important features of the Schottky-barrier formation process—but also created some controversy. There is general agreement that for interfaces between silicon and simple metals the Fermi level is pinned in its interface position by localized interface states, as indicated by photoemission and energy-loss experiments. For III-V metal interfaces the experiments are yielding apparently contradictory results.[39] On one hand, several interface properties exhibit a general dependence on the chemical parameters of the metal and of the semiconductor. For example, the Schottky-barrier heights on InP can assume either one of two possible values, depending on the interface reactivity. On the other hand, the Schottky barrier is generally established at a very early stage of formation of the metal overlayer, and it appears related to a limited number of pinning positions for E_F. These features were explained by Spicer and co-workers[11] in terms of their "defect model," which attributes the pinning of E_F to surface defects created by the metal chemisorption process on the semiconductor surface. The experimental basis and the theoretical implications of the above two results have been discussed in detail in a number of recent reviews,[39] which also propose possible ways to reconcile them. Therefore, we shall not give here a full discussion of those issues. The relevant points to our present results are that some of the above results find their counterparts in our present data on heterojunction interfaces.

Similar to silicon simple-metal interfaces, localized electronic states have been detected at the Si-Ge interface and theoretically explained in terms of Si-Ge chemisorption bonds.[25] However, this is the only heterojunction interface for which chemisorption-induced interface states are easily detected with angle-integrated photoemission. For the other interfaces we studied, the information on the local electronic states responsible for the Fermi-level pinning is indirect, and primarily given by the study of E_F as a function of the overlayer thickness.

One important point which was raised in support of the defect model[11] is that the pinning position of E_F for several III-V compounds appears independent of the nature of the overlayer. For example, for *n*-type GaAs several different kinds of overlayers were reported to pin the Fermi level ~0.75 eV above the top of the valence band. Mönch and Gant[40] found that the adsorption of Ge gives the same pinning positions of the Fermi level on GaAs as that of metal atoms, suggesting an extension of the defect model to heterojunction interfaces. This hypothesis is strengthened and generalized by our present results. The results of Table III show that the pinning positions for Ge or Si on *n*-type GaAs—as measured by Mönch *et al.*[34] for ordered or disordered Ge overlayers and by ourselves—are coincident with the above value of 0.75 eV within the experimental uncertainty. This observation is generalized by the results of Table III, which shows that the pinning position is the same for a given substrate, independent of the overlayer. This is consistent with the predictions of the defect model (which was originally developed for interfaces involving III-V compounds). However, the chemical properties of Ge and Si are too close to each other to consider this a very strong argument in favor of the defect model. The above similarity of the pinning positions on GaAs for different classes of overlayers remains the strongest indication from our work that the defect model could be extended to semiconductor-semiconductor interfaces.

Other features of the data in Table III are related to the defect model. It was suggested that the study of the chemical trends upon varying the substrate is an effective approach to study the nature of the Fermi-level-pinning defects.[41] Recently, Allen and Dow calculated the different energy levels for surface antisite defects on GaAs and GaP.[41] The calculated acceptor levels are not far from the pinning positions of E_F shown in Table III for n-type substrates. Much more interesting, however, is the fact that the distance between E_v and E_F changes on going from GaAs to GaP as qualitatively predicted by the theory.[41] These results, therefore, appear consistent with a role of surface antisite defects in the Fermi-level pinning. One interesting fact is that the theoretical results given by *interface* antisite defects show a much poorer correlation with the experimental data.

The Fermi-level pinning at heterojunction interfaces raises interesting questions about its correlation with the establishment of the band discontinuities. The pinning positions of E_F in the two gaps are trivially related to ΔE_v and ΔE_c. One could, therefore, propose a *gedanken* experiment in which the clean surfaces of the two semiconductors chemisorb just enough foreign atoms to reach the final pinning position of E_F (the real experiments show that less than 0.1 monolayer of foreign atoms are sufficient for most III-V substrates), and then they are brought together by aligning the E_F's to form the interface. In this approach, ΔE_v would be given, at least in first approximation, by the difference of the distances between the Fermi level and the valence-band edge for the two surfaces. There are of course some very fundamental problems with this *gedanken* experiment. For example, the defect levels—and therefore the pinning positions of E_F in the two gaps—could be substantially changed by the formation of the interface. However, many experiments have revealed that the pinning position of E_F, established at submonolayer coverage, does not change much in many cases when the overlayer grows thicker.[39] Interestingly enough, the difference between the pinning positions for GaAs and ZnSe reported in Table III gives ~1 eV, which coincides with the measured ΔE_v for the ZnSe-GaAs interface. Without further experimental tests, it is impossible to decide if this is just a coincidence. Otherwise, it could indicate that the above *gedanken* experiment is valid within reasonable limits, and it would explain why the empirical accuracy limit underlying all the linear discontinuity models, ~0.15 eV, is after all so surprisingly good. In that case, however, one would have to find an explanation for the agreement between our data and the ΔE_v's given by the modified tight-binding and pseudopotential models, as discussed in Sec. IV B.

V. SUMMARY

The main results of our systematic study are the following. The valence-band discontinuity and the interface Fermi-level-pinning positions were measured for Ge and Si overlayers on Si and Ge substrates and on 11 compound-semiconductor substrates. The measured ΔE_v's were used to empirically estimate an underlying, average accuracy limit of ~0.15 eV for all the linear discontinuity models. There are the models which express ΔE_v and ΔE_c as the difference of two terms related to the two semiconductors—and in particular the models most widely used in heterojunction research such as the electron-affinity rule.

We then used the experimental data to estimate the accuracy of each linear model without questioning *a priori* its theoretical soundness. The best average accuracy, 0.15–0.2 eV, was found for empirically modified versions of the Harrison model and of the Frensley-Kroemer model. We also proposed an empirical optimization of all linear models, based on the use of the terms in Table V which, in turn, were deduced from experimental ΔE_v's. This approach appears able to reach the general accuracy limits for linear models.

Some features in the measured pinning positions of E_F indicate that the basic assumption of a local-defect-related pinning mechanism could be extended from III-V–semiconductor-metal interfaces to heterojunction interfaces. We also raised the problem of the correlation between the band discontinuities and the pinning of E_F in the two gaps. However, a satisfactory treatment of this problem requires more experimental tests and a considerable amount of fundamental theoretical work.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grant No. DMR-82-00518. The experiments were made possible by the friendly and expert assistance of the staff of the University of Wisconsin Synchrotron Radiation Center (supported by the National Science Foundation, Grant No. DMR-80-20164). We are grateful to N. G. Stoffel for participating in these experiments and for critically reading the manuscript. R. R. Daniels and Te-Xiu Zhao actively helped us in the experimental work, and we had several illuminating scientific interactions with H. Kroemer, W. Harrison, W. R. Frensley, A. Nussbaum, R. S. Bauer, W. Mönch, R. W. Grant, E. A. Kraut, S. P. Kowalczyk, and P. Perfetti.

---

[1] A. D. Katnani, R. R. Daniels, Te-Xiu Zhao, and G. Margaritondo, J. Sci. Technol. 20, 662 (1982); A. D. Katnani, N. G. Stoffel, R. R. Daniels, Te-Xiu Zhao, and G. Margaritondo, J. Vac. Sci. Technol. A 1, 692 (1983).

[2] G. Margaritondo, A. D. Katnani, N. G. Stoffel, R. R. Daniels, and Te-Xiu Zhao, Solid State Commun. 43, 163 (1982).

[3] J. R. Waldrop and R. W. Grant, Phys. Rev. Lett. 26, 1686 (1978).

[4] R. W. Grant, J. R. Waldrop, and E. A. Kraut, Phys. Rev. Lett. 40, 656 (1979).

[5] J. R. Waldrop, S. P. Kowalczyk, R. W. Grat, E. A. Kraut, and D. L. Miller, J. Vac. Sci. Technol. 19, 573 (1981).

[6] R. L. Anderson, Solid State Electron. 5, 341 (1962).

[7] W. R. Frensley and H. Kroemer, Phys. Rev. B 15, 2642 (1977).

[8] W. Harrison, J. Vac. Sci. Technol. 14, 1016 (1977).

[9] M. J. Adam and Allen Nussbaum, Solid State Electron. 22, 783 (1979).

[10] Oldwig Von Ross, Solid State Electron. 23, 1069 (1980).

[11] W. E. Spicer, P. W. Chye, P. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. 16, 1422 (1979); W. E. Spicer, I. Lindau,

P. Skeath, and C. Y. Su, *ibid.* 17, 1019 (1980).

[12] A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972).

[13] W. G. Oldham and A. G. Milnes, Solid State Electron. 7, 153 (1964); J. Jerhot and V. Snejdar, Phys. Status Solidi A 34, 505 (1976).

[14] H. C. Card, J. Appl. Phys. 50, 2822 (1979).

[15] H. Kroemer, CRC Crit. Rev. Solid State Sci. 5, 555 (1975).

[16] G. A. Baraff, Joel A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. 38, 237 (1977).

[17] Warren Pickett, Steven G. Louis, and Marvin Cohen, Phys. Rev. Lett. 39, 109 (1977); Phys. Rev. B 17, 815 (1978).

[18] C. A. Swarts, W. A. Goddard, and T. G. McGill, J. Vac. Sci. Technol. 19, 551 (1981).

[19] J. Pollman and S. Pantelides, J. Vac. Sci. Technol. 16, 1498 (1979).

[20] P. Perfetti, D. Denley, K. A. Mills, and D. A. Shirley, Appl. Phys. Lett. 33, 66 (1978).

[21] R. S. Bauer and J. C. McMenamin, J. Vac. Sci. Technol. 15, 1444 (1978).

[22] W. Mönch and H. Gant, J. Vac. Sci. Technol. 17, 1094 (1980).

[23] D. Denley, K. A. Mills, P. Perfetti, and D. A. Shirley, J. Vac. Sci. Technol. 16, 1501 (1979).

[24] P. Zurcher, G. J. Lapeyre, J. Anderson, and D. Frankel, J. Vac. Sci. Technol. 21, 476 (1982).

[25] P. Perfetti, N. G. Stoffel, A. D. Katnani, G. Margaritondo, C. Quaresima, F. Patella, A. Savoia, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. B 24, 6174 (1981); G. Margaritondo, N. G. Stoffel, A. D. Katnani, H. S. Edelman, and C. M. Bertoni, J. Vac. Sci. Technol. 18, 290 (1981); G. Margaritondo, N. C. Stoffel, A. D. Katnani, and F. Patella, Solid State Commun. 36, 215 (1980).

[26] S. P. Kowalczyk, W. J. Schlaffer, E. A. Kraut, and R. W. Grant, J. Vac. Sci. Technol. 20, 705 (1981).

[27] S. P. Kowalczyk, E. A. Kraut, J. R. Waldrop, and R. W. Grant, J. Vac. Sci. Technol. 21, 482 (1982).

[28] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, Phys. Rev. Lett. 44, 1620 (1980). A comparison of the results of these authors with those obtained by linear extrapolation confirms the accuracy of the latter method quoted in the text.

[29] R. H. Williams, R. R. Varma, and V. Montegomery, J. Vac. Sci. Technol. 16, 1143 (1979).

[30] P. Skeath, I. Lindau, P. W. Chye, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. 16, 1143 (1979).

[31] L. J. Brillson, C. F. Brucker, N. G. Stoffel, A. D. Katnani, and G. Margaritondo, Phys. Rev. Lett. 46, 838 (1981).

[32] M. S. Daw and D. L. Smith, Phys. Rev. B 20, 5150 (1979); Appl. Phys. Lett. 36, 690 (1980).

[33] J. D. Dow and R. E. Allen, J. Vac. Sci. Technol. 20, 659 (1982).

[34] W. Mönch, R. S. Bauer, H. Gant, and R. Murschall, J. Vac. Sci. Technol. 21, 498 (1982).

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

[36] F. F. Fang and W. H. Howard, J. Appl. Phys. 35, 3 (1964).

[37] P. Zurcher and R. S. Bauer, J. Vac. Sci. Technol. A 1, 695 (1983).

[38] A. D. Katnani and G. Margaritondo, J. Appl. Phys. 5, 2522 (1983), and references therein.

[39] For a complete discussion of these problems and for further references see G. Margaritondo, Solid State Electron. 26, 499 (1983), or L. J. Brillson, Surf. Sci. Rep. 2, 123 (1982).

[40] W. Mönch and H. Gant, Phys. Rev. Lett. 48, 512 (1982).

[41] A. D. Katnani, G. Margaritondo, R. E. Allen, and J. D. Dow, Solid State Commun. 44, 1231 (1982).