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Low-temperature photoemission measurements of valence-band discontinuities at buried heterojunctions

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Synchrotron-radiation photoemission studies of CdTe-GaAs(110) heterojunctions prepared *in situ* were performed at room temperature and after the interface was cooled to 35 K. At room temperature we observe a valence-band offset $\Delta E_v = 0.20 \pm 0.07$ eV, together with band bending in opposite directions of the substrate and overlayer bands. After cooling to 35 K the synchrotron-radiation-induced saturation photovoltage yields flat-band conditions for the two semiconductors in the whole CdTe-coverage range explored (1-50 Å). A valence-band offset $\Delta E_v = 0.21 \pm 0.05$ eV could then be measured directly from the valence-band spectra. We conclude that photoinjection compensates the long-range component of the electrostatic potential across the junction, while the local interface dipole remains essentially invariant with temperature and photoinjected-carrier density. In these conditions, low-temperature photoemission becomes an ideal tool to study valence-band offsets at buried heterojunctions.

Photoemission spectroscopy has been very successful in providing a systematic picture of semiconductor heterojunction parameters.[1,2] One of the most commonly used methods to determine band discontinuities involves measurements of the position of the valence-band maximum and characteristic core levels for the semiconductor substrate prior to heterojunction formation, followed by layer-by-layer deposition of the semiconductor overlayer to build the heterostructure. Valence-band photoemission is used to determine the final position of the valence-band maximum in the overlayer, while the coverage-dependent position of the substrate and overlayer core levels is used to monitor band bending.

A major source of uncertainty is possible core line shape changes and binding energy shifts due to interface chemistry rather than band-bending variations. Furthermore, the relatively short photoemission sampling depth effectively prevents the study of heterojunctions "buried" below a few tens of angstroms from the surface since band-bending variations might go undetected in this case. For these reasons it would be desirable to measure band discontinuities in ideal flat-band conditions, which are, unfortunately, generally incompatible with thermodynamic equilibrium. Recently, low-temperature surface photovoltage effects[3,4] have been shown to produce steady-state conditions in which the band bending is reduced or eliminated at a number of semiconductor surfaces and metal-semiconductor interfaces. We selected the CdTe-GaAs(110) heterojunction as a test case, and present here synchrotron-radiation measurements of the valence-band offset and semiconductor band bending at room temperature and at 35 K. To our knowledge this is the first *in situ* photoemission study of the CdTe-GaAs(110) heterojunction, the first study of the temperature dependence of the CdTe-GaAs valence-band offset, and the first demonstration that a synchrotron-radiation-induced saturation photovoltage can be used to measure heterojunction parameters in flat-band conditions.

CdTe-GaAs heterostructures have been grown and studied by a number of authors in connection with $Hg_{1-x}Cd_xTe$-CdTe-GaAs infrared optoelectronic technology.[5,6] We employed an ultrahigh-vacuum CdTe deposition chamber connected through a gate valve to our photoelectron spectrometer.[7] GaAs(110) substrates were obtained by cleaving *n*-type Te-doped (10^{14} cm^{-3}) GaAs single-crystal posts in the photoelectron spectrometer (operating pressure 3×10^{-11} Torr). Only mirrorlike surfaces with unpinned Fermi levels (as judged from the photoemission core-level positions) were transferred to the deposition chamber (operating pressure less than 10^{-10} Torr) for heterojunction formation. CdTe was deposited from a single effusion cell. Due to the special sample holder employed in order to allow sample cooling, the GaAs substrate could not be heated above room temperature during growth. In these conditions, amorphous or polycrystalline CdTe layers are generally obtained and reflection-high-energy-electron-diffraction (RHEED) intensity oscillations are not observed.[7] Core photoemission intensities were used to monitor the stoichiometry of the deposits *vis-à-vis* of the evaporation material. A 1:1 Cd:Te stoichiometry was observed in all cases within an experimental uncertainty of (1-3)%. Since RHEED oscillations could not be monitored, the thickness of the CdTe overlayer was measured by means of a quartz thickness monitor, at a typical growth rate of 1 Å/min. At selected CdTe coverages growth was interrupted, and the sample transferred to the photoelectron spectrometer for photoemission characterization.

The photoemission measurements were performed in the angle-integrated mode in the $45 < h\nu < 110$ eV photon-energy range using radiation from the electron storage ring Aladdin at the Synchrotron Radiation Center of the University of Wisconsin-Madison, a 6-m toroidal grating monochromator, and a hemispherical analyzer. Overall energy resolution ranged from 0.2 to 0.3 eV.[7] For low-temperature measurements the sample holder was connected to a closed-cycle refrigerator by means of a copper braid and indium-coated clamps. The sample temperature was monitored using a Chromel-Alumel thermocouple calibrated by means of a silicon diode clamped to silicon test samples. Sample temperatures of 35 ± 5 K were reproducibly obtained with this experimental arrangement. At each CdTe coverage, angle-integrated photoelectron energy distribution curves for the valence band, Ga 3*d* and Cd 4*d* core levels[8] were obtained both at room temperature and upon cooling at 35 K. The sample was then reheated at room temperature, a new cleave was obtained to expose a pristine GaAs(110) surface, and the substrate was transferred back to the deposition chamber for a new deposition-measurement cycle.

In Figs. 1 and 2 we show energy distribution curves (EDC's) for the Ga 3*d* and Cd 4*d* core emission from CdTe-GaAs(110) at representative CdTe coverages (in angstroms). The EDC's have been normalized to the main emission feature, and the photoelectron intensity is given in arbitrary units as a function of the photoelectron kinetic energies.[9] Solid symbols in Figs. 1 and 2 correspond to the data obtained at room temperature, open symbols to those obtained at 35 K. The bottommost EDC in Fig. 1 shows the Ga 3*d* emission from the pristine GaAs(110) surface. The solid and dashed lines superimposed on these data show the results of a least-squares fit of the data in terms of a bulk (*B*) and surface (*S*) 3*d* doublet,[7] also shown (dotted line). At CdTe coverages of 1 and 5 Å we observe a shift of the Ga 3*d* core levels to higher kinetic energies (lower binding energies) in the room-temperature data, reflecting a progressive upward band bending of the GaAs bands[10] (vertical solid lines). The total shift of the Ga 3*d* core levels is 0.20 ± 0.05 eV in the 0–5 Å coverage range, as estimated from the peak position. Upon cooling at 35 K (open circles), the band-bending shift is consistently removed, and the Ga 3*d* core levels remain at the flat-band position (dashed vertical line) within an experimental uncertainty of 0.05 eV.

In Fig. 2 the Cd 4*d* core-levels measured at room temperature (solid circles) show a progressive shift to lower kinetic energies with CdTe coverage. The shift of 0.15 eV in the 1 to 50 Å coverage range (solid vertical lines) is consistent with a downward bending of the CdTe bands which more than compensates for the upward band bending of the GaAs substrate. Upon cooling (Fig. 2, open cir-

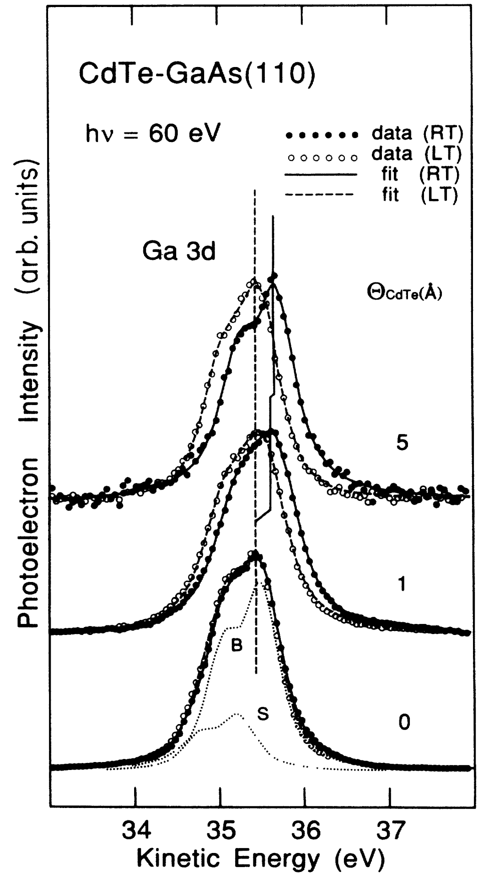

FIG. 1. Photoelectron energy distribution curves for the Ga 3*d* core emission at both room temperature (solid circles) and 35 K (open circles) for CdTe coverages of 0, 1, and 5 Å. The experimental data are shown superimposed on the result of a least-squares fitting procedure described in Ref. 10 (solid line, room temperature; dashed line, 35 K). The fit for the Ga 3*d* core emission prior to CdTe deposition contains a bulk and a surface contribution (dotted line). The vertical lines denote the peak position (solid lines, room temperature; dashed line, 35 K).

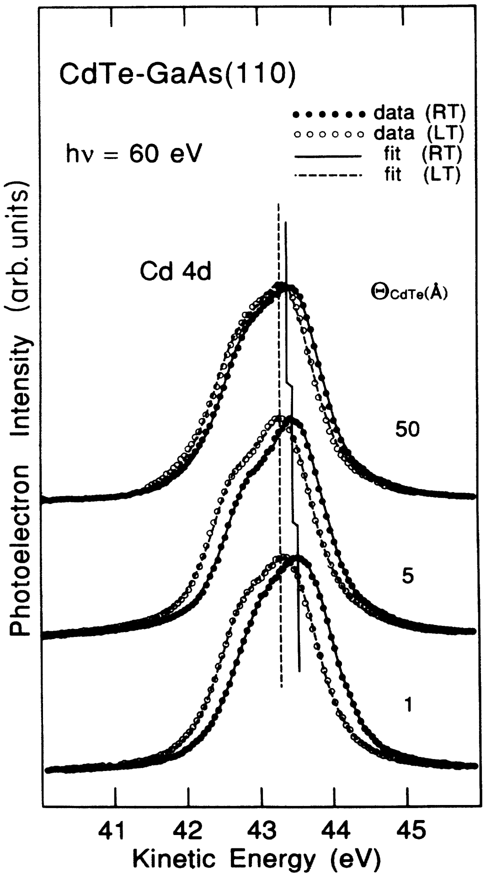

FIG. 2. EDC's for the Cd 4*d* core emission at room temperature (solid circles) and 35 K (open circles) for the CdTe coverages of 1, 5, and 50 Å. The experimental data are shown superimposed on the result of a least-squares fit (Ref. 10). The vertical lines denote the peak positions (solid line, room temperature; dashed line, 35 K).

cles) the Cd $4d$ core levels appear at the same position (dashed vertical line) within an experimental uncertainty of 0.05 eV, and no coverage-dependent downward band bending can be detected.

In Fig. 3 we show the valence-band emission prior to CdTe deposition, and for a CdTe thickness of 50.0 ± 0.1 Å, a thickness far exceeding the experimental sampling depth.[1] In Fig. 3(a), we show EDC's at room temperature, and in Fig. 3(b) we show results obtained upon cooling at 35 K. The spectra have been normalized to the main emission features, and are given in arbitrary units. The binding-energy scale is referred to the position of E_v in GaAs,[11] as determined from a linear extrapolation of the leading valence-band edge (also shown).

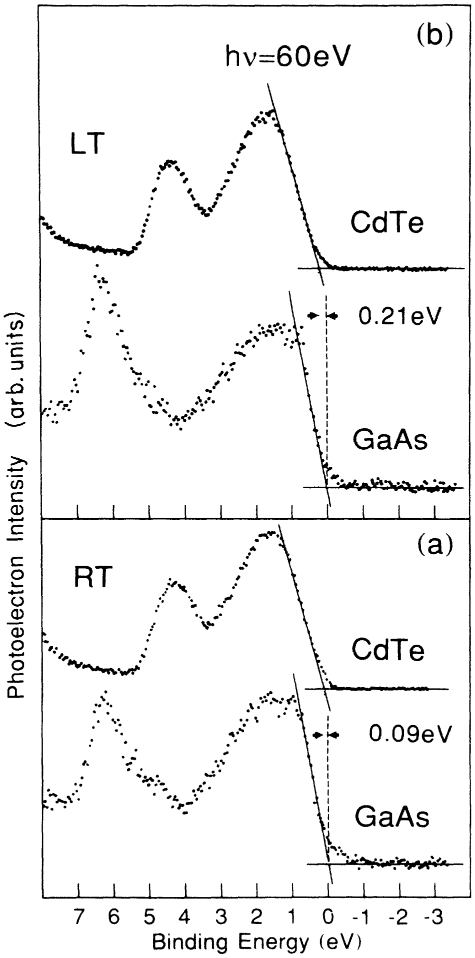

FIG. 3. (a) EDC's for the valence-band emission of GaAs(110) and a 50-Å CdTe overlayer on GaAs(110) at room temperature (RT). (b) EDC's for the valence-band emission of GaAs(110) and a 50-Å CdTe overlayer on GaAs(110) after cooling to 35 ± 5 K (LT). The valence-band maxima (denoted by vertical-dashed lines for GaAs and vertical-dotted lines for CdTe), determined through a linear extrapolation of the leading valence-band edge, are also shown. The energy separation of the valence-band maxima in (b) directly corresponds to the valence-band offset $\Delta E_v = 0.21 \pm 0.05$ eV, since at 35 K the interface is in nonequilibrium flat-band conditions due to a synchrotron-radiation-induced saturation photovoltage. The energy separation of the valence-band maxima at room temperature [0.09 eV in (a)] can be used to determine ΔE_v if one uses core-level results to determine the band bending. From the EDC's in Figs. 1 and 2 we derive $\Delta E_v = 0.20 \pm 0.07$ eV at room temperature.

At 35 K, since the band bending is removed, we can directly determine ΔE_v from the separation of the linearly extrapolated positions of E_v(GaAs) and E_v(CdTe) in Fig. 3(b) (dashed and dotted vertical lines, respectively). The resulting value of $\Delta E_v = 0.21 \pm 0.05$ eV is in remarkable agreement with the theoretical predictions of Anderson's model (0.22 eV, Ref. 12), the empirical deep-level model (0.23 eV, Ref. 13), and Harrison's tight-binding model (0.21 eV, Ref. 14).

At room temperature the energy separation of the linearly extrapolated positions of E_v [0.09 eV in Fig. 3(a)] does not give ΔE_v directly because of the presence of band bending. Using standard procedures,[15] we can express ΔE_v in terms of the position of the Ga $3d$ core levels relative to the valence-band maximum prior to CdTe deposition, the corresponding position of the Cd $4d$ core levels in the high CdTe-coverage limit, and the energy difference of the Ga $3d$ and Cd $4d$ core levels at the interface. Using subscripts CL and v for quantities pertaining to the core levels and valence-band maximum, respectively, we can write

$$\Delta E_v = [E_{\mathrm{CL}}(\mathrm{Ga}\ 3d) - E_v(\mathrm{GaAs})] - [E_{\mathrm{CL}}(\mathrm{Cd}\ 4d) - E_v(\mathrm{CdTe})] + \Delta E^0_{\mathrm{CL}}\,, \qquad (1)$$

where ΔE^0_{CL} is the Ga $3d$–Cd $4d$ binding-energy difference at the interface. The core separation ΔE^0_{CL} appears coverage dependent in the room-temperature results of Figs. 1 and 2. This type of phenomenon has been observed during formation of Ge-GaAs and Ge-InP interfaces (Ref. 2) and is associated with a reported coverage-dependent valence-band offset due to the gradual conversion of the vacuum/III-V interface to the amorphous Ge/III-V interface.[2] Along these lines, in Figs. 1 and 2, we would measure a core separation ΔE^0_{CL} of 7.97 ± 0.05 eV at a coverage of 1 Å, gradually decreasing to about 7.82 ± 0.05 eV at a coverage of 5 Å, and using Eq. (1) and the data of Figs. 1–3 (Ref. 16) we would derive a ΔE_v value that varies with coverage from 0.12 ± 0.07 to 0.27 ± 0.07 eV in the 1–5 Å CdTe-coverage range with an average value of 0.20 eV in the range. This interpretation, however, is in conflict with our low-temperature results of Figs. 1 and 2, which indicate that upon band-bending removal the core separation ΔE^0_{CL} remains constant at 7.87 ± 0.05 eV *at all coverages explored*, so that there is no gradual formation of the band offset. If we use the value of 7.87 eV for ΔE^0_{CL}, we obtain from Eq. (1) (Ref. 16) $\Delta E_v = 0.22 \pm 0.07$ eV, which is fully consistent with the low-temperature value determined in Fig. 3(b) and the average room-temperature value determined above. The implication is that there is no detectable coverage dependence nor temperature dependence of the valence-band offset in our results.

In conclusion, the mechanism for which electron-hole pairs excited by ambient light sources or by synchrotron radiation are separated by the built-in field at a surface or interface to produce a voltage is becoming quantitatively well understood.[3,4,17] This effect is enhanced at low temperature due to the increased junction resistance[17] so that a saturation photovoltage can be obtained to induce flat-band conditions. The present results show that the short-range variation of the electrostatic potential across semiconductor heterojunctions remains unchanged by this effect, so that low-temperature photoemission can be successfully used to determine valence-band offsets in nonequilibrium steady-state flat-band conditions. Correspondingly, we were able to measure $\Delta E_v = 0.21 \pm 0.05$ eV at buried CdTe-GaAs(110) heterojunctions and rule out any coverage dependence and temperature dependence of the valence-band offset within an experimental uncertainty of 0.07 eV.

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[8] Other accessible core levels included the As 3*d* and Te 4*d* cores. Since these appear partially superimposed on one another, they are not suitable for the type of analysis presented here. In any case, it has been pointed out that the cation core shifts are scarcely affected, in general, by interface chemistry and should be preferably used to monitor band bending. See A. D. Katnani and G. Margaritondo, Phys. Rev. B **28**, 1944 (1983).

[9] The coverage dependence of the integrated intensities of the Ga 3*d* and Cd 4*d* core levels, to be discussed in Ref. 7, show an exponential and complementary exponential dependence, respectively, on the CdTe coverage in quantitative agreement with that expected for layer-by-layer growth with no atomic interdiffusion.

[10] The solid and dashed line superimposed on the data in Figs. 1 and 2 have been obtained through a least-squares fit of the data to a superposition of Lorentzian functions convoluted with a Gaussian function. For the bottommost EDC's in Fig. 1 we used four Lorentzian functions to reproduce the surface and bulk-related Ga 3*d* doublets. The resulting fitting parameters (spin-orbit splitting, branching ratio, surface shift, Lorentzian and Gaussian widths, etc.) are in good agreement with values provided in the literature (Ref. 7). For the other Ga 3*d* results in Fig. 1 the reduced surface-doublet intensity allowed a good fit in terms of a single Ga 3*d* doublet. For the Cd 4*d* results in Fig. 2, the superposition of Te 5*s* and Cd 4*d* bulk and surface-related doublets made a deconvolution more difficult. We elected to use a single broadened 4*d* doublet for simplicity, so that the solid and dashed lines superimposed on the data in Fig. 2 should be considered only as a guide to the eye. See Ref. 7.

[11] The corresponding measured kinetic energies for E_v(GaAs) in Figs. 3(a) and 3(b) are 53.86 ± 0.05 and 53.75 ± 0.05 eV, respectively.

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[16] The average $E_{\rm CL}$(Ga 3*d*) $- E_v$(GaAs) from twenty mirrorlike cleaves was 18.44 eV. The average value of $E_{\rm CL}$(Cd 4*d*) $- E_v$(CdTe) from five 50-Å CdTe films deposited on GaAs was 10.35 eV.

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