# Nonmagnetic-semimagnetic semiconductor heterostructures: $Ge-Cd_{1-x}Mn_xTe(110)$

X. Yu,\* A. Raisanen,<sup>†</sup> G. Haugstad, N. Troullier, G. Biasiol, and A. Franciosi

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

(Received 16 June 1992; revised manuscript received 8 March 1993)

Synchrotron-radiation photoemission studies of heterovalent heterojunctions involving Ge and  $Cd_{1-x}Mn_xTe$  alloys (x = 0, 0.35, and 0.60) were performed on interfaces prepared *in situ* by Ge deposition on cleaved (110) semimagnetic semiconductor surfaces. The valence-band offsets  $\Delta E_v$  were obtained with consistent results through a nonlinear least-squares fit of the interface valence-band emission in terms of a superposition of valence-band spectra for the individual semiconductors, and with a more conventional method utilizing the Te 4d and Ge 3d core-level emission. We find valence-band offsets  $\Delta E_v = 0.80-0.83$  eV largely independent of semimagnetic composition and band gap. In the framework of the linear models of semiconductor heterojunction behavior, this result would indicate that CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te heterojunctions will follow the common anion rule.

### INTRODUCTION

Semiconductor heterostructures involving ternary semimagnetic semiconductors such as  $Cd_{1-x}Mn_x$  Te have been attracting increasing attention since the original idea of a spin superlattice.<sup>1</sup> Quantum wells where a semimagnetic semiconductor is coupled with a nonmagnetic counterpart of similar energy gap and conductionband electron effective mass will exhibit strong modification of the electronic properties in a magnetic field due to the large difference in the electronic g factors of the two materials.<sup>2,3</sup> For example, the spin splitting of electronic states in semimagnetic semiconductors may be two orders of magnitude greater than in the adjacent nonmagnetic layer<sup>2,4</sup> and comparable to the ionization energy of shallow impurities. The consequent tunability of the depth of the quantum wells by the magnetic field may give rise to phenomena such as enhancement of electronic g factors in shallow nonmagnetic wells surrounded by semimagnetic barriers, magnetically induced transitions from type-I to type-II superlattice,<sup>5</sup> boil-off and freeze-out of electrons to and from quantum wells, and selective spin tunneling across the barriers.<sup>2,3</sup>

Observation of the magnetic effects described above is crucially dependent on the presence of heterojunction band discontinuities of suitable magnitude. For most nonmagnetic-semimagnetic (NM-SM) heterojunctions, however, no information is available at present about conduction- and valence-band offsets. Even for the most studied NM-SM heterojunction system, CdTe- $Cd_{1-x}Mn_xTe$ , the situation is somewhat unclear. Photoluminescence results in external magnetic fields have been interpreted<sup>6</sup> as indicating a valence-band discontinuity  $\Delta E_v = 25 \text{ meV}$  (for x = 0.24, 0.6% lattice mismatch), corresponding to a conduction- to valence-band offset ratio  $\Delta E_c / \Delta E_v$  of about 14:1 or  $\Delta E_v = 6.7\%$  of the band-gap energy difference  $\Delta E_g$ . This would imply that the valence-band discontinuity for a hypothetical strain-free case is virtually zero. $^{6,7}$  However, a magnetic-fieldinduced type-I to type-II transition in CdTe-Cd<sub>0.93</sub>Mn<sub>0.07</sub>Te superlattices (0.2% strain) has been recently interpreted in terms of a valence band offset of up to 20% of the band-gap energy difference.<sup>5</sup>

A study of NM-SM heterojunction band offsets by means of photoemission spectroscopy seems therefore timely. Photoemission spectroscopy has clarified in the past many of the systematic trends in heterojunction behavior<sup>8</sup> and can in favorable cases directly visualize the band offset in the valence-band spectra.<sup>9,10</sup> We selected as a first test case the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te system for a number of reasons. Systematic studies exist of Ge deposition on a variety of semiconductors,<sup>11</sup> including CdTe.<sup>12</sup> Amorphous layers can be easily obtained through deposition at room temperature, so that the overlayer is unstrained.<sup>11</sup> At the same time, epitaxial Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te structures are likely to be the first NM-SM heterostructure involving a group-IV material to be synthesized, since epitaxial CdTe layers have been successfully grown with both (100) and (111) orientation<sup>13,14</sup> on GaAs(100), which is lattice-matched to Ge. The Ge-CdTe valenceband offset is also known to be large,<sup>12</sup> so that direct visualization of the offset by photoemission may be possible.

Photoemission measurements of the valence-band offset for Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te interfaces prepared in situ with x=0, 0.35, and 0.60 were conducted using two different methods. We used the initial (Ge coverage  $\theta = 0$ ) and final ( $\theta > 20$  Å) positions of the valence-band maximum, together with the variation in Ge 3d and Te 4d core separation as a function of coverage to obtain  $\Delta E_v$ . We also used a new fitting procedure to visualize  $\Delta E_v$  directly from the interface valence-band emission. The valence-band offset was found to be independent of the semimagnetic ternary composition within experimental uncertainty. Given a maximum change in the valence-band offset in the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te series of only 0.03 eV, application of the transitivity rule of heterojunction behavior would yield an upper limit of only 6.5% of the band-gap energy difference for  $\Delta E_v$  in CdTe- $Cd_{1-x}Mn_xTe$ .

4545

## **EXPERIMENTAL DETAILS**

The  $Cd_{1-x}Mn_xTe$  crystals used in the present studies were grown at Purdue University through a modified Bridgmann method, and characterized through x-ray diffraction and x-ray microprobe analysis as to crystallographic phase and composition. The same samples were used in studies of the bulk electronic structure of  $Cd_{1-x}Mn_xTe$  semiconductors (Refs. 15 and 16) and metastable  $Cd_{1-x}Mn_xTe$  alloy formation through Mn-CdTe thin-film reaction.<sup>17</sup> All results presented here were obtained on single-phase single crystals (x = 0, 0.35, and 0.60) cleaved in situ in a photoelectron spectrometer. Operating pressure was  $<5 \times 10^{-11}$  Torr. Heterojunctions were synthesized by depositing Ge in situ from a tungsten basket evaporator onto mirrorlike cleavage surfaces kept at room temperature. In these conditions amorphous Ge overlayers are known to form.<sup>12</sup> The Ge coverage  $\theta$  (in Å) was monitored by means of a quartz microbalance. The pressure during deposition never exceeded  $5 \times 10^{-10}$  Torr.

Angle-integrated photoemission measurements were performed as a function of Ge overlayer thickness in the 1-20-Å range. Synchrotron radiation from the 1-GeV electron storage ring Aladdin at the Synchrotron Radiation Center of the University of Wisconsin-Madison was monochromatized by means of a 3-m toroidal grating monochromator and focused onto the samples. Photoelectrons were collected at an average emission angle of 45° by means of a commercial hemispherical energy analyzer. Angle-integrated photoelectron energy distribution curves (EDC's) were recorded with an overall energy resolution (electrons and photons) ranging from 0.2 to 0.3 eV in the photon-energy range from 45 to 110 eV, as determined from the width of the Fermi cutoff in spectra from metallic standards deposited in situ onto the sample.

### **RESULTS AND DISCUSSION**

In Fig. 1 we show representative EDC's for the valence-band emission from Ge-CdTe(110), Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te(110), and Ge-Cd<sub>0.40</sub>Mn<sub>0.60</sub>Te(110) interfaces for Ge coverages  $\theta$  (shown to the right of each spectrum) in the 1–5-Å range, at a photon energy of 80 eV. The bottom-most spectrum of each series shows the valence-band emission from the cleaved substrate surface prior to Ge deposition. The zero of the binding-energy scale was taken at the position of the substrate valence-band maximum  $E_v$ , as estimated from a linear extrapolation of the leading valence-band edge.

A word of caution is required when measuring the valence-band offset between an amorphous and a crystalline semiconductor. Electronic-structure calculations have shown that several characteristics of the electronenergy spectrum of semiconductors are sensitive to topological disorder.<sup>18</sup> In particular, it is possible to define a valence and a conduction band for amorphous semiconductors, but the corresponding density of states (DOS) may differ substantially from those of the corresponding



FIG. 1. Photoelectron energy distribution curves for the valence-band emission from  $\text{Ge-Cd}_{1-x}\text{Mn}_x\text{Te}(110)$  interfaces for x = 0 (bottom), 0.35 (midsection), and 0.60 (top) at a photon energy of 80 eV. Ge coverages  $\theta$  in Å are shown to the right of each spectrum. The bottom-most spectrum of each series shows the valence-band emission from the cleaved substrate surface prior to Ge deposition. The zero of the binding-energy scale was taken at the position of the substrate valence-band maximum  $E_v$ , as estimated from a linear extrapolation of the leading valence-band edge. The topmost EDC (20-Å coverage) is representative of the bulk amorphous Ge valence-band emission.

crystalline semiconductors. The general trend, as observed by photoemission spectroscopy, is a smearing of the DOS structure;<sup>18</sup> for the valence band of amorphous Ge (and similarly for amorphous Si and C), this results mainly in a broadening of the double structure occurring some 7-10 eV below the top of the valence-band maximum of crystalline Ge (Refs. 19 and 20) and associated with the six-membered rings in the diamond structure.<sup>20</sup> In addition, it is difficult to define unequivocally a band gap in the amorphous material, because of the existence of states in the gap that above a characteristic energy are increasingly delocalized in r space.<sup>18</sup> Finally, photoemission measurements have shown that the electron density of states of amorphous Ge depends on the growth conditions, such as the substrate temperature<sup>21</sup> and the angle between the source and the sample normal.<sup>22</sup> Therefore, the magnitude of the band gap is not a well-defined physical constant. From a phenomenological point of view, photoelectron spectroscopy allows one to locate a valence-band edge,<sup>12</sup> but determination of the corresponding band-gap discontinuity and conduction-band offset remains difficult. In what follows we will discuss the systematics of the valence band offsets in Ge- $Cd_{1-x}Mn_xTe$  interfaces by using the photoemissiondetermined phenomenological position of the valenceband maximum.

The Ge coverage range in Fig. 1 was selected to emphasize emission from both substrate and overlayer features. At higher coverages the valence-band emission converges rapidly to a bulklike amorphous Ge emission. This is illustrated by the topmost EDC in Fig. 1, obtained upon deposition of 20 Å of Ge on  $Cd_{0.40}Mn_{0.60}Te$  and representative of elemental Ge.<sup>12,23</sup>

The valence-band emission from CdTe(110) (the bottom-most EDC) reflects the major Te p-derived density-of-states feature in the 0-3-eV binding-energy range, and the smaller DOS feature with mixed Cd s – Te p character in the 3-5-eV range. Upon Ge deposition, Ge-related states give rise to a shoulder on the lowbinding-energy side of the main DOS feature. By  $\theta = 5$ Å, a new Ge-derived leading valence-band edge is clearly visible below the original CdTe valence-band edge. Analogous results are shown in the midsection of Fig. 1 for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te(110). The spectrum for the ternary semimagnetic substrate prior to Ge deposition shows the emergence of a new emission feature located some 3.5 eV below  $E_v$  relative to CdTe.<sup>15,24,25</sup> This structure becomes the dominant valence-band feature in  $Cd_{0,40}Mn_{0,60}Te$  and is primarily due to the 3d emission from substitutional Mn atoms in the spin-polarized  $d^{5}sp$ configuration.<sup>15,17</sup> All of the spectra for  $\theta = 5$  Å in Fig. 1, irrespective of the substrate, exhibit a second Ge-induced valence-band edge below the original substrate DOS.

The qualitative trends in Fig. 1 suggest that the valence-band emission from the interface is, to a first approximation, simply a superposition of substrate-related and overlayer-related valence-band spectra. The exponential attenuation observed for all substrate core features as a function of Ge coverage (not shown) also argues against interface reactions and the formation of new mixed phases. We therefore attempted to fit the experi-

mental interface spectra in Fig. 1 to a superposition of substrate and elemental Ge emission. The results are shown in Fig. 2 for the three interfaces at a Ge coverage of 5 Å. EDC's prior to Ge deposition (dashed line) were selected for each interface to represent the substrate emission. EDC's at Ge coverages  $\theta > 20$  Å were selected to represent the bulk Ge emission (dotted line). The experimental data in the region of the leading valence-band edge (solid circle) were fitted to a superposition of substrate and overlayer spectra. A nonlinear least-squares fit, implementing a modified Levenberg-Marquardt algorithm,<sup>26</sup> was performed as a function of two parameters, namely, the relative amplitude and energy offset of substrate and overlayer EDC's. The result of the best fit is



FIG. 2. Fit of selected experimental interface spectra from Fig. 1 (solid circles) in terms of a superposition of  $Cd_{1-x}Mn_x$  Te (dashed line) and elemental Ge (dotted line) valence-band spectra. A nonlinear least-squares fit was performed as a function of the relative amplitude and energy offset of substrate and overlayer EDC's. The result of the best fit is shown by the solid line superimposed on the experimental data for each interface. The resulting offset between the linearly extrapolated values of the valence-band maxima for substrate and overlayer spectra was found to be 0.80 eV for Ge-CdTe, 0.83 eV for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te, and 0.81 eV for Ge-Cd\_{0.40}Mn<sub>0.60</sub>Te. The uncertainty of the systematic variation of the offset in the series is 0.03 eV; on each individual value it is 0.07 eV.

also shown in Fig. 2 as the solid line superimposed on the data.

The best fits in Fig. 2 were obtained for similar values of the relative amplitude and shift. In particular, the offset between the linearly extrapolated values of  $E_v$  for substrate and overlayer spectra was found to be 0.80 eV for Ge-CdTe, 0.83 eV for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te, and 0.81 eV for Ge-Cd<sub>0.40</sub>Mn<sub>0.60</sub>Te. The reliability of the results is demonstrated by the consistent value of the offset obtained for each sample at different Ge coverages.<sup>27</sup> The reliability of the procedure is also supported by the values of the Ge-substrate relative intensity obtained from the fit, which closely matched (within  $\pm 5\%$ ) the values expected from the observed Ge 3d-Cd 4d and Ge 3d-Te 4d integrated core intensity ratios (not shown).

The experimental uncertainty of the valence-band offsets determined through the above procedure has two components. First, there is the uncertainty deriving from the fitting procedure, which is of the order of the smallest variation in parameter space which gives comparable total least-squares differences. This was estimated at  $\pm 0.02$ eV, and affects the systematic variation of the valenceband offset in the Ge-CdTe, Ge-Cd $_{0.65}$ Mn $_{0.35}$ Te, and Ge- $Cd_{0.40}Mn_{0.60}$ Te series. The measured valence-band offset is therefore quantitatively consistent in the series within experimental uncertainty. In addition, there is a substantial experimental uncertainty which derives from the determination of the position of  $E_v$  through a linear extrapolation of the leading valence-band edge of substrate and overlayer spectra. We estimate the corresponding combined uncertainty at  $\pm 0.07$  eV (Ref. 16). Such a higher uncertainty affects the numerical value of each single offset, but does not affect the variation of the offset in the series, because of the cancellation of possible systematic errors due to the linear-extrapolation method.

Since the procedure explored in Fig. 2 is new, we elected to compare its results with those of a more conventional method to evaluate band offsets. Conventional photoemission determinations of the valence-band offset would rely on the measured position of a characteristic substrate core level  $E_{cl}$  (CdTe) relative to the valence-band maximum  $E_v$  prior to Ge deposition, the position of a Ge core level  $E_{cl}$  (Ge) relative to the valence-band maximum in thick overlayers, and the energy difference  $\Delta E_{cl}$  of the Cd and Ge core levels at the interface obtained following deposition of thin overlayers onto the substrate:<sup>8,28,29</sup>

$$\Delta E_v = [E_{cl}(\mathbf{Ge}) - E_v(\mathbf{Ge})] - [E_{cl}(\mathbf{CdTe}) - E_v(\mathbf{CdTe})] - \Delta E_{cl} .$$
(1)

Since in this picture the core levels are used as markers of the position of the bulk electronic states and to monitor band bending, care must be taken to select core levels which are not modified by chemical bonding at the interface and reflect the bulk environment. In Fig. 3 we show representative EDC's for the Te 4d emission and the Ge 3d core emission (solid circles) from Ge-CdTe (110) at a photon energy of 57 eV as a function of Ge coverage. It can be seen that while the Te 4d line shape remains unchanged in Fig. 3 and exhibits only a rigid shift of 0.13 eV (from  $\theta=0$  to 5 Å) to higher kinetic energies (lower binding energies), the Ge 3d line shape changes dramatically with increasing coverage, suggesting that a portion of the Ge atoms is affected by the interface environment. The Cd 4d line shape (not shown) exhibits only minor changes in the same coverage range, with a rigid shift to lower binding energies consistent with that of the Te 4d cores. However, at higher coverages evidence of small amounts of segregated or alloyed Cd is found. We associate the rigid shift of the substrate core levels to a Geinduced change in band bending, and elect to use the Te 4d core levels to evaluate  $\Delta E_n$  through Eq. (1).



FIG. 3. EDC's for the Te 4d emission and the Ge 3d core emission (solid circles) from Ge-CdTe(110) at a photon energy of 57 eV as a function of Ge coverage. The Te 4d line shape remains unchanged, and exhibits only a band-bending-related rigid shift to higher kinetic energies (lower binding energies), in agreement with an analogous behavior of the Cd 4d core levels (not shown). The Ge 3d line shape changes with increasing coverage. We obtained good fits of the Ge 3d line shape (solid line) in terms of interface-related and bulk-related 3d doublets. The individual doublets resulting from the fit are also shown, shifted downward for clarity. From the coverage-dependent core-level position and the initial ( $\theta = 0$ ) and final positions ( $\theta = 20$  Å) of the valence-band maxima, we determined a valence-band offset of  $0.81\pm0.07$  eV for Ge-CdTe(110). With an analogous procedure, we obtained offsets of 0.85±0.07 eV for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te(110), and  $0.85 {\pm} 0.07$ eV for Ge- $Cd_{0.40}Mn_{0.60}Te(110).$ 

A coverage-dependent change in the Ge 3d line shape has been observed during Ge deposition on III-V semiconductors.<sup>30</sup> A deconvolution of the Ge 3d core emission in terms of interface-related and bulk-related contributions proved necessary to obtain reliable Ge-III-V valence-band offsets.<sup>29</sup> Along the same lines, we obtained good fits of the overall Ge 3d line shape in terms of two spin-orbit split 3d doublets. Each doublet comprised Gaussian-convoluted Lorentzian functions. Position, intensity, branching ratio, and spin-orbit splitting of each doublet, together with the Gaussian and Lorentzian width of each core level, were treated as fitting parameters and determined through a least-squares minimization.<sup>31,32</sup> The result of the fit is shown in Fig. 3 by the solid line superimposed on the experimental points. The individual doublets resulting from the fit are also shown, shifted downward for clarity.

At a Ge coverage of 1 Å, the dominant contribution to the Ge 3d emission comes from Ge atoms directly bound to the CdTe surface. A second, smaller Ge 3d doublet shifted by 0.36 eV to lower binding energies reflects the development of the bulk Ge band structure and becomes dominant at coverages  $\theta > 3$  Å. With increasing Ge coverage, the two Ge 3d doublets shift rigidly to lower binding energy by 0.29 eV (from  $\theta = 1$  to 20 Å), while maintaining a constant separation. We associate the rigid shift of Te 4d, Cd 4d, and Ge 3d features to a Ge-induced band-bending variation. We used the position of the bulk-related Ge 3d doublet in Fig. 3 to determine the core-level separation  $\Delta E_{cl}$  in Eq. (1). With this procedure we calculated  $\Delta E_v = 0.81 \pm 0.07$  eV for Ge-CdTe(110).

Results analogous to those depicted in Fig. 3 were obtained for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te and Ge-Cd<sub>0.40</sub>Mn<sub>0.60</sub>Te interfaces. Through a line-shape analysis of the Ge 3d line shape, we obtained  $\Delta E_v = 0.85 \pm 0.07$  eV for Ge-Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te(110), and  $\Delta E_v = 0.85 \pm 0.07$  eV for Ge-Cd<sub>0.40</sub>Mn<sub>0.60</sub>Te(110). The two methods to determine the valence-band offsets yield, therefore, quite similar results, with a maximum discrepancy of 0.04 eV for Ge-Cd<sub>0,40</sub> $Mn_{0,60}$ Te(110). There is good agreement between the value of the offset obtained here for Ge-CdTe  $(0.81\pm0.07 \text{ eV})$  and that reported earlier by Katnani and Margaritondo<sup>12</sup> ( $0.85\pm0.10 \text{ eV}$ ).

Any determination of  $\Delta E_n$ , through Eq. (1) may in principle require corrections when residual strains are present in the overlayer. Tersoff and Van de Walle pointed out<sup>33</sup> that the effect of strain on the position of the core levels relative to the valence-band maximum should be carefully evaluated. The position of the core levels in the overlayer will change due to hydrostatic and uniaxial effects. The separation between the core levels and the centroid of the valence bands at  $\Gamma$  in the Brillouin zone is only influenced by hydrostatic strain. Conversely, uniaxial strain removes the valence-band degeneracy at  $\Gamma$  and modifies the position of the spin-split band, but does not shift the centroid.<sup>34</sup> The resulting required correction to the core position might be quite large. For example, Schwartz et al.<sup>34</sup> estimated a strain-related correction between 0.39 and 0.52 eV for Si-Ge(100) (4.0% in-plane strain), and we obtained<sup>35</sup> corrections of 0.44 and 0.45 eV

for Si-GaAs(100) and Si-AlAs(100), respectively (4.1%) and 4.2% in-plane strain), based on an extrapolation of the results of Yu *et al.*<sup>36</sup>

The method of valence-band-offset determination illustrated in Fig. 2 is, instead, far less affected by possible residual strains in the overlayer.<sup>37</sup> For the Ge- $Cd_{1-x}Mn_x$  Te interface series examined, we obtained consistent results with the two methods, and this supports the presence of complete strain relaxation in the Ge overlayer as a result of the amorphous nature of the overlayer.<sup>12</sup> We emphasize that the large lattice mismatch between Ge and  $Cd_{1-x}Mn_x$  Te (>14%) also promotes complete strain relaxation at the lowest coverages explored, in analogy to what has been found for CdTe(100)-GaAs(100).<sup>13,14</sup>

The existence of a common value of the valence-band offset for the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te heterojunctions examined is especially interesting, since the band-gap energy difference  $\Delta E_g$  varies widely in the series, because of the increase of the band gap of Cd<sub>1-x</sub>Mn<sub>x</sub>Te with x. The band gap of the alloy is 1.47, 1.93, and 2.13 eV for the three compositions (x = 0, 0.35, and 0.60) examined. As a consequence, the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te systems must exhibit large variations in the valence-band percentile contribution to the band-gap difference, a behavior that is relatively uncommon in semiconductor heterostructures.<sup>8</sup>

The observed systematics of the band offset in Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te can be used to infer the behavior of the band offset in the CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te system. Using the transitivity rule of heterojunction behavior, the CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te band offset can be inferred from the variation of the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te band offset. The transitivity rule states that, given two semiconductors A and B and a third semiconductor C, the valence-band offset satisfies the relation

$$\Delta E_v(A,B) = \Delta E_v(A,C) - \Delta E_v(B,C) . \qquad (2)$$

This transitivity has been experimentally verified for a number of semiconductors, within an accuracy of 0.1-0.15 eV.<sup>11</sup> If we use Eq. (2) to infer the CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te band offsets from the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te experimental results, we find  $\Delta E_v$  (CdTe, Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te) =  $\Delta E_v$  (CdTe, Ge) -  $\Delta E_v$  (Ge, Cd<sub>0.65</sub>Mn<sub>0.35</sub>Te) = 0.03 eV in modulus, and, similarly,

$$\Delta E_v(CdTe, Cd_{0.40}Mn_{0.60}Te) = 0.01 \text{ eV}$$
.

This suggests that, unlike most of the binary-ternary alloy heterojunctions studied to date, this system may follow closely the common anion rule of heterojunction behavior.<sup>8</sup> We can derive an upper limit for the valenceband contribution to the band-gap difference in CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te as

$$0.03/(1.93-1.47)=6.5\%$$
.

Such an estimate is in good agreement with those proposed by Chang *et al.*<sup>6</sup> and Nurmikko<sup>7</sup> and somewhat at variance with that proposed by Deleporte *et al.*<sup>5</sup>

#### CONCLUSIONS

The band discontinuities in nonmagnetic-semimagnetic Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te(110) semiconductor heterojunctions involving amorphous relaxed overlayers were determined by means of high-resolution synchrotron-radiation photoemission spectroscopy for different values of the Mn concentration x. The two different analysis methods employed point both to a valence-band offset largely independent of semimagnetic composition and band gap in the series. Consequently, because of the 0.66-eV variation in the Cd<sub>1-x</sub>Mn<sub>x</sub>Te band gap with increasing x from 0 to 0.6, the valence- and conduction-band contributions to the band-gap difference  $\Delta E_g$  for GeCd<sub>1-x</sub>Mn<sub>x</sub>Te vary considerably with x.

The observed independence of the Ge-Cd<sub>1-x</sub>Mn<sub>x</sub>Te valence-band offset on x suggests the CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te heterojunctions may follow the common anion rule of heterojunction behavior. This is somewhat surprising, since the rule does not appear to work for other common

- \*Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831.
- <sup>†</sup>Present address: Xerox Corporation, Webster Research Center, Webster, NY 14580.
- <sup>1</sup>M. von Ortenberg, Phys. Rev. Lett. 49, 1041 (1982).
- <sup>2</sup>J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).
- <sup>3</sup>G. Y. Wu, D. L. Smith, C. Mailhiot, and T. C. McGill, Appl. Phys. Lett. **49**, 1551 (1986).
- <sup>4</sup>Diluted Magnetic Semiconductors, edited by J. K. Furdyna and J. Kossut, Semiconductors and Semimetals, Vol. 25 (Academic, New York, 1988).
- <sup>5</sup>E. Deleporte, J. M. Berroir, G. Bastard, C. Delalande, J. M. Hong, and L. L. Chang, Phys. Rev. B **42**, 5891 (1990).
- <sup>6</sup>S.-K. Chang, A. Nurmikko, J.-W. Wu, L. A. Kolodziejski, and R. L. Gunshor, Phys. Rev. B 37, 1191 (1988).
- <sup>7</sup>A. V. Nurmikko, Surf. Sci. **196**, 632 (1988).
- <sup>8</sup>Heterojunction Band Discontinuities, Physics and Device Applications, edited by F. Capasso and G. Margaritondo (North-Holland, Amsterdam, 1987).
- <sup>9</sup>G. Margaritondo, C. Quaresima, F. Patella, F. Sette, C. Capasso, A. Savoia, and P. Perfetti, J. Vac. Sci. Technol. A 2, 508 (1984).
- <sup>10</sup>G. Margaritondo and A. Franciosi, Annu. Rev. Mater. Sci. 14, 67 (1984).
- <sup>11</sup>A. D. Katnani, Heterojunction Band Discontinuities, Physics and Device Applications (Ref. 8), p. 115.
- <sup>12</sup>A. D. Katnani and G. Margaritondo, Phys. Rev. B 28, 1944 (1983).
- <sup>13</sup>Y. Gobil, J. Cibert, K. Saminadayar, and S. Tatarenko, Surf. Sci. 211/212, 969 (1989); E. Ligeon, C. Chami, R. Danielou, G. Feuillet, J. Fontenille, K. Saminadayar, A. Ponchet, J. Cibert, Y. Gobil, and S. Tatarenko, J. Appl. Phys. 67, 2428 (1990).
- <sup>14</sup>F. A. Ponce, G. B. Anderson, and J. M. Ballingall, Surf. Sci. 168, 564 (1986); N. Otsuka, L. A. Kolodziejsi, R. L. Gunshor, S. Datta, R. N. Bicknell, and J. F. Schetzina, Appl. Phys. Lett. 46, 860 (1985).
- <sup>15</sup>A. Franciosi, A. Wall, Y. Gao, J. H. Weaver, M.-H. Tsai, J. D. Dow, R. Reifenberger, and F. Pool, Phys. Rev. B 40,

anion heterojunctions with good lattice matching, such as GaAs-AlAs and HgTe-CdTe. Based on our results, we estimated an upper limit of 6.5% of the band-gap difference for the valence-band offset in CdTe-Cd<sub>1-x</sub>Mn<sub>x</sub>Te heterojunctions.

## ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research under Grant No. N00014-89-J-1407 and by the Center for Interfacial Engineering of the University of Minnesota. We are indebted to J.K. Furdyna and R. Reifenberger for the samples used in the present studies. We thank J.K. Furdyna, M. Hybertsen, G. Margaritondo, G. P. Schwartz and C.G. Van de Walle for useful discussions and for providing us with the results of their work prior to publication. We are happy to acknowledge the assistance of the entire staff of the Synchrotron Radiation Center, supported by the National Science Foundation.

12009 (1989); M.-H. Tsai, J. D. Dow, R. V. Kasowski, A. Wall, and A. Franciosi, Solid State Commun. 69, 1131 (1989).

- <sup>16</sup>A. Wall, Y. Gao, A. Raisanen, A. Franciosi, and J. R. Chelikowsky, Phys. Rev. B 43, 4988 (1991).
- <sup>17</sup>A. Wall, A. Raisanen, G. Haugstad, L. Vanzetti, and A. Franciosi, Phys. Rev. B 44, 8185 (1991).
- <sup>18</sup>D. Wearie and E. O'Reilly, in *Noncrystalline Semiconductors*, edited by M. Pollak (CRC Press, Boca Raton, 1987), Vol. I, p. 1.
- <sup>19</sup>L. Ley, S. Kowalczyk, R. Pollak, and D. A. Shirley, Phys. Rev. Lett. **29**, 1088 (1972).
- <sup>20</sup>N. J. Shevchik, in *Tetrahedrally Bonded Amorphous Semiconductors (Yorktown Heights)*, Proceedings of the International Conference on Tetrahedrally Bonded Amorphous Semiconductors, edited by M. H. Brodsky, S. Kirkpatrick, and D. Wearie, AIP Conf. Proc. No. 20 (AIP, New York, 1974), p. 72, and references therein.
- <sup>21</sup>C. G. Ribbing, D. T. Pierce, and W. E. Spicer, Phys. Rev. B 4, 4417 (1971).
- <sup>22</sup>B. Orlowski, W. E. Spicer, and A. D. Baer, in *Tetrahedrally Bonded Amorphous Semiconductors (Yorktown Heights)* (Ref. 20), p. 241.
- <sup>23</sup>The photoelectron escape depth in the photon-energy range explored is  $\sim 4$  Å.
- <sup>24</sup>M. Taniguchi, L. Ley, R. L. Johnson, J. Ghijsen, and M. Cardona, Phys. Rev. B **33**, 1206 (1986).
- <sup>25</sup>S.-H. Wei and A. Zunger, Phys. Rev. B **35**, 2340 (1987), and references therein.
- <sup>26</sup>See A. Raisanen, G. Haugstad, X. Yu, and A. Franciosi, J. Appl. Phys. **70**, 3115 (1991), and references therein.
- <sup>27</sup>In the coverage range examined the typical maximum variation observed for  $\Delta E_v$  at different Ge coverages was less than  $\pm 0.03$  eV.
- <sup>28</sup>E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, Phys. Rev. B 28, 1965 (1983).
- <sup>29</sup>G. Margaritondo and A. Franciosi, Annu. Rev. Mater. Sci. 14, 67 (1984).
- <sup>30</sup>C. M. Aldao, I. M. Vitomirov, F. Xu, and J. H. Weaver, Phys. Rev. B 40, 3711 (1989).

- <sup>31</sup>More details on the fitting procedure can be found in Ref. 26.
- <sup>32</sup>Typical values obtained for the fitting parameters were the following: Branching ratio, 0.62; spin-orbit splitting, 0.60 eV; Lorentzian half width at half maximum, 0.09 eV; Gaussian width at half maximum, 0.51 eV.
- <sup>33</sup>J. Tersoff and C. G. Van de Walle, Phys. Rev. Lett. **59**, 946 (1987).
- <sup>34</sup>G. P. Schwartz, M. S. Hybertsen, J. Bevk, R. G. Nuzzo, J. P. Mannaerts, and G. J. Gualtieri, Phys. Rev. B **39**, 1235 (1989); M. S. Hybertsen (private communication).
- <sup>35</sup>G. Bratina, L. Sorba, A. Antonini, L. Vanzetti, and A. Fran-

ciosi, J. Vac. Sci. Technol. B 9, 2225 (1991).

- <sup>36</sup>E. T. Yu, E. T. Croke, D. H. Chow, D. A. Collins, M. C. Phillips, T. C. McGill, J. O. McCaldin, and R. H. Miles, J. Vac. Sci. Technol. B 8, 908 (1990).
- <sup>37</sup>The method directly determines the two valence-band maxima at the interface. Admittedly, since the overlayer contribution in the fits of Fig. 2 was approximated using EDC's for 20-Åthick Ge films and the interface spectra were analyzed at lower Ge coverages (5 Å in Fig. 2), errors due to possible variations in the shape of the Ge leading valence-band edge with progressive strain relaxation cannot be ruled out.