X-ray photoelectron spectroscopy measurement of valence-band offsets for Mg-based semiconductor compounds

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We have used x-ray photoelectron spectroscopy to measure the valence-band offsets for the lattice matched $MgSe/Cd_{0.54}Zn_{0.46}Se$ and $MgTe/Cd_{0.88}Zn_{0.12}Te$ heterojunctions grown by molecular beam epitaxy. By measuring core level to valence-band maxima and core level to core level binding energy separations, we obtain values of 0.56 ± 0.07 eV and 0.43 ± 0.11 eV for the valence-band offsets of $MgSe/Cd_{0.54}Zn_{0.46}Se$ and $MgTe/Cd_{0.88}Zn_{0.12}Te$, respectively. Both of these values deviate from the common anion rule, as may be expected given the unoccupied cation d orbitals in Mg. Application of our results to the design of current II-VI wide band-gap light emitters is discussed.

The importance of Mg-based semiconductor compounds for II-VI wide band-gap light emitters has recently been demonstrated. In particular, the blue-green laser diodes (LDs) initially demonstrated by Haase et al.[1] are now fabricated with $Zn_{1-x}Mg_xS_ySe_{1-y}$ cladding layers,[2] resulting in the demonstration of the first blue LD[3] and pseudomorphic blue-green LDs with pulsed operation up to temperatures as high as 394 K.[4] In addition, compositionally graded $Mg_xCd_{1-x}Se$ is used as an electron injector in the green light emitting diode (LED) design proposed by Phillips et al.,[5] resulting in a device with favorable current-voltage characteristics and device lifetimes.[6] There is also interest in $Mg_xCd_{1-x}Te$ for light emitter applications, and growth of $Mg_xCd_{1-x}Te$ by molecular beam epitaxy (MBE) has recently been achieved.[7] Finally, simulations have shown that $Mg_yZn_{1-y}Te$ layers can be used to shorten the wavelength of light emission in graded electron injector devices.[8]

For the ZnSe-based devices, knowledge of the valence-band offset (ΔE_v) arising from the addition of Mg in the $Zn_{1-x}Mg_xS_ySe_{1-y}$ cladding layers is needed to design LDs with adequate carrier confinement, and to predict general trends in the dopability of the cladding layers. For the graded electron injector devices, ΔE_v is needed to design for efficient electron injection. Currently, both types of devices are designed using band lineups based primarily on the common anion rule. Since the common anion rule[9] was originally observed not to apply to the one cation, Al, then studied from the third row of the periodic table, we should not expect it to necessarily apply to Mg, another third row cation. Similarly, Wei and Zunger[10] predict that the common anion rule should only apply when the d orbitals of the cations on both sides of a heterojunction, e.g., $MgSe/Cd_{0.54}Zn_{0.46}Se$, interact with their respective valence bands in a comparable manner.

Therefore, since the $3d$ orbitals in Mg are unoccupied, as in the case of Al, we might expect to observe a deviation from the common anion rule similar to that in the AlAs/GaAs system.

In this letter, we report the measurement of ΔE_v in the lattice matched $MgSe/Cd_{0.54}Zn_{0.46}Se$ [5.89 Å, zincblende (Ref. 2)] and $MgTe/Cd_{0.88}Zn_{0.12}Te$ [6.435 Å, zincblende (Ref. 11)] heterojunctions by x-ray photoelectron spectroscopy (XPS). $Cd_{0.54}Zn_{0.46}Se$ and $Cd_{0.88}Zn_{0.12}Te$ were chosen to avoid difficulties associated with measuring band offsets in lattice mismatched systems, and to test the validity of the common anion rule for Mg-based compounds.

The structures studied were grown in two Perkin-Elmer 430P MBE systems, one devoted to III-V and the other to II-VI semiconductor growth. After GaSb buffer layers were grown on GaSb (100) substrates to provide a smooth growth surface, the samples were transferred via an ultrahigh vacuum (UHV) transfer tube to the II-VI growth chamber. Thick, relaxed layers of $Cd_{0.54}Zn_{0.46}Se$ ($Cd_{0.88}Zn_{0.12}Te$), followed by the band offset measurement structures, were then grown at a substrate temperature of 270 °C (300 °C). The ternary compositions were calibrated using XPS and x-ray diffraction to keep the lattice mismatch to less than 0.5%. The reflection high-energy electron diffraction patterns showed no indications of deviation from the cubic zincblende structure. Following the II-VI growth, the samples were transferred via an UHV transfer tube to a Perkin-Elmer model 5500 analysis system with a monochromatic Al $K\alpha$ x-ray source for the XPS measurements. The base pressure in the XPS chamber was typically $\sim 3 \times 10^{-10}$ Torr.

To determine ΔE_v using XPS, we used the following relation:

$$\Delta E_v = (E_{Zn3p3/2} - E_v^{CdZnX}) - (E_{Mg2s} - E_v^{MgX})$$
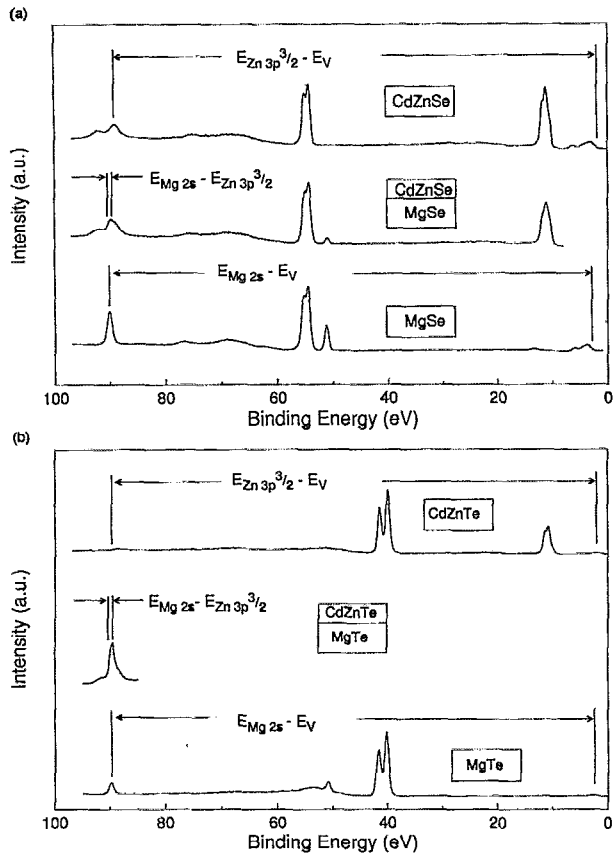$$- (E_{Zn3p3/2} - E_{Mg2s}), \tag{1}$$

FIG. 1. XPS spectra for (a) MgSe/Cd$_{0.54}$Zn$_{0.46}$Se, and (b) MgTe/Cd$_{0.88}$Zn$_{0.12}$Te band offset measurements. Energy separations used in the band offset measurements are labeled.

FIG. 2. Least-squares fit of Zn $3p$ and Mg $2s$ core level peaks for 20 Å MgSe on Cd$_{0.54}$Zn$_{0.46}$Se. Four parameters (intensity and binding energy of each peak) were used in the fit.

followed the procedure outlined in Ref. 12. Briefly, this involves using a calculated band structure for each material to determine a theoretical valence-band density of states (VBDOS). This VBDOS is then convolved with the instrumental resolution function, determined from measured Au $4f$ core level peaks. Finally, the instrumentally broadened theoretical VBDOS is fit to the experimental VBDOS to obtain the position of the valence-band maximum. The VBDOS were calculated using either the pseudopotential method [13] or the semi-empirical linear combination of atomic orbitals method.[14] Details of the procedure used are outlined in Ref. 15.

Figure 3 shows fitted valence-band spectra for MgSe, MgTe, Cd$_{0.54}$Zn$_{0.46}$Se, and Cd$_{0.88}$Zn$_{0.12}$Te. To verify the validity of the calculated band structures, we followed the pro-

where the X in CdZnX and MgX refers to either Te or Se. The core level to valence-band maximum, E_v, binding energy separations were measured on bulk CdZnX and bulk MgX samples. The core level binding energy separations were measured on thin ($\sim$20 Å) CdZnX on MgX samples, and thin MgX ($\sim$20 Å) on CdZnX samples. XPS binding energy separations measured on the same sample under identical conditions were typically reproducible to better than $\pm$0.02 eV, and energy separations measured on the same structure but different samples were reproducible to within experimental error. Commutativity of the MgSe/Cd$_{0.54}$Zn$_{0.46}$Se band offset was tested and confirmed. Commutativity was not tested for the MgTe/Cd$_{0.88}$Zn$_{0.12}$Te band offset. Figure 1 shows sample XPS spectra used in the band offset measurements.

To determine the core level peak positions, we first performed an integrated background subtraction, and then fit the peaks to Voigt functions, allowing the binding energy, linewidth, Lorentzian fraction, and intensity to vary. For the heterojunction samples the Zn $3p$ and Mg $2s$ core levels overlap, and it was necessary to constrain the peak shapes to those obtained from the bulk samples in order to reduce the number of fit parameters. A typical fit for the Zn $3p$ and Mg $2s$ core levels is shown in Fig. 2.
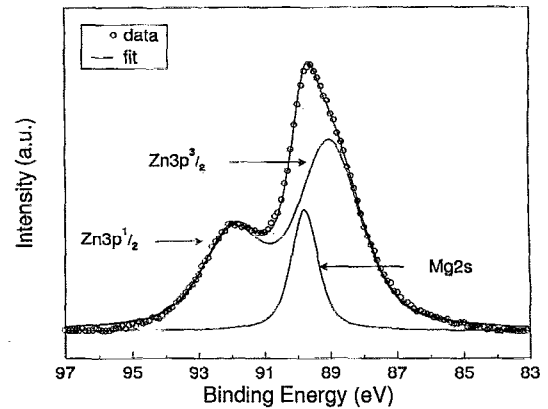
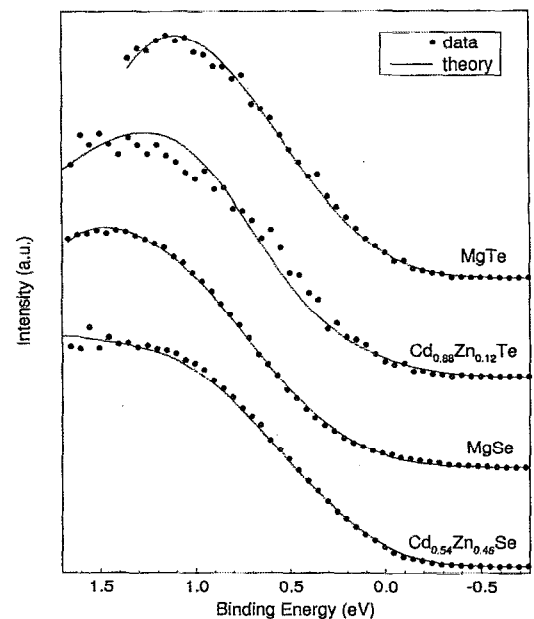To determine the valence-band maximum position, we

FIG. 3. Fit of experimental VBDOS (dots), and instrumentally broadened theoretical VBDOS (solid lines) for MgTe, Cd$_{0.88}$Zn$_{0.12}$Te, MgSe, and Cd$_{0.54}$Zn$_{0.46}$Se.

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cedure in Ref. 12, and varied the valence-band maximum fit region. Only a small variation of the fitted valence-band maximum position was observed as a function of fit region, indicating that the VBDOSs used accurately modeled the experimental VBDOSs.

The results from the XPS measurements are $E_{Zn3p3/2} - E_v^{CdZnSe} = 87.52 \pm 0.04$, eV, $E_{Mg2s} - E_v^{MgSe} = 87.76 \pm 0.04$ eV, and $E_{Zn3p3/2} - E_{Mg2s} = 0.80 \pm 0.04$ eV for the MgSe/ $Cd_{0.54}Zn_{0.46}Se$ heterojunction, and $E_{Zn3p3/2} - E_v^{CdZnTe} = 87.80 \pm 0.04$ eV, $E_{Mg2s} - E_v^{MgTe} = 88.16 \pm 0.05$ eV, and $E_{Zn3p3/2} - E_{Mg2s} = 0.79 \pm 0.09$ eV for the MgTe/$Cd_{0.88}Zn_{0.12}$Te heterojunction. From Eq. (1) we obtain $\Delta E_v(\text{MgSe}/Cd_{0.54}Zn_{0.46}Se) = 0.56 \pm 0.07$ eV, and $\Delta E_v(\text{MgTe}/Cd_{0.88}Zn_{0.12}Se) = 0.43 \pm 0.11$ eV with the valence-band maximum of MgX below that of CdZnX. Both of these values deviate from the common anion rule in the same direction and with roughly the same magnitude as in the AlAs/GaAs system. Since both Mg and Al are third row elements in the periodic table and have unoccupied d orbitals, this supports the importance of including the repelling effects of cation d orbitals on the valence-band maximum in band offset predictions for common anion systems.

Our results thus indicate that in the ZnSe-based LD structures, the addition of Mg in $Zn_{1-x}Mg_xS_ySe_{1-y}$ tends to pull down the valence-band maximum. As a consequence, the Mg and S concentrations in the $Zn_{1-x}Mg_xS_ySe_{1-y}$ layers may need to be increased in the ZnSe-based LD designs for optimal electron confinement, especially as the wavelength of light emission is extended into the blue. Also, since addition of Mg lowers E_v we would also expect the inherent p-type dopability of $Zn_{1-x}Mg_xS_ySe_{1-y}$ and Mg_yZn_{1-y}Te layers to decrease, since p-type dopability tends to be more difficult for semiconductors with lower E_v. This effect has already been observed in the form of compensation in nitrogen-doped $Zn_{1-x}Mg_xS_ySe_{1-y}$ and phosphorus-doped Mg_yZn_{1-y}Te, although the mechanism responsible for the compensation was attributed to impurities in both cases.[16,17] For the graded electron injection devices, our results indicate that the Mg concentration in the graded $Mg_xCd_{1-x}Se$ layer will need to be adjusted for efficient electron injection, although the exact amount is dependent on the MgSe band gap used.

In conclusion, using XPS we have measured ΔE_v in the lattice matched MgSe/$Cd_{0.54}Zn_{0.46}Se$ and MgTe/ $Cd_{0.88}Zn_{0.12}$Te heterojunctions. We obtained values of 0.56 ± 0.07 eV, and 0.43 ± 0.11 eV, respectively, with the valence-band maximum of MgX below that of CdZnX. Both of these values deviate significantly from the common anion rule, and support the importance of including the effect of cation d orbitals in ΔE_v predictions for common anion heterojunctions. Based on our results, the Mg concentrations in both the $Zn_{1-x}Mg_xS_ySe_{1-y}$ cladding layers and the graded $Mg_xCd_{1-x}Se$ layers must be adjusted for optimal performance of the respective devices. Also, our results indicate that the inherent p-type dopability of $Zn_{1-x}Mg_xS_ySe_{1-y}$ and Mg_yZn_{1-y}Te layers may decrease with increasing Mg concentration.

[1] M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheng, Appl. Phys. Lett. **59**, 1272 (1991).

[2] H. Okuyama, K. Nakano, T. Miyajima, and K. Akimoto, Jpn. J. Appl. Phys. **30**, L1620 (1991).

[3] H. Okuyama, T. Miyajima, Y. Morinaga, F. Hiei, M. Ozawa, and K. Akimoto, Electron. Lett. **28**, 1798 (1992).

[4] J. M. Gaines, R. R. Drenten, K. W. Haberern, T. Marshall, P. Mensz, and J. Petruzzello, Appl. Phys. Lett. **62**, 2462 (1993).

[5] M. C. Phillips, M. W. Wang, J. F. Swenberg, J. O. McCaldin, and T. C. McGill, Appl. Phys. Lett. **61**, 1962 (1992).

[6] J. F. Swenberg, M. C. Phillips, M. W. Wang, J. O. McCaldin, and T. C. McGill, J. Cryst. Growth (to be published).

[7] A. Waag, H. Heinke, S. Scholl, C. R. Becker, and G. Landwehr, J. Cryst. Growth **131**, 607 (1993).

[8] M. W. Wang, M. C. Phillips, J. F. Swenberg, E. T. Yu, J. O. McCaldin, and T. C. McGill, J. Appl. Phys. **73**, 4660 (1993).

[9] J. O. McCaldin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **36**, 56 (1976).

[10] S. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987).

[11] A. Waag, H. Heinke, S. Scholl, C. R. Becker, and G. Landwehr, J. Cryst. Growth **131**, 607 (1993).

[12] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, Phys. Rev. B **28**, 1965 (1983).

[13] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

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

[15] M. W. Wang, J. F. Swenberg, R. J. Miles, M. C. Phillips, E. T. Yu, J. O. McCaldin, R. W. Grant, and T. C. McGill, J. Cryst. Growth (to be published).

[16] P. M. Mensz, S. Herko, K. W. Haberern, J. Gaines, and C. Ponzoni, Appl. Phys. Lett. **63**, 2800 (1993).

[17] K. Somogyi, J. Chevallier, J. F. Rommeluere, J. Marine, and B. Schaub, IEEE Trans. Electron Devices **26**, 1198 (1979).