Correlation between the ordered structure and the valence-band splitting in highly strained CdxZn1−xTe epilayers

T. W. Kim, K. D. Kwack, J. G. Park, H. S. Lee, J. Y. Lee et al.

Citation: Appl. Phys. Lett. **83**, 269 (2003); doi: 10.1063/1.1592622
View online: http://dx.doi.org/10.1063/1.1592622
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v83/i2
Published by the American Institute of Physics.

Correlation between the ordered structure and the valence-band splitting in highly strained $Cd_xZn_{1-x}Te$ epilayers

T. W. Kim,[a] K. D. Kwack, and J. G. Park
Advanced Semiconductor Research Center, Division of Electrical and Computer Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Scoul 133-791, Korea

H. S. Lee[b] and J. Y. Lee
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Gusung-dong, Yusung-ku, Daejon 305-701, Korea

M. S. Jang and H. L. Park
Department of Physics, Yonsei University, Seoul 120-749, Korea

(Received 11 March 2003; accepted 12 May 2003)

Selected-area electron diffraction pattern (SADP) results showed two sets of {1/2 1/2 1/2} superstructure reflections with symmetrical intensities along the [110] axis, and the corresponding high-resolution transmission electron microscopy images indicated a doublet periodicity in the contrast of the {111} lattice planes. Photoluminescence spectra from highly strained $Cd_xZn_{1-x}Te$/GaAs heterostructures showed that the valence-band splitting into the heavy hole and the light hole bands occurred as the Cd mole fraction was increased. The valence-band splitting is strongly correlated to the $CuPt_B$-type ordered structure in highly strained heterostructures. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1592622]

Ternary semiconductor epitaxial films with large energy gaps have become particularly attractive because of interest in investigations of the fundamental physical properties of the films in their applications for many promising devices.[1–5] However, since there are inherent problems due to possible cross-doping effects resulting from interdiffusion or intermixing during growth,[6,7] by comparison with III–V ternary epilayers grown on III–V binary substrates, relatively little work has been done on ternary II–VI/binary III–V heterostructures.[8] Among these mixed heterostructures, $Cd_xZn_{1-x}Te$/GaAs heterostructures have been particularly interesting due to their potential applications for optoelectronic devices operating in the blue-green region of the spectrum.[9,10] Since the optical properties of semiconductor thin films grown on substrates are strongly affected by the microstructural properties of the films,[10] correlation studies of the microstructural and the optical properties of these layers are very important for improving the efficiencies of electronic and optoelectronic devices.

Since the existence of ordering in the epitaxial layers of ternary compound semiconductors significantly affects their optical properties,[11] investigations of ordering in ternary compound semiconductors are particularly important for understanding the optical properties of the layers. Some studies concerning several kinds of ordered structures in ternary semiconductors, such as CuAu,[12–14] chalcopyrite,[15–17] and CuPt,[18–21] have been reported. However, studies concerning the correlation behavior between the existence of the ordered structures and the optical properties of the ternary semiconductors have not been performed yet.

This letter reports the correlation properties between ordered structures and the valence-band splitting in highly strained $Cd_xZn_{1-x}Te$ epilayers grown on GaAs substrates by using molecular-beam epitaxy (MBE). Selected-area electron diffraction pattern (SADP), and transmission electron microscopy (TEM) measurements were performed to investigate the atomic and the ordered structures of the lattice-mismatched $Cd_xZn_{1-x}Te$ epilayers grown on GaAs substrates. Photoluminescence (PL) measurements were carried out to investigate the excitonic transition behavior of the $Cd_xZn_{1-x}Te$ thin films. A possible atomic arrangement for the ordered structure is described on the basis of the experimental results.

Elemental Cd, Zn, and Te with purities of 99.9999% were used as the source materials and were precleaned by repeated sublimation. The $Cd_xZn_{1-x}Te$ epilayers were deposited on GaAs substrates by using MBE at a substrate temperature of 320 °C and a system pressure of 10^{-6} Torr. The temperatures of the Cd, Zn, and Te sources for $Cd_xZn_{1-x}Te$ with various Cd mole fractions were changed, and the typical growth rate was 0.2 μm/h. The typical thickness of a $Cd_xZn_{1-x}Te$ film was 0.8 μm.

Figure 1 shows a SADP obtained from a $Cd_{0.61}Zn_{0.39}Te$ epitaxial layer grown on a GaAs (100) substrate. While the fundamental zinc-blende spots appeared along the $[1\bar{1}0]$ zone axis, as shown in Fig. 1(a), {1/2 1/2 1/2} superstructure reflections, together with fundamental zinc-blende spots, were observed along the [110] zone axis, as shown in Fig. 1(b). The extra {1/2 1/2 1/2} spots are attributed to $CuPt_B$-type ordering, which is typically observed in III–V or II–VI compound semiconductors.[20] An unequivalent crystallographic atomic arrangement of four {111} planes distinguishes the $CuPt_A$- and the $CuPt_B$-ordered structures from each other. The $CuPt_A$-ordered structure is related to the (111) and the $(\bar{1}\bar{1}\bar{1})$ planes and generates extra $(h \pm 1/2, k$

[a]Electronic mail: twk@hanyang.ac.kr
[b]Electronic mail: hoseong@kaist.ac.kr

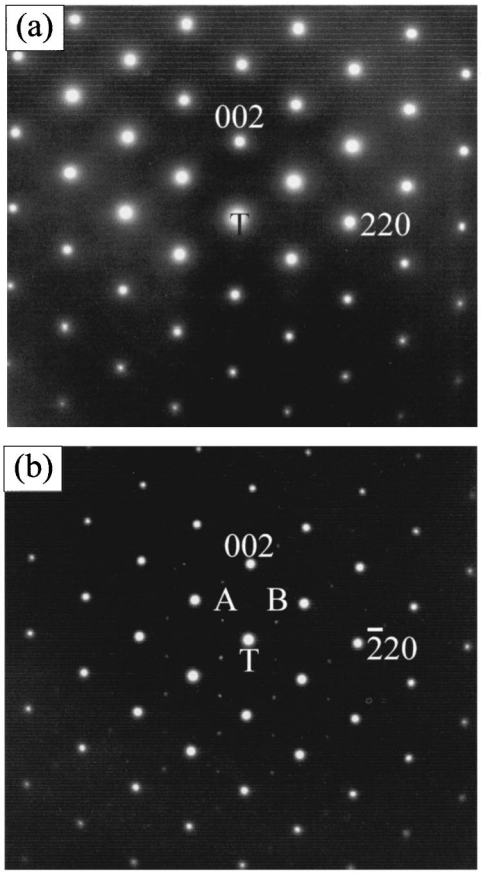

FIG. 1. SADP pattern of the $Cd_{0.61}Zn_{0.39}Te$ epilayer showing (a) no superstructure reflection along the $[1\bar{1}0]$ zone axis and (b) two symmetric sets of extra {1/2 1/2 1/2} spots along the [110] zone axis.

$\pm 1/2, \ell \pm 1/2)$ and $(h \mp 1/2, k \mp 1/2, \ell \pm 1/2)$ spots in the SADP. The $CuPt_B$-ordered structure, which produces $(h \pm 1/2, k \mp 1/2, \ell \pm 1/2)$ and $(h \mp 1/2, k \pm 1/2, \ell \pm 1/2)$ superstructure reflections, is thought to exist in the $(\bar{1}11)$ and the $(1\bar{1}1)$ planes. The extra {1/2 1/2 1/2} spots denoted by A and B in Fig. 1(b) have almost the same intensity, and their shapes are not sharp, but slightly diffusive. This result indicates that perfect ordering does not occur in $Cd_xZn_{1-x}Te$ epilayers.

Figure 2 shows a high-resolution TEM (HRTEM) image

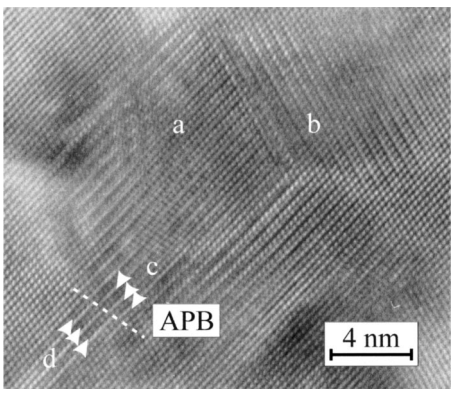

FIG. 2. Cross-sectional HRTEM image of the $Cd_{0.61}Zn_{0.39}Te$ epilayer showing an ordered structure having a doublet periodicity on the {111} lattice planes. Two different variants can be seen along the $\langle 111 \rangle$ directions, variant 1 being "a" and variant 2 being "b." An antiphase boundary exists between the "c" and the "d" regions of variant 1.

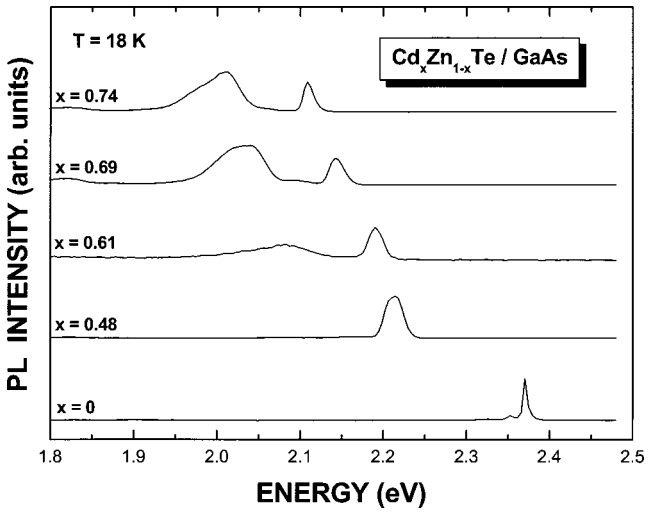

FIG. 3. PL spectra at 18 K from $Cd_xZn_{1-x}Te$/GaAs heterostructures with various Cd mole fractions.

along the [110] zone axis. The image has a doublet periodicity in the contrast of the {111} lattice planes of the $Cd_{0.61}Zn_{0.39}Te$ epitaxial layer grown on GaAs (100). The doublet periodicities seen in Fig. 2, which exist in the $(\bar{1}11)$ and the $(1\bar{1}1)$ planes, are similar to the superstructure reflections in the SADP shown in Fig. 1(b). The "a" in Fig. 2 is attributed to $CuPt_B$ ordering, and the "b" is related to another type of ordering. The ordering domains are about 10–20 nm. The doublet periodicity of the $(\bar{1}11)$ and the $(1\bar{1}1)$ planes in the $CuPt_B$ ordering consists of two overlapping structures with a 180° rotation.[20] An antiphase boundary for the CuPt-type ordering exists between the "c" and the "d" regions in Fig. 2.

Since the atomic ordering typically depends on valence-band splitting in compound semiconductors,[4] PL measurements were performed on a highly strained $Cd_xZn_{1-x}Te$/GaAs heterostructure to clarify the degenerate valence-band splitting in the substrates. Figure 3 shows the PL spectra obtained at 18 K for $Cd_xZn_{1-x}Te$/GaAs heterostructures with various Cd mole fractions. The PL spectra show that the peaks corresponding to the neutral acceptor bound exciton (A°, X) lines shift to lower energies with an increase up to the Cd mole fraction of 0.69, and the full width at half maximum (FWHM) of the (A°, X) bound exciton line increases with an increase up to Cd mole fraction of 0.69. The increase in the FWHM for the (A°, X) exciton with increasing Cd mole fraction originates from compositional fluctuations of the cations. While one peak, corresponding to the principal (A°, X) line, appears for $Cd_xZn_{1-x}Te$/GaAs heterostructures with low Cd mole fractions, two peaks related to the (A°, X) are observed for $Cd_xZn_{1-x}Te$/GaAs heterostructures with high Cd mole fractions. The two peaks for $Cd_xZn_{1-x}Te$/GaAs heterostructures with high Cd mole fractions originate from degenerate valence-band splitting into the heavy-hole and the light-hole bands due to strain effect resulting from the larger lattice mismatch between the $Cd_xZn_{1-x}Te$ epilayer and the GaAs substrate.

According to the results of SADP, HRTEM, and PL measurements, valence-band splitting in $Cd_xZn_{1-x}Te$ epilayers might be strongly correlated with the existence of CuPt-type ordered structures. The PL peaks shown in Fig. 3 showed a

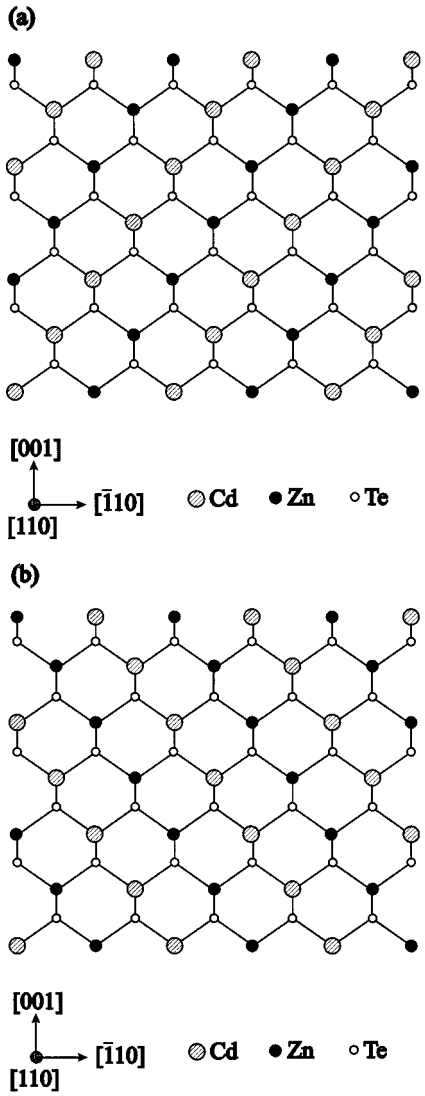

FIG. 4. Schematic diagrams of the two variants of CuPt-type ordered $Cd_xZn_{1-x}Te$ along the [110] projection: (a) $(1\bar{1}1)$ and (b) $(\bar{1}11)$.

broad luminescence, which was due to an inhomogeneity in the ordered structures in the $Cd_xZn_{1-x}Te$ layer. The values of valence-band splitting energies (ΔE_{VBS}) in the $Cd_xZn_{1-x}Te$ epilayers with x values of 0.61, 0.69, and 0.74 were 110, 102, and 99 meV, respectively, and they were affected by the degree of ordering. The value of the ΔE_{VBS} decreased with increasing Cd mole fraction in the $Cd_xZn_{1-x}Te$ film. Thus, the $Cd_{0.74}Zn_{0.26}Te$ epilayer had the least ordering among our samples because the magnitude of the ΔE_{VBS} for the $Cd_{0.74}Zn_{0.26}Te$ epilayer was smaller than those for the $Cd_{0.61}Zn_{0.34}Te$ and the $Cd_{0.69}Zn_{0.31}Te$ epilayers. Therefore, the value of ΔE_{VBS} might be affected by compositional fluctuations due to changes in the band gap which depend on the Cd composition and on the influence of strain at the band edges.

Figure 4 presents schematic diagrams of the two types of $CuPt_B$ ordering structures. CuPt ordering has doublet periodicities in the (111) planes. The atomic arrangements in the $Cd_xZn_{1-x}Te$ epitaxial layers are given by a repeated CdTe/ZnTe ordering along the [111] direction, as shown in Figs. 4(a) and 4(b). Atoms are also arranged in a repeating CdTe/ZnTe order along the $[1\bar{1}0]$ directions. Therefore, the doublet periodicities of the $(1\bar{1}1)$ and the $(\bar{1}11)$ planes in the HRTEM image of Fig. 2 are thought to be due to a $CuPt_B$ ordering with two different structures.

In summary, the results of the SADP and the HRTEM measurements showed the existence of CuPt-type ordered structures in the $Cd_xZn_{1-x}Te$ epilayers. The observed ordered structure had the typical features of two variations of $CuPt_B$ ordering along the [110] zone axis. An antiphase boundary was observed in the CuPt-type ordered structure of the $Cd_xZn_{1-x}Te$ epitaxial layer. PL spectra from highly strained $Cd_xZn_{1-x}Te$/GaAs heterostructures showed that splitting of the valence band in the $Cd_xZn_{1-x}Te$ epilayer into the heavy-hole and the light hole bands occurred as the Cd mole fraction increased. The existence of CuPt-type ordered structures in the $Cd_xZn_{1-x}Te$ epilayers was strongly correlated with valence-band splitting. A possible atomic arrangement for the ordered structure was described on the basis of the experimental results.

The work at Hanyang University was supported by the Korea Science and Engineering Foundation through the Quantum Functional Science Research Center at Dongguk University, and the work at Korea Advanced Institute of Science and Technology was supported by the Ministry of Science and Technology through the National Research Laboratory program.

[1] R. F. C. Farrow, G. R. Jones, G. H. Williams, and I. M. Young, Appl. Phys. Lett. **39**, 954 (1981).
[2] *Properties of Wide Bandgap II–VI Semiconductors*, edited by R. Bhargava (INSPEC, London, 1997).
[3] A. Iribarren, R. Castro-Rodriguez, F. Caballero-Briones, and J. L. Pena, Appl. Phys. Lett. **74**, 2957 (1999).
[4] N. Amir, K. Choen, S. Stolyarova, A. Chack, R. Beserman, R. Weil, and Y. Nemirovsky, J. Phys. D **33**, L9 (2000).
[5] A. Cavallini, B. Fraboni, W. Dusi, M. Znarini, and P. Siffert, Appl. Phys. Lett. **77**, 3212 (2000).
[6] T. W. Kim, H. L. Park, J. Y. Lee, and H. J. Lee, Appl. Phys. Lett. **65**, 2597 (1994).
[7] B. J. Wu, G. M. Haugen, J. M. DePuydt, L. H. Kou, and L. Salamanca-Riba, Appl. Phys. Lett. **68**, 2828 (1996).
[8] D. J. Olego, J. P. Faurie, S. Sivananthan, and P. M. Racah, Appl. Phys. Lett. **47**, 1172 (1985).
[9] K. Yasuda, K. Mori, Y. Kubota, K. Kojima, F. Inukai, Y. Asai, and T. Nimura, J. Electron. Mater. **27**, 948 (1998).
[10] K. Cohen, R. Beserman, S. Stolyarova, R. Weil, and Y. Nemirovsky, Thin Solid Films **336**, 205 (1998).
[11] L. C. Su, S. T. Ru, G. B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, Appl. Phys. Lett. **62**, 3496 (1993).
[12] T. S. Kuan, W. I. Wang, and E. L. Wilkie, Appl. Phys. Lett. **51**, 51 (1987).
[13] A. Gomyo, T. Suzuki, S. Iijima, H. Hotta, H. Fujii, S. Kawata, K. Kobayashi, Y. Ueno, and I. Hino, Jpn. J. Appl. Phys., Part 2 **27**, L2370 (1988).
[14] T. W. Kim, D. U. Lee, H. S. Lee, J. Y. Lee, and M. D. Kim, J. Appl. Phys. **89**, 2503 (2001).
[15] O. Ueda, T. Fujii, Y. Nakada, H. Yamada, and I. Umebu, J. Cryst. Growth **95**, 38 (1989).
[16] H. R. Jen, M. J. Jou, Y. T. Cherng, and G. B. Stringfellow, J. Cryst. Growth **85**, 175 (1987).
[17] H. R. Jen, M. J. Cherng, and G. B. Stringfellow, Appl. Phys. Lett. **48**, 1603 (1986).
[18] M. Kondow, H. Kakibayashi, T. Tanaka, and S. Minagawa, Phys. Rev. Lett. **63**, 884 (1989).
[19] K. T. Chang and E. Goo, J. Vac. Sci. Technol. B **10**, 1549 (1992).
[20] M. S. Kwon and J. Y. Lee, J. Cryst. Growth **191**, 51 (1998).
[21] T. W. Kim, D. U. Lee, D. C. Choo, H. S. Lee, J. Y. Lee, and H. L. Park, Appl. Phys. Lett. **78**, 922 (2001).