Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thin Solid Films 429 (2003) 211–215

www.elsevier.com/locate/tsf

The growth of the $Cd_xZn_{1-x}Te$ epilayers by low-pressure metalorganic vapor-phase epitaxy

Z.Z. Zhang, D.Z. Shen*, C.X. Shan, J.Y. Zhang, Y.M. Lu, Y.C. Liu, X.W. Fan

Key Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 140 Renmin Street, Changchun 130022, PR China

Received 1 June 2001; received in revised form 8 January 2003; accepted 13 January 2003

Abstract

In this paper, $Cd_xZn_{1-x}Te$ epilayers with different Cd contents ranging from 0 to 1 were grown on GaAs (1 0 0) substrates by low-pressure metalorganic vapor-phase epitaxy. The $Cd_xZn_{1-x}Te$ epilayers were characterized by using the X-ray diffraction, scanning electron microscopy and photoluminescence measurements. When the flow rates of the precursors were kept at constants, the Cd content in the $Cd_xZn_{1-x}Te$ epilayers decreased with the increase of the substrate temperature. This phenomenon was considered to be related to absorption and desorption characters of the reactants.

PACS: 68.55.Nq; 78.55.Et; 81.05.Dz; 81.15.Gh

Keywords: Metalorganic vapor-phase epitaxy; $Cd_xZn_{1-x}Te$ epilayer; Substrate temperature; Cd content

1. Introduction

Recently, the $Cd_xZn_{1-x}Te$ alloy is attracting much interest due to the application in optical devices. Because the band gap can be tuned from 1.5 to 2.3 eV by changing the Cd content, the $Cd_xZn_{1-x}Te$ alloy is considered to be an ideal material for optical devices operating inside the red–green wave band. Additionally, $Cd_xZn_{1-x}Te/ZnTe$ quantum wells (QWs) are type-I QWs with strong exciton luminescence at room temperature [1] with varying the Cd contents from 0 to 1. Recently, some studies have been performed on low-dimensional $Cd_xZn_{1-x}Te$ materials grown by molecule beam epitaxy [2], hot wall epitaxy [3] and metalorganic vapor-phase epitaxy (MOVPE) [4,5]. However, a few studies concerning the effect of substrate temperature on the growth of $Cd_xZn_{1-x}Te$ by MOVPE have been reported [6,7]. In this work, a series of $Cd_xZn_{1-x}Te$ epilayers with different Cd contents were fabricated by low-pressure MOVPE. The effect of substrate temperature on the Cd contents in the epilayers was investigated. The $Cd_xZn_{1-x}Te$ epilayers were characterized by means of X-ray diffraction (XRD) method, scanning electron microscopy (SEM) images and photoluminescence (PL) measurements.

2. Experiment

The $Cd_xZn_{1-x}Te$ epilayers were grown on GaAs (1 0 0) substrates by low-pressure MOVPE using dimethyl zinc (DMZn), dimethyl cadmium (DMCd) and diethyl tellurium (DETe) as the precursors. The gas flow rates of DMZn, DMCd and DETe were fixed at 9.55×10^{-6}, 1.30×10^{-6} and 1.12×10^{-5} mol/min, respectively. H_2 was used as the carrier gas and the total gas flow rate was kept at 2 l/min. The pressure of the growth chamber was kept at 220 Torr. To desorb impurity molecules, the substrates were pretreated at 600 °C for 10 min before the growth. The epilayers were grown at 320, 350, 420, 480 and 540 °C, respectively. The composition of the $Cd_xZn_{1-x}Te$ epilayers was measured by using an X-ray diffractometer (D/max-RA) with the line of 0.154 nm. The surface morphology was studied by using a field emission scanning electron microscope (S4200). All the PL measurements were performed at

---

*Corresponding author. Tel.: +86-431-5937596; fax: +86-431-5955378.

E-mail address: shen@public.cc.jl.cn (D.Z. Shen).

doi:10.1016/S0040-6090(03)00145-7

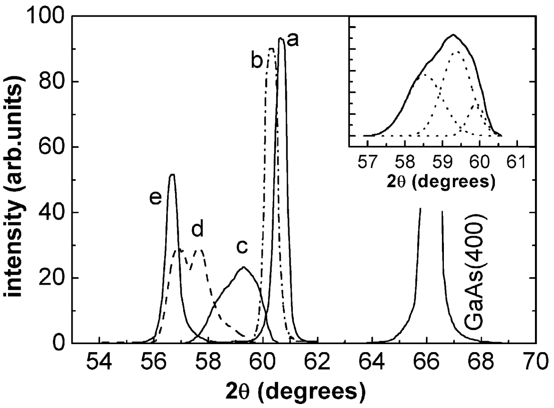


Fig. 1. XRD spectra of the $Cd_xZn_{1-x}Te$ epilayers grown at different temperatures: (a) $T_g = 540$ °C; (b) $T_g = 480$ °C; (c) $T_g = 420$ °C; (d) $T_g = 350$ °C; (e) $T_g = 320$ °C. The inset shows the Gaussian fit result of line c, in which the solid line is the original XRD peak of sample c and the dot lines are the result of Gaussian fit.

77 K. Here, a N_2-laser with a wavelength of 337.1 nm was used as the excitation source, and a SPEX1404 spectrometer with RCA-C31034 photomultiplier tube was used as the detector.

3. Result

Fig. 1 shows the XRD spectra of the $Cd_xZn_{1-x}Te$ epilayers grown at 320, 350, 420, 480 and 540 °C, respectively. The peak for the sample grown at 540 °C, which is located at 60.7°, agrees well with [0 0 4] diffraction peak of ZnTe. The peak for the sample grown at 320 °C, which is located at 56.7°, agrees with that of CdTe. For the other samples, the diffraction peaks are located between 56.7 and 60.7°. As shown in Fig. 1, the peak position of the epilayers shifts to large degree side gradually with increasing the growth temperature. The line width shows a significant change. The line width increases until the substrate temperature increases to 420 °C, and then decreases with the further increase of the temperature. The peak (marked with letter d, dash line) found between 56 and 58° for the sample grown at 350 °C has a double-peak structure, which indicates the epilayer is a mixture of two phases with different Cd contents. Furthermore, for the sample grown at 420 °C, the peak is broad compared to the others and the line shape is not symmetric. A Gaussian peak fit performed on this peak showed that it is composed of three peaks. This suggests that the sample grown at 420 °C has also more than one phase. The Cd contents in the $Cd_xZn_{1-x}Te$ alloys were obtained from the Bragg equation and the Vegard law. For the multiphase samples, the Cd contents were mean values of every phase in the epilayers, which were obtained by calculating statistically. The calculated x values of the $Cd_xZn_{1-x}Te$ layers, which were grown at 320, 350, 420, 480 and 540 °C, were 1, 0.82, 0.39, 0.11 and 0, respectively. The dependence of the Cd content on the substrate temperature is illustrated in Fig. 2, where x decreases as the substrate temperature increases.

The SEM surface images of the samples, which were grown at 320, 350, 420 and 480 °C, are shown in Fig. 3. The surfaces of the epilayers become increasingly rougher as the Cd content increases with decreasing the substrate temperature. When the epilayer was grown at low temperature, the mobility of surface atoms will be reduced. Once occupy some positions on the surface, the atoms are difficult to be transferred. It will result in unequal growth rates at different areas on the surface, which brings the roughness. In addition, as shown in the XRD spectra, multiphase was formatted in the $Cd_{0.39}Zn_{0.61}Te$ and $Cd_{0.82}Zn_{0.18}Te$ epilayers. It will affect the epilayer smoothness more or less.

Fig. 4 shows the PL spectra measured at 77 K. Lines a, b and c are the PL peaks of the epilayers with Cd contents of 0, 0.11 and 0.39, which were grown at 540, 480 and 420 °C, respectively. The PL signals of CdTe and $Cd_{0.82}Zn_{0.18}Te$ epilayers are too weak to be detected. When the growth temperature decreases to a certain level, the surface atoms have not enough mobility to form high quality films, which leads to large numbers of defects in the epilayers during the growth. Impurity atoms doped randomly in the films are apt to congregate around these defects. In general, these impurities act as nonradiative recombination centers due to their complex energy levels. It is these nonradiative recombination centers that lead to the luminescence quenching. In Fig. 4, the PL peaks of the epilayers exhibit obvious red shift with increasing the Cd content. The peak positions of the three epilayers at 77 K are 528, 569 and 651 nm, which correspond to the energy values of 2.348, 2.179 and 1.905 eV, respectively. The energy gaps at room temperature that were calculated according to Ref. [8] are 2.264, 2.167 and 1.937 eV, respectively. Being considered the energy gap narrowing with temperature increasing, the experimental result is in accordance with

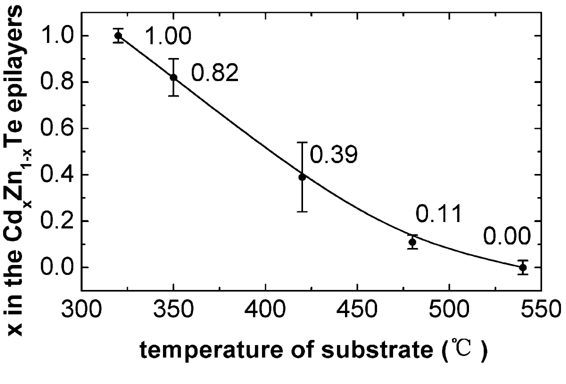


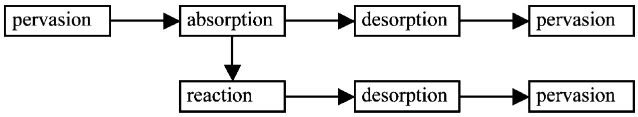
Fig. 2. Influence of substrate temperature on the Cd content in the $Cd_xZn_{1-x}Te$ epilayers.

the calculated values on the whole. In addition, the PL peak of the $Cd_{0.39}Zn_{0.61}Te$ epilayer is broader than the other peaks. As mentioned in the discussion of the XRD result, the $Cd_{0.39}Zn_{0.61}Te$ layer is multiphase. So the broad PL peak should be the superimposition of several PL peaks that originate from these phases with different Cd content.

4. Discussions

As shown in Fig. 2, the Cd content in the $Cd_xZn_{1-x}Te$ epilayers decreases as the substrate temperature increases with keeping the flow rates of all the precursors. This phenomenon will be discussed using the theory of gas/solid-phase-reaction kinetics and referring to related Refs. [9–12].

Above the graphite susceptor, there exists a boundary layer. According to the theory of gas/solid-phase-reaction kinetics, reactants would experience a course as follows:



After moving through the boundary layer, the organic molecules are absorbed on the substrate and the M–R bonds are broken induced by thermal energy. The letter M denotes the Cd, Zn or Te atom, and the R is alkyl.

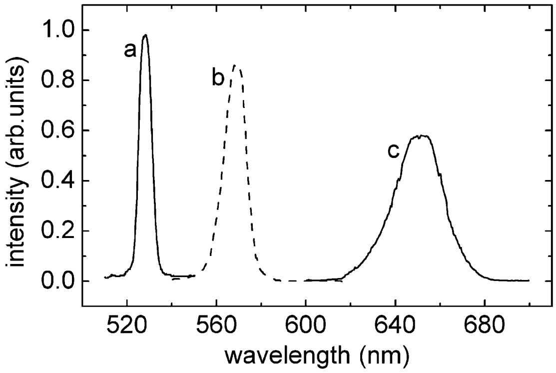


Fig. 4. PL spectra of the $Cd_xZn_{1-x}Te$ epilayers with different composition: (a) ZnTe, $T_g=540$ °C; (b) $Cd_{0.11}Zn_{0.89}Te$, $T_g=480$ °C; (c) $Cd_{0.39}Zn_{0.61}Te$, $T_g=420$ °C.

This epilayer growth process can be described by the following equations.

$$\mathrm{Cd_{ad}+Te_{ad}\xrightarrow{H_2}CdTe} \tag{1}$$

$$\mathrm{Zn_{ad}+Te_{ad}\xrightarrow{H_2}ZnTe} \tag{2}$$

Eqs. (3)–(6) describes desorption of the reactants.

$$\mathrm{CH_3Cd_{ad}\xrightarrow{\Delta}CH_3Cd_{gas}+V_{II}} \tag{3}$$

$$\mathrm{Cd_{ad}\xrightarrow{\Delta}Cd_{gas}+V_{II}} \tag{4}$$

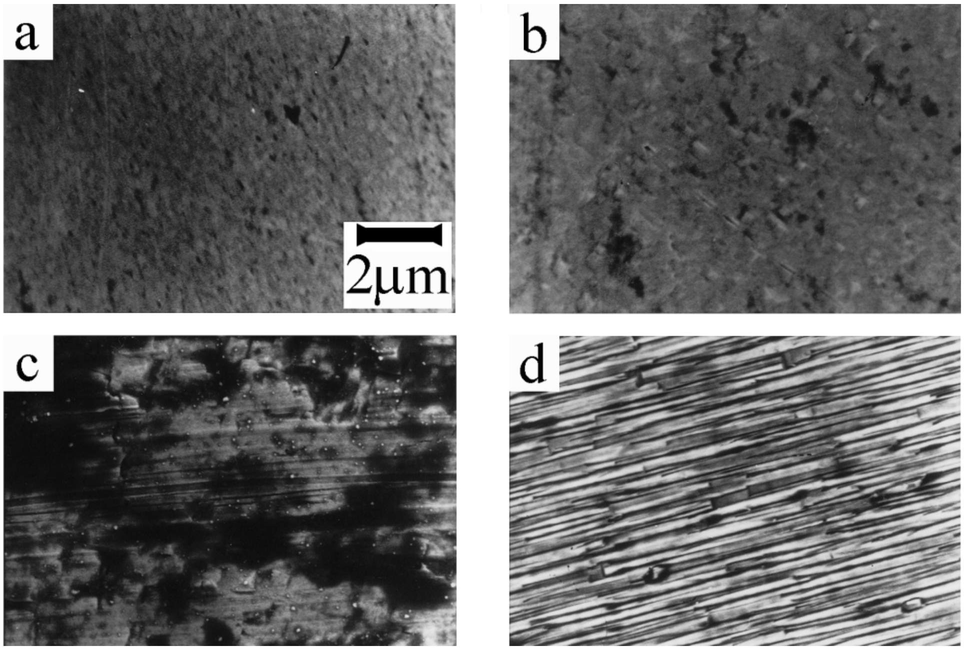


Fig. 3. SEM images of the $Cd_xZn_{1-x}Te$ epilayers: (a)ZnTe, $T_g=540$ °C; (b) $Cd_{0.11}Zn_{0.89}Te$, $T_g=480$ °C; (c) $Cd_{0.39}Zn_{0.61}Te$, $T_g=420$ °C; (d) $Cd_{0.82}Zn_{0.18}Te$, $T_g=350$ °C.

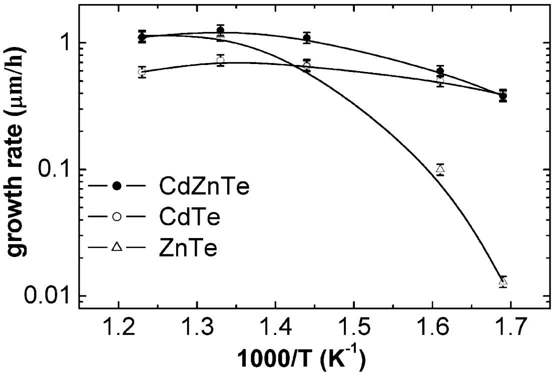


Fig. 5. Relationship between the growth rates and the substrate temperature: The flow rates: DMCd = 1.30×10^{-6} mol/min; DMZn = 9.55×10^{-6} mol/min; DETe = 1.12×10^{-5} mol/min.

$$CH_3Zn_{ad} \overset{\Delta}{\rightarrow} CH_3Zn_{gas} + V_{II} \tag{5}$$

$$Zn_{ad} \overset{\Delta}{\rightarrow} Zn_{gas} + V_{II} \tag{6}$$

V_{II} denotes group II vacancy on the surface, and the symbol Δ denotes heating. Symbols with subscripts such as gas and ad denote the corresponding species in gas phase and absorbed phase, respectively.

Fig. 5 depicts the relationship between the growth rates and the substrate temperature. As the substrate temperature rises, the growth rate of ZnTe increases rapidly, but the change of the CdTe growth rate is not evident. It is known that the Zn–CH_3 bond is stronger than the Cd–CH_3 bond because of the difference in their atomic radius, which results in the active energy of ZnTe decomposition being larger than that of CdTe [13]. According to reaction kinetics, the growth rate can be expressed with the equation:

$$v = kf(\theta_1\theta_2\cdots\theta_n)g(\theta_v), \quad \text{where } k = A\exp(-E_a/k_BT) \tag{7}$$

is the rate constant, $f(\theta_1\theta_2\cdots\theta_n)$is a function of the surface coverage of the species, and $g\theta_v$ is a function of vacant sites, A is a pre-exponential factor, k_B is Boltzmann constant, and T is substrate temperature. From Eq. (7), it can be deduced that, the larger the activation energy E_a is, the more obviously the temperature impacts the growth rate.

For the samples grown at low temperature, the Cd contents in the $Cd_xZn_{1-x}Te$ epilayers are rather high. In the case where the DMZn flow rate is higher than the DMCd flow rate, the difference in chemical property between the two precursors is the principal factor affecting the Cd content of the films. The energy necessary for breaking the first M–R bond of DMZn and DMCd are 276 kJ/mol [14] and 182 kJ/mol (43.5 kcal/mol) [15], respectively. It means that at a given temperature the absorption and the decomposition of the DMCd molecules occur more frequently than those of the DMZn molecules.

As the substrate temperature is increased, the increase extent of the decomposition rate of DMCd is less than that of DMZn. Because the bond energy of Cd-CH_3, which is proportional to the activation energy of decomposition, is less than that of Zn-CH_3, the effect of temperature on the decomposition rate of DMCd is less than that of DMZn. Therefore, the increase of growth temperature results in decrease of the Cd content in the epilayers.

If the substrate temperature is increased to a certain level, the desorption rates of species on the substrate surface become sizable. The desorption processes are described by Eqs. (3)–(6). As the substrate temperature increases, the deposition rate of DMZn arrives to a higher level, which would expend large numbers of DETe molecules. In the absence of any DETe, Eq. (4) occurs more easily [11]. It means that the increase of the DMZn deposition rate will bring the decrease of the DMCd deposition rate. As shown in Fig. 5, the growth rate of $Cd_xZn_{1-x}Te$ layer is not equal to the sum of the growth rates of the ZnTe and CdTe layers at high temperature. These processes result that the $Cd_xZn_{1-x}Te$ epilayer having approaching that of ZnTe.

5. Conclusion

In this work, $Cd_xZn_{1-x}Te$ epilayers with different Cd content were grown by low-pressure MOVPE. XRD, SEM and PL were employed to characterize the epilayers. With keeping the flow rates of precursors, the Cd content of the $Cd_xZn_{1-x}Te$ epilayer decreased as the substrate temperature increased. This was discussed by using gas/solid-phase-reaction kinetics theory and attributed to the difference on the absorption and desorption properties of the reactants.

Acknowledgments

This work was supported by the National Fundamental and Applied Research Project, the Key Project of the National Natural Science Foundation of China, the Program of CAS Hundred Talents and the National Natural Science Foundation of China.

References

[1] R.P. Stanley, B.J. Hawdon, J. Hegarty, Appl. Phys. Lett. 58 (1991) 2972.
[2] V.S. Bagaev, V.V. Zaitsev, E.E. Onishchenko, Yu.G. Sadofyev, J. Crystal Growth 214/215 (2000) 250.
[3] B. Koo, J. Wang, Y. Ishikawa, M. Isshiki, Jpn. J. Appl. Phys. 37 (1998) 5674.

[4] K. Yasuda, M. Minamide, K. Kawamoto, T. Maejima, J. Crystal Growth 159 (1996) 121.
[5] P.W. Sze, N.F. Wang, M.P. Houng, Y.H. Wang, J.S. Hwang, W.Y. Chou, Y.T. Cherng, C.H. Wang, C.D. Chiang, J. Crystal Growth 180 (1997) 177.
[6] J.J. Reinoso, E.I. Ko, P.L. Sides, J. Crystal Growth 174 (1997) 713.
[7] K. Cohen, S. Stolyarova, N. Amir, A. Chack, R. Beserman, R. Weil, Y. Nemirovsky, J. Crystal Growth 198/199 (1999) 1174.
[8] P.W. Sze, N.F. Wang, M.P. Houng, Y.H. Wang, J.S. Hwang, W.Y. Chou, Y.T. Cherng, C.H. Wang, C.D. Chiang, J. Crystal Growth 180 (1997) 177.
[9] B. Mullin, S.J.C. Irvine, D.J. Ashen, J. Crystal Growth 55 (1981) 92.
[10] B. Liu, A.H. McDaniel, R.F. Hicks, J. Crystal Growth 112 (1991) 192.
[11] N. Lovergine, M. Longo, P. Prete, C. Gerardi, L. Calcagnile, R. Cingolani, A.m. Mancini, J. Appl. Phys. 81 (2) (1997) 685.
[12] I.B. Bhat, N.R. Taskar, S.K. Ghandhi, J. Electrochem. Soc. 134 (1987) 195.
[13] D.W. Kisker, J. Crystal Growth 98 (1989) 127.
[14] R.L. Jackson, Chem. Phys. Lett. 163 (1989) 315.
[15] C.M. Laurie, L.H. Long, Trans. Faraday Soc. 53 (1957) 939.