# Low-pressure metalorganic vapor phase epitaxy growth of ZnTe

**6 AUTHORS**, INCLUDING:

Qixin Guo
Saga University
**268** PUBLICATIONS **3,552** CITATIONS

W Z Shen
Shanghai Jiao Tong University
**381** PUBLICATIONS **4,506** CITATIONS

ELSEVIER

# Low-pressure metalorganic vapor phase epitaxy growth of ZnTe

Yusuke Kume[a], Qixin Guo[a],*, Tooru Tanaka[a], Mitsuhiro Nishio[a],
Hiroshi Ogawa[a], Wenzhong Shen[b]

[a]*Department of Electrical and Electronic Engineering, Saga University, Saga 840-8502, Japan*
[b]*Department of Physics, Shanghai Jiao Tong University, Shanghai 200030, China*

Available online 20 November 2006

## Abstract

The homoepitaxial growth of ZnTe on the (1 0 0)-oriented ZnTe substrate has been investigated at different reactor pressures using dimethylzinc and diethyltelluride as source materials. The growth rate of ZnTe layers increases with increasing reactor pressure and then it eventually becomes saturated. The longitudinal optical phonon mode of ZnTe and a strong free exciton emission are clearly observed for all samples, indicating the ZnTe layers are of good crystal quality.
© 2006 Published by Elsevier B.V.

## 1. Introduction

Zinc telluride (ZnTe) is a semiconductor of the II–VI family which has attracted growing interest because of its applications in a variety of optoelectronic devices such as pure-green light-emitting devices, terahertz detectors, solar cells, waveguides and modulators. These have generated a great deal of effort toward the growth and characterization of this material [1–13]. Recently, we have succeeded in fabricating a ZnTe light-emitting diode (LED) using the Al diffusion technique and observed pure-green electroluminescence at a wavelength of 550 nm at room temperature [14]. In order to achieve high-efficiency LEDs and laser diodes (LDs), it is necessary to establish the epitaxial growth technique of high-quality ZnTe layer. Metalorganic vapor phase epitaxy (MOVPE) is one of the promising growth techniques for obtaining epitaxial layer, and is suitable for mass production. The fabrication of optical and electronic devices, particularly those containing structures with low dimensionality such as quantum well and quantum dot, requires highly controlled growth rate of epitaxial layers. Reactor pressure in MOVPE growth is expected to be one of the important factors for accurate control of the thickness of ZnTe layers. To the best of our knowledge, however, no systematic study has been carried out on the effect of reactor pressure on MOVPE growth of ZnTe. In this work, we try to clarify the relationship between the reactor pressure and growth rate or optical properties of ZnTe epitaxial layers in a MOVPE system.

## 2. Experimental procedure

ZnTe layers were grown by MOVPE at different reactor pressures. Dimethylzinc (DMZn) and diethyltelluride (DETe) were used as source materials and $H_2$ as carrier gas. Commercially available undoped ZnTe (1 0 0) were used as substrates. The ZnTe substrate was ultrasonically cleaned by organic solvents, and dipped in a 1% Br–methanol solution. In order to remove the native oxide on the surface of ZnTe substrate before the growth, it was cleaned by thermal annealing in $H_2$ at 470 °C for 30 min. The transport rates of DMZn and DETe were kept at 15 μmol/min. The reactor pressure was widely varied from 200 to 760 Torr while the substrate temperature was kept at 400 °C. Typical growth conditions are summarized in Table 1. The growth rate was evaluated using surface step profile analyzer. Raman measurements were performed on

Table 1
Typical growth conditions for ZnTe

| | |
|---|---|
| Substrate | Undoped ZnTe (1 0 0) |
| Source material | DMZn ((CH$_3$)$_2$Zn) |
| | DETe ((C$_2$H$_5$)$_2$Te) |
| Carrier gas | H$_2$ |
| Substrate temperature | 400 °C |
| Transport rate of DMZn | 15 μmol/min |
| Transport rate of DETe | DETe 15 μmol/min |
| Growth pressure | 200–760 Torr |
| Growth time | 180 min |

a Jobin Yvon LabRAM HR 800 UV–VIS–NIR micro-Raman system with an Andor DU402 classic charge-coupled device detector. The surface morphology of the ZnTe layers was investigated by a field-emission scanning electron microscope (FESEM). Cathodoluminescence (CL) experiments were conducted at room temperature in the FESEM equipped with a MonoCL2 system designed by Oxford Research Instruments. The photoluminescence (PL) spectra of the epitaxial layers were measured at 4.2 K using a 488 nm Ar$^+$ laser as the excitation source. The power density on the surface of the sample was kept at 50 mW/cm$^2$.

## 3. Results and discussion

Fig. 1 shows the dependence of the growth rate on the reactor pressure. In the low reactor pressure region, the growth rate increases monotonically with the reactor pressure. After reaching a maximum value of 2 μm/h around reactor pressure of 600 Torr, however, the growth rate becomes saturated. The result suggests that low-pressure growth is suitable for accurate control of the thickness. Since the transport rate of each source supplied into the reactor is kept at a constant value, the rise of the reactor pressure causes the increase in partial pressure of the reactants. As a result, the absorption of each reactant will increase with increasing reactor pressure and then becomes saturated at a high partial pressure of the reactant. On the other hand, the desorption of each reactant will be suppressed with increase reactor pressure. These may be the reason why the growth rate is low at a low pressure of 200 Torr and increases monotonically with increasing reactor pressure followed by saturation above a pressure of 600 Torr.

Fig. 2 shows a typical Raman spectrum at room temperature for the ZnTe layer grown at a reactor pressure of 200 Torr. Similar spectra were observed for other samples. The Raman scattering was recorded in back-scattering geometry of $z(x, -)\bar{z}$ configuration using a He–Cd laser at 325 nm. The longitudinal optical (LO) and 2LO phonon modes of ZnTe are clearly observed at 206 and 411 cm$^{-1}$, respectively, for all samples. The Raman scattering of phonons in crystals can be explained by the interactions of phonons and photons. It has been shown that Raman spectroscopy is a sensitive method for
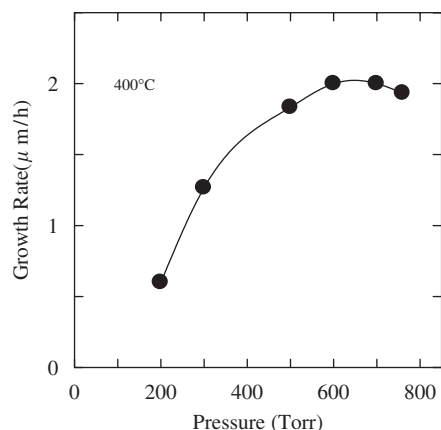


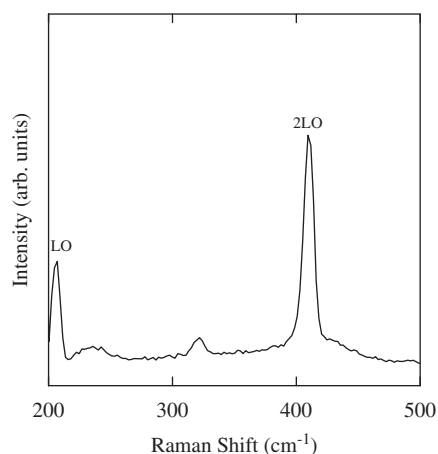Fig. 1. Dependence of growth rate on reactor pressure.



Fig. 2. Typical Raman spectrum of ZnTe layers grown at 200 Torr.

characterizing the crystal quality because the extended defects can give rise to a broadening of the Raman peaks [15,16]. The full-width at half-maximum of 2LO peaks in all spectra is almost same, indicating the crystal quality of the ZnTe layers seems not to depend on reactor pressure.

Fig. 3 shows surface morphology and CL panchromatic images of the epilayers grown at different reactor pressures and the substrate. Compared with smooth surface of the substrate (Fig. 3(d)), the surface morphology of the epilayers strongly depends on the growth pressure as shown in Fig. 3(a)–(c). The surface is marked by a dense ridging when the reactor pressure is as high as 760 Torr while the surface of the epitaxial layer grown at a low pressure of 200 Torr shows morphology consisted of pyramid-like hillocks. Relatively smooth surface was observed for the epitaxial layer grown at 500 Torr. However, the morphological features do not produce panchromatic CL contrast as shown in Fig. 3(a′)–(c′), suggesting that no impurity segregation exists in the ZnTe epilayers. The difference in the surface morphology between the epitaxial layers grown at different reactor pressures may be due to the difference of the growth mechanism. Lovergine et al. [17] have studied the morphology and structure of MOVPE grown homoepitaxial (1 0 0)ZnTe layers as a function of growth temperature.
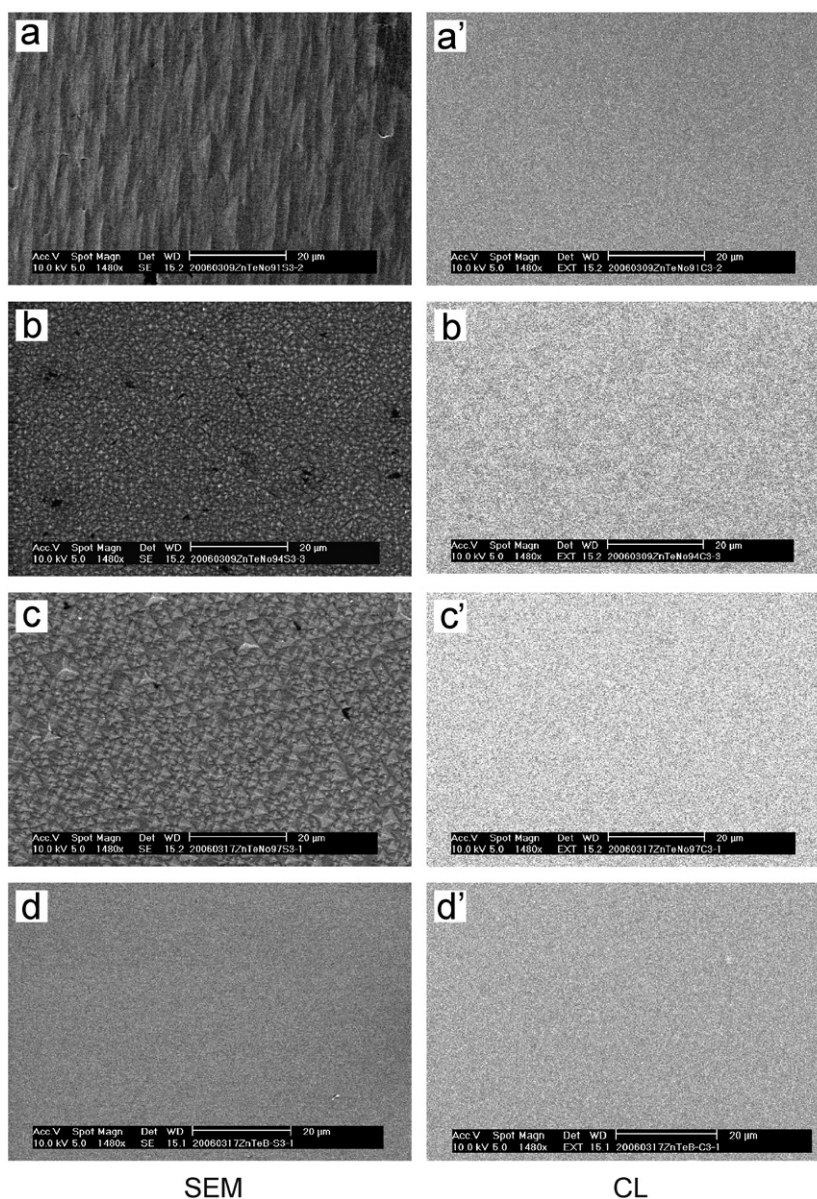
Fig. 3. FESEM micrographs and panchromatic CL images of the ZnTe layers grown at different reactor pressures: (a,a′) 760, (b,b′) 500, (c,c′) 200 Torr, and the substrate (d,d′).

They showed that mass transport-limited growth regime leads to a dense surface ridging along one of the ⟨1 1 0⟩ in-plane directions whereas surface kinetics limits growth regimes large pyramid-like hillocks. They also found that flat and featureless morphology is achieved for epilayers grown within a narrow temperature interval which corresponds to the transition between mass-transport and surface kinetics-limited growth regimes. Thus we believe that the morphology of the ZnTe layers can be improved by optimizing growth temperature or reactor pressure.

Next, we have measured the PL spectra in order to assess the optical properties of ZnTe layers. The penetration depth of the laser light is about one-third of a micron [18]. Therefore, ZnTe layers with thickness between 1.5 and 6 μm were investigated in order to avoid influence from the ZnTe substrate. Fig. 4 shows a typical PL spectrum from the ZnTe layer grown at a reactor pressure of 200 Torr. No significant difference in the feature was found for other samples. The PL spectrum is dominated by a strong free exciton (FE) emission at 2.381 eV. The excitonic peak (Ia) observed at 2.375 eV is attributed the recombination of excitons bound to neutral shallow acceptors such as Li, Cu, or Na. This peak is observed widely for undoped ZnTe grown by other growth method. Previous secondary ion mass spectroscopy analysis on nominally undoped ZnTe epitaxial layers showed that Na acts as a dominant impurity. It is worth to note that Y lines at 2.185 and 2.148 eV, which are known to arise due to extended structural defects, are not observed in the ZnTe sample. The absence of defect-related lines under strong FE emission indicates the ZnTe layer is of good quality in terms of crystallinity.
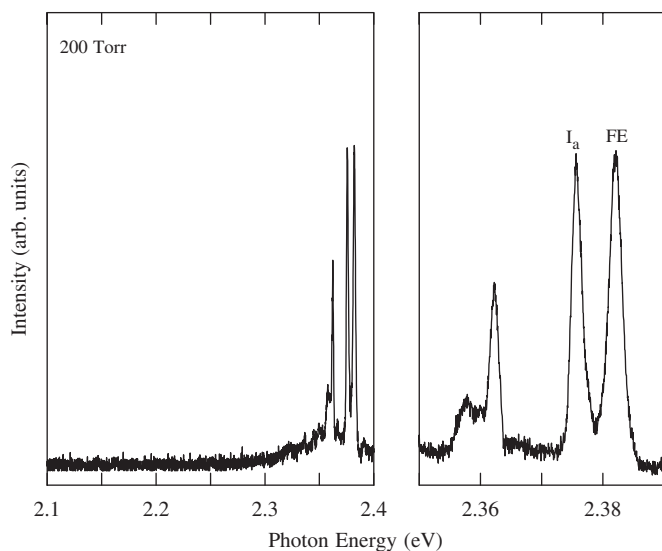
Fig. 4. Typical photoluminescence spectrum of ZnTe layer grown at 200 Torr.

## 4. Conclusions

We have investigated the homoepitaxial growth of ZnTe on the (1 0 0)-oriented ZnTe substrate at different reactor pressures using DMZn and DETe as source materials. The growth rate of ZnTe layers increases with increasing the reactor pressure and then it eventually becomes saturated. The longitudinal optical phonon mode of ZnTe and a strong free exciton emission are clearly observed for all samples, indicating the ZnTe layers are of good crystal quality.

## References

[1] A. Garica, A. Remon, V. Munoz, R. Triboulet, J. Crystal Growth 191 (1998) 685.
[2] M. Nishio, Q.X. Guo, H. Ogawa, Thin Solid Films 343/344 (1999) 508.
[3] M. Nishio, Q.X. Guo, H. Ogawa, Thin Solid Films 343/344 (1999) 512.
[4] K. Sato, T. Asahi, M. Hanafusa, A. Noda, A. Arakawa, M. Uchida, O. Oda, Y. Yamada, T. Taguchi, Phys. Stat. Sol. (A) 180 (2000) 26.
[5] K. Hayashida, M. Nishio, H. Harada, S. Furukawa, Q.X. Guo, H. Ogawa, J. Crystal Growth 221 (2000) 404.
[6] V.I. Kozlovsky, A.B. Krysa, Yu.V. Korostelin, Yu.G. Sadofyev, J. Crystal Growth 214/215 (2000) 35.
[7] Q.X. Guo, M. Matsuse, T. Tanaka, M. Nishio, H. Ogawa, Y. Chang, S.L. Wang, J. Wang, J. Vac. Sci. Technol. A 19 (2001) 2232.
[8] M. Nishio, K. Hayashida, Q.X. Guo, H. Ogawa, Appl. Surf. Sci. 169/170 (2001) 226.
[9] Q.X. Guo, T. Tanaka, M. Nishio, H. Ogawa, X. Mei, H. Ruda, Jpn. J. Appl. Phys. 41 (2002) L118.
[10] Q.X. Guo, Y. Matsumoto, S. Wang, T. Tanaka, M. Nishio, H. Ogawa, Jpn. J. Appl. Phys. 41 (2002) 5069.
[11] T. Tanaka, K. Hayashida, M. Nishio, Q.X. Guo, H. Ogawa, J. Appl. Phys. 93 (2003) 5302.
[12] S. Wu, Z.Q. Ren, W.Z. Shen, H. Ogawa, Q.X. Guo, J. Appl. Phys. 94 (2003) 3800.
[13] J.H. Sun, W.B. Xie, W.Z. Shen, H. Ogawa, Q.X. Guo, J. Appl. Phys. 94 (2003) 7144.
[14] T. Tanaka, Y. Kume, M. Nishio, Q.X. Guo, H. Ogawa, A. Yoshida, Jpn. J. Appl. Phys. 42 (2003) L362.
[15] Z.G. Qian, W.Z. Shen, H. Ogawa, Q.X. Guo, J. Phys.: Condens. Matter 16 (2004) R381.
[16] I. Oja, M. Nanu, A. Katerski, M. Krunks, A. Mere, J. Raudoja, A. Goossens, Thin Solid Films 480/481 (2005) 82.
[17] N. Lovergine, M. Traversa, P. Prete, T. Di Luccio, L. Tapfer, A.M. Mancini, J. Crystal Growth 275 (2005) e1189.
[18] K. Wolf, A. Naumovl, T. Reisinger, M. Kastner, H. Stanzl, W. Kuhn, W. Gebhardt, J. Crystal Growth 135 (1994) 113.