

Effect of reactor pressure upon photoluminescence properties of ZnTe homoepitaxial layer

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ZnTe homoepitaxial layers on (100)-oriented ZnTe substrates were fabricated at different reactor pressures and their photoluminescence (PL) spectra and X-ray rocking curve (XRC) were measured. The measurement results show that reducing reactor pressure leads to the enhancement of the free excitonic emissions relative to the impurity-related emissions and the decrease of XRC linewidth. This indicates that both the PL property and the crystallinity for the ZnTe epilayer are significantly improved with reducing reactor pressure during growth.

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1. Introduction

Zinc telluride (ZnTe) is one of the promising materials for pure green light emitting diodes (LEDs) because of its direct transition band gap of 2.26 eV at room temperature. This compound does not contain expensive rare metals such as In and Ga, leading to the fabrication of LED with low cost. In addition to LED, ZnTe has been applied in a variety of optoelectronic devices such as terahertz detectors, solar cells, waveguides and modulators. A lot of efforts have been performed toward the growth and characterization of this material [1-4]. Recently, a ZnTe LED using the Al diffusion technique has been fabricated successfully and pure-green electroluminescence at a wavelength of 550 nm at room temperature was observed [5]. 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 has been confirmed to be a crucial factor for accurate control of the thickness of ZnTe layers [6]. To the best of our knowledge, however, no detailed study has been carried out on the reactor pressure dependence of the

optical properties and crystallinity of ZnTe homoepitaxial layers, especially in low reactor pressure range.

In this work, ZnTe epilayers on (100)-oriented ZnTe substrates were grown by MOVPE at reactor pressures of 300, 500 and 700 Torr, and their photoluminescence (PL) spectra and X-ray rocking curve (XRC) were examined. The measurement results show that the PL property and crystallinity of ZnTe epilayer depend markedly on the reactor pressure.

2. Experimental

ZnTe epilayers were grown by MOVPE at reactor pressures of 300 (sample A), 500 (sample B) and 700 Torr (sample C). Dimethylzinc (DMZn) and diethyltelluride (DETe) were used as source materials and H₂ as carrier gas. Commercially available undoped ZnTe (100) were used as substrates. The ZnTe substrate was ultrasonically cleaned by organic solvents, and dipped in a 1% Br-methanol solution. It was then cleaned by thermal annealing in H₂ at 470 °C for 30 min to remove the native oxide on the surface of ZnTe substrate before the growth. The transport rates of DMZn and DETe were kept at 15 μmol/min. The substrate temperature was kept at 400 °C. The thickness of ZnTe homoepitaxial layers is about 5 μm.

For PL measurements, the samples were mounted in a closed-cycle He cryostat and the temperature changed from 6 to 300 K. The 442 nm line of a He-Cd laser was

used as an excitation light source with the spot size of $\sim 250 \mu\text{m}$, and the excitation power changed from $1 \mu\text{W}$ to 10 mW . The PL signal from the sample was dispersed by a Jobin-Yvon iHR320 monochromator and detected by a thermoelectrical cooled Synapse CCD detector. The structural properties of the samples were examined by conventional θ - 2θ X-ray diffraction (XRD), and their crystalline qualities were evaluated by XRC of a high-resolution double-crystal method.

3. Results and discussion

Fig. 1 shows the PL spectra of the samples measured under an excitation power of 2 mW at 6 K . For sample A grown at the lowest reaction pressure of 300 Torr , as shown in Fig. 1(a), the PL spectrum is dominated by a strong ground state emission centered around 2.3814 eV of free excitons (FE), which is denoted as FE(1s). The peaks at 2.3570 and 2.3909 eV are assigned to the longitudinal optical phonon replica (FE(1s)-LO) of the FE(1s) peak and the first excited state (FE(2s)) of FE, respectively [7]. In addition, the weak peak (I_x) located at 2.3650 eV is the emission of the exciton bound to a neutral double acceptor, which may be a group IV impurity, replacing the Te site, namely carbon [8]. While the peak (I_a) at 2.3750 eV is attributed to an emission from the excitons bound to neutral acceptors such as Li, Cu or Na. This peak is observed widely for undoped ZnTe grown by other growth methods. Previous secondary ion mass spectroscopy analysis on nominally undoped ZnTe epitaxial layer showed that Na is a dominant impurity [9].

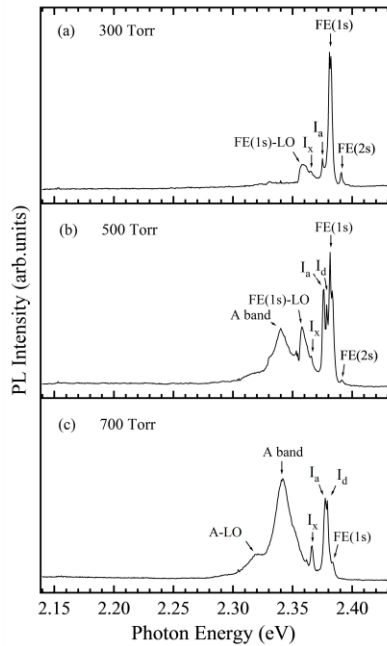


Fig. 1. 6 K PL spectra of ZnTe epilayers grown at different reactor pressures of 300 (a), 500 (b) and 700 Torr (c). $P = 2 \text{ mW}$.

In contrast, however, the I_a peak for sample B grown at 500 Torr obviously increases in intensity relative to the FE(1s) peak, and meanwhile a new emission peak (I_d) at 2.3785 eV and a new emission band (A band) at around 2.340 eV appear, as shown in Fig. 1(b). The peak I_d is attributed to a neutral donor excitonic emission, which closely matches the 2.3780 eV emission reported in moderately Al-doped ZnTe homoepitaxial layers grown by molecular beam epitaxy [10], and in the I- or Al-doped ZnTe homoepitaxial layers grown by MOVPE [1,11]. The A band is considered to be originating from a defect- or impurity-related emission. Furthermore, for sample C grown at 700 Torr , it is found from Fig. 1(c) that the peak I_a , peak I_d and A band further increase in intensity relative to the FE(1s) peak compared with sample B, while the FE(2s) peak almost disappears. In addition, it is worth noting for all the PL spectra shown in Fig. 1 that the Y lines usually located at 2.188 and 2.147 eV which are known to arise due to extended structural defects [12], are not observed, and that the oxygen-bound-exciton (OBE) emission band around 650 nm whose zero-phonon line locates at around 1.986 eV , reported by Ekawa and Taguchi [13] and Zhang et al. [14], also does not appear. The above mentioned measurement results show that although all these ZnTe homoepitaxial layers have good PL property due to the absence of the Y lines and OBE emission, their optical quality depends clearly on the reactor pressure, as Fig. 1 shows, the free excitonic emission intensity gradually weakens relative to the impurity-related emission intensity with increasing reactor pressure. Moreover, the PL spectra of the epilayers at room temperature display that the ZnTe epilayer grown at 300 Torr has the strongest PL emission (not shown here), indicating the ZnTe epilayer grown at 300 Torr is of the best optical property among the samples whether at low temperature or at room temperature.

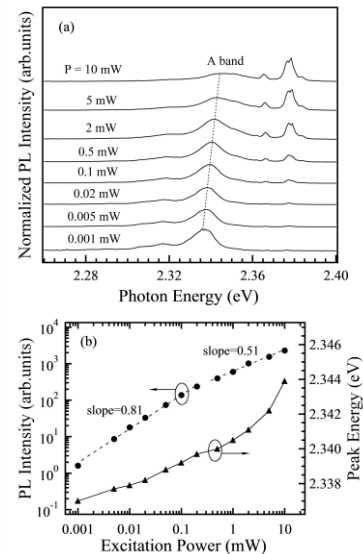


Fig. 2. (a) Excitation power dependence of PL spectra of ZnTe epilayer grown at a reactor pressure of 700 Torr ; (b) The intensity and peak energy of the A band as a function of excitation power, obtained from raw data in Fig. 2(a). $T = 6 \text{ K}$.

To determine the origin of the A band, Fig. 2(a) shows the typical PL spectra of sample C as a function of excitation power measured at 6 K, and the excitation power dependences of the peak energy and intensity of the A band in the PL spectra are summarized in Figs. 2(b). As clearly seen from Fig. 2(b), when the excitation power increases from 1 μ W to 10 mW, the A band shifts to higher-energy side, while its PL intensity increases exponentially first with a factor of 0.81 below 0.2 mW and then with a fact of 0.51 showing that the emission intensity of the A band is trending toward saturation with increasing the excitation power. This is a typical characteristic of donor-acceptor pair (DAP) emission often observed in the spectra of the ZnTe bulks and ZnTe homoepitaxial epilayers [1,15]. Consequently, the A band is considered to be a DAP emission, which may result from the carriers transition between Al donor and Na (or Li) acceptor [1]. The above mentioned peak blueshift is due to the saturation of the PL components from distant pairs emitting in the low-energy part of a spectrum.

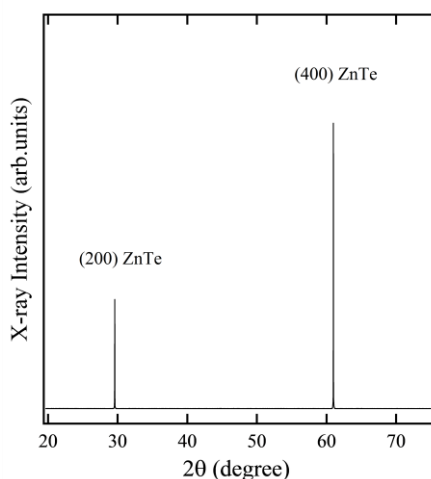


Fig. 3. A typical XRD profile of the ZnTe homoepitaxial layer grown at a reactor pressure of 300 Torr.

To obtain the structural property of ZnTe epilayer, the XRD measurement for the samples was performed. Fig. 3 shows a typical XRD profile of sample A. Only two peaks from (200) and (400) reflections of ZnTe are observed, supporting the epitaxial growth of ZnTe films on ZnTe substrate. In order to further clarify reactor pressure effect on crystalline quality of the ZnTe epilayer, the XRC measurements of the (400) reflections from the ZnTe epilayers are performed. As shown in Fig. 4, the full width at half maximum (FWHM) value of the XRC increases rapidly from 32 to 75 and 136 arcsec with increasing reactor pressure from 300 to 500 and 700 Torr. This indicates that reducing reactor pressure can improve the crystallinity of ZnTe epilayer. It is in good agreement with the PL measurement results obtained in Fig. 1.

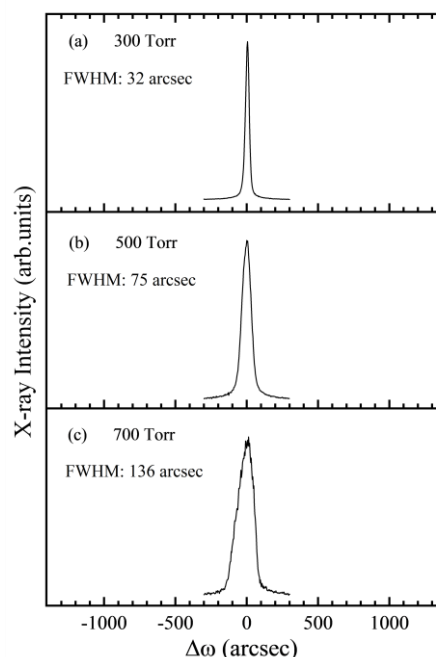


Fig. 4. XRCs for (400) reflection from ZnTe epilayers grown at different reactor pressures of 300 (a), 500 (b) and 700 Torr (c).

The above mentioned results obtained by the PL and XRC measurements, can be qualitatively explained as follows. In our previous work [6], we have shown that with increasing reactor pressure the growth rate of the ZnTe epilayer first increases monotonically below 600 Torr and then becomes saturated. This suggests that the low-pressure growth in the reactor pressure range below 600 Torr is suitable for accurate control of the epilayer thickness, while the reaction rate of the precursors increases with increasing reactor pressure below 600 Torr. Consequently, the better PL property and crystallinity of the ZnTe epilayer grown at 300 Torr can be ascribed to the fact that since the growth rate of the ZnTe epilayer, corresponding to the reaction rate of the precursors, is smaller at 300 Torr, the adsorbed precursors have enough time to diffuse over the surface to find its proper position, thus facilitating recrystallization of the adsorbed precursors. However, an increasing reactor pressure can result in the increase of the precursor reaction rate to yield ZnTe epilayer, thus leading to the formation of vacancy or inclusion of impurities easily [16,17]. Furthermore, the low-pressure MOVPE growth process also has following advantages [18-20]: firstly, elimination of parasitic nucleation in the gas phase. This is due to the fact that the low reactor pressure increases the temperature gradient near the surface of the substrate, and reduces the thickness of the high-temperature region above the substrate, thereby suppressing the occurrence of parasitic reactions; secondly, reduction of autodoping (i.e. the doping of an epitaxial layer by volatile impurities that originate from the substrate). This is because the

volatile impurities can be taken away from the reactor by the main gas flow due to the greater diffusion coefficient of impurities at low reactor pressure. All the above mentioned factors result in the improvement of the PL property and crystallinity of the ZnTe epilayer grown at the low reactor pressures, especially at 300 Torr.

4. Conclusion

ZnTe homoepitaxial layers on the (100)-oriented ZnTe substrates were fabricated at reactor pressures of 300, 500 and 700 Torr using dimethylzinc and diethyltelluride as source materials by MOVPE. The reactor pressure dependences of the PL spectrum and XRC of the ZnTe epilayer manifest that reducing reactor pressure results in the enhancement of the free excitonic emission relative to the impurity-related emissions as well as the decrease of XRC linewidth, indicating that the reducing reactor pressure can improve the PL property and crystallinity of ZnTe epilayer. The facts can be explained as that the adsorbed precursors have enough time to diffuse over the surface to find its proper position at low reactor pressure due to the low reaction rate of the precursors, thus facilitating recrystallization of the adsorbed precursors. At the same time, the growth process at low reactor pressure also results in the elimination of parasitic nucleations in the gas phase and the reduction of autodoping.

Acknowledgements

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