Improvement of MOVPE grown ZnTe:P layers by annealing treatment

K Saito, K Fujimoto, K Yamaguchi, T Tanaka, M Nishio, Q X Guo and H Ogawa

1Synchrotron Light Application Center, Saga University, 1 Honjo, Saga 840-8502, Japan
2Department of Electrical and Electronic Engineering, Saga University, 1 Honjo, Saga 840-8502, Japan
saikatsu@vbl.saga-u.ac.jp

Abstract. The effects of annealing treatment in nitrogen flow upon the optical and electrical properties of ZnTe:P homoepitaxial layers grown by metalorganic vapour phase epitaxy at various substrate temperatures have been investigated. The photoluminescence properties at 4.2 K of the layers are drastically improved by the annealing treatment independent of the substrate temperature. Donor-acceptor pair emission vanishes and instead free-to-bound transition emission becomes significant, and also broadened acceptor-related excitonic emission slightly shifts towards longer wavelength side, indicating reduction of compensation effect and the activation of the P atoms. These are conformed with the fact that the carrier concentration of ZnTe:P layers are increased significantly for any substrate temperature.

1. Introduction
ZnTe is a promising material for pure green light emitting diodes (LEDs). Phosphorus (P) is considered to be a suitable $p$-type dopant in ZnTe, since the pure green LEDs is obtainable by a thermal diffusion of Al into $p$-type ZnTe:P [1]. As for metalorganic vapour phase epitaxy (MOVPE), which is a promising growth technique for mass production, we have successfully grown ZnTe:P homoepitaxial layers by MOVPE using tris-dimethylaminophosphorus (TDMAP) as a P source [2-4]. A use of a substrate temperature of 500 ºC leads to a high carrier concentration such as $1.3\times10^{18}$ cm$^{-3}$, but brings about roughly surface morphology for ZnTe:P layer on (100) ZnTe substrate. For a relatively lower substrate temperature such as 400 ºC which gives relatively good surface morphology for ZnTe:P layer on the (100) ZnTe substrate, on the other hand, a carrier concentration is as low as $2\times10^{17}$ cm$^{-3}$ even for the layer grown at high TDMAP transport rate and the photoluminescence (PL) spectrum at 4.2 K shows only donor-acceptor pair emission (DAP) [2-4]. Recently, we have discovered that the annealing treatment in nitrogen flow (ATN) improves the PL properties for such ZnTe:P layers grown at a substrate temperature of 420 ºC significantly [5]. It is also expected to give improvement of electrical properties of ZnTe:P layers. In this study, we investigated the effects of ATN upon the optical and electrical properties of ZnTe:P layers grown by MOVPE over wide substrate temperature range.
2. Experimental procedures
The ZnTe:P layers were grown in the atmospheric pressure MOVPE system with horizontal reactor, different from the previous studies in which a conventional vertical type was used [2-5]. Dimethylzinc (DMZn) and diethyltelluride (DETe) were used as source materials, while TDMAP as a dopant source. Hydrogen was employed as a carrier gas with the total flow rate of 4.8 slm. In order to facilitate the electrical properties of ZnTe:P layers, high-resistive (100) ZnTe:Ga substrates were used. The substrate temperature was varied from 360 to 500 ºC, while the transport rates of DMZn, DETe and TDMAP were fixed at 92, 83 and 3 μmol/min, respectively. ATN for the as-grown layers was performed in nitrogen flow at a low temperature of 420 ºC for 2 hours. The characterization of as-grown and annealed ZnTe:P layers was performed by PL and electrical measurements. PL measurement was performed at 4 K using a 488 nm Ar⁺ laser as an excitation light source. The power density on the surface of the layers was kept at about 50 mW/cm². The laser power was attenuated by neutral density filters only when the excitation intensity dependence of PL was investigated. The electrical properties of the layers were determined by van der Pauw’s method using electroless Pd electrode as ohmic contacts. The growth rate of each as-grown layer was estimated from the cross sectional image using cathode luminescence microscopy.

3. Results and discussion
Figure 1 shows the PL spectra at 4.2 K of as-grown and annealed ZnTe:P layers for various substrate temperatures. In the PL spectra of as-grown layers (dotted lines), two or three distinct peaks of an excitonic emission line (Iₐ) and an emission band A and/or B are found. For the A band, as

- **Figure 1.** PL spectra of as-grown and annealed ZnTe:P layers for various substrate temperatures.
- **Figure 2.** Excitation power dependent PL spectra of (a) A band and (b) B band.
shown in figure 2(a), the peak energy is independent of the excitation power and also the difference between the band gap of ZnTe [6] and this peak energy is comparable to P accepter level [7,8], indicating that this band is due to free-to-bound transition emission (FB). Figure 2(b) shows the behaviour of B band excited at various excitation powers at 4.2 K. The peak B shifts to higher energy side as the excitation power increases, which is a characteristic of DAP [9]. In the spectra of the layers grown at substrate temperature ($T_s$) < 390 °C, $I_a$ and overlapped FB and DAP are observed. When the substrate temperature is increased up to 395 °C, it is noteworthy that the spectrum is marked by $I_a$ with FB while DAP disappears, indicating the as-grown layer of good crystalline quality. As seen in figure 3, which shows the relationship between substrate temperature and growth rate of the ZnTe:P layer, the substrate temperature of 395 °C corresponds to a transition region of growth modes from the mass transport to surface kinetics. At a substrate temperature as high as 405 °C, DAP dominates over FB. The variation for as-grown layers up to the substrate temperature of 405 °C is consistent with the previously study [3], except for the broadening and slight shift towards longer wavelength side of $I_a$. For the layers grown at $T_s \geq 425$ °C corresponding to the mass transport-limited mode, on the other hand, $I_a$ and FB are clearly observed instead of DAP, indicating a good optical quality. This means that, a compensation is reduced for the ZnTe:P layers grown at $T_s \geq 425$ °C. According to the previous study [5], hydrogen may induce the formation of defect-related donor.

For ZnTe:P layers after ATN, as shown by solid lines in figure 1, the PL spectra of the ZnTe:P layers grown at $T_{sub} \leq 405$ °C are changed significantly except for the layer grown at 395 °C. DAP vanishes, and instead FB becomes predominant. As for $I_a$, it broadens and shifts towards longer wavelength side, for any substrate temperature. This may be due to the increase in the number of P acceptors. Thus, it is expected that ATN is also effective for improving the electrical properties of ZnTe:P layers independent of the substrate temperature.

Figure 4 shows the electrical properties of as-grown and annealed ZnTe:P layers as a function of substrate temperature. For as-grown ZnTe:P layers, the carrier concentration (open circles) increases monotonically with increasing substrate temperature and then become saturated slightly. On the other hand, the mobility (open triangles) slightly decreases with increasing substrate temperature. The increase of carrier concentration with substrate temperature may be due to the increase of the efficiency in thermal decomposition of TDMAP, in agreement with the previous study [3]. The maximum carrier concentration reaches $1.7 \times 10^{18}$ cm$^{-3}$ at a substrate temperature of 500 °C, while a substrate temperature of 395 °C gives a low carrier concentration of $2.5 \times 10^{17}$ cm$^{-3}$. It should be noted that the highest hole concentration obtained here is higher than that obtained using tertiary-butylphosphine [7]. For ZnTe:P layers after ATN, as shown by filled circles in figure 4, the carrier concentration is increased for any substrate temperature. Even for ZnTe:P layers grown at a low

![Figure 3. Relationship between substrate temperature and growth rate of ZnTe:P layer.](image)

![Figure 4. Electrical properties of as-grown and annealed ZnTe:P layers for various substrate temperatures.](image)
substrate temperature of 380 ºC, a high carrier concentration of $1.3 \times 10^{18} \text{cm}^{-3}$ is obtained, which is comparable to as-grown ZnTe:P layer grown at 500 ºC. On the other hand, the mobility is almost unchanged independent of ATN as shown by filled triangles in figure 4. Thus, ATN improves the electrical properties as well as PL properties dramatically. Since ZnTe:P layers grown at low substrate temperatures which exhibit the presence of DAP in PL spectra, the enhancement in the carrier concentration due to hydrogen passivation. However, the enhancement in the carrier concentration by ATN may be due to an activation of the P atoms rather than the reduction of a compensation effect, since it is noticeable that a carrier concentration is enhanced to be $4.3 \times 10^{18} \text{cm}^{-3}$ for ZnTe:P layer grown at a substrate temperature of 450 ºC which does not show DAP in PL spectrum.

4. Conclusions
We have investigated the effects of annealing treatment in nitrogen flow upon the optical and electrical properties of ZnTe:P homoepitaxial layers grown by horizontal MOVPE at various substrate temperatures. ATN improves the electrical properties as well as PL properties dramatically for any substrate temperature. The enhancement in the carrier concentration by ATN may be due to an activation of the P atoms rather than the reduction of a compensation effect. Through this study, high carrier concentration as high as $4.3 \times 10^{18} \text{cm}^{-3}$ is attained.

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References
[1] Tanaka T, Kume Y, Nishio M, Guo Q X, Ogawa H and Yoshida A 2003 *Jpn. J. Appl. Phys.* **42** L362
[2] Hayashida K, Tanaka T, Nishio M, Guo Q X and Ogawa H 2004 *Phys. Status Solidi* (c) **1** 718
[3] Hayashida K, Tanaka T, Nishio M, Guo Q X, Tanikawa T and Ogawa H 2006 *Phys. Status Solidi* (c) **3** 1172
[4] Tanaka T, Nishio M, Hayashida K, Fujimoto K, Guo Q X and Ogawa H 2007 *J. Cryst. Growth* **298** 437
[5] Saito K, Fujimoto K, Yamaguchi K, Tanaka T, Mitsuhiro N, Guo Q X and Ogawa H 2007 *Phys. Status Solidi* (b) **244** 1634
[6] Dean P J, Venghaus H and Simmonds P E 1978 *Phys. Rev. B* **18** 6831
[7] Wolf K, Stanzl H, Naumov A, Wagner H P, Kuhn W, Hahn B and Gebhardt W 1994 *J. Cryst. Growth* **138** 412
[8] Wolf K, Naumov A, Wagner H P, Gilg F, Sahin H, Stanzl H and Gebhardt W 1994 *J. Lumin.* **60/61** 544
[9] Williams E W and Bebb H B 1972 Photoluminescence II: Gallium Arsenide (*Semiconductors and Semimetals* vol 8) ed R K Willardson and A C Beer (New York: Academic Press) p 321