Annealing Effects of a High-Quality ZnTe Substrate

KENJI YOSHINO,1,4 MINORU YONETA,2 KENZO OHMORI,2 HIROSHI SAITO,2 MASAKAZU OHISHI,2 and TAKAYUKI YABE3

1.—Department of Electrical and Electronic Engineering, Miyazaki University, Miyazaki 889-2192, Japan. 2.—Department of Applied Physics, Okayama University of Science, Okayama 700-0005, Japan. 3.—Innovative Materials Development Center, Nikko Materials Co. Ltd., Saitama 335-8502, Japan. 4.—E-mail: yoshino@pem.miyazai-u.ac.jp

The sharp photoluminescence (PL) and optical-reflection spectra in the band-edge region of the high-quality nondoped ZnTe substrate (100) were observed at 4.2 K. Free exciton, associated with lower and upper polaritons (EXL and EXU) at 2.382 eV and 2.381 eV, respectively, were clearly observed. This meant that this substrate was high quality. The intensity of a bound exciton peak (2.375 eV), which is caused by a Zn vacancy, of a neutral acceptor decreased with an increase of the Zn vapor pressures.

Key words: ZnTe, substrates, annealing

INTRODUCTION

Zinc telluride (ZnTe), a II-VI compound semiconductor and a zincblende structure, has been accepted for optical devices, such as pure-green light emitting diodes (LEDs) and laser diodes because it has an energy gap of 2.26 eV at room temperature and the band structure is of direct optical-transition type. It is, however, difficult to realize p-n junctions because of the well-known compensation effect specific to II-VI materials. The p-type ZnTe can be easily obtained, but n-type ZnTe cannot be realized because of self-compensation. Low-resistivity ZnTe crystals can be used as lattice-matching substrates for these electroluminescence devices.

Recently, ZnTe-based LEDs were successfully demonstrated by Sato et al.1,2 They obtained high-quality, 80-mm-diameter ZnTe crystals grown by the vertical gradient freeze (VGF) method without seed crystals3-5 and fabricated p-n junctions by thermal diffusion of Al in p-type ZnTe substrates. Electroluminescence of 550 nm was clearly visualized under room light at room temperature. To develop ZnTe-based LEDs, it is indispensable to clarify the property of n- and p-type ZnTe.

Furthermore, ZnTe also attracts our attention for electro-optic (EO) devices because of a relatively high EO coefficient and dielectric constant. A free-space EO sampling technique for the coherent characterization of THz beams was developed, and the conversion of a time-resolved far-infrared image into a time-resolved optical image using a ZnTe sensor was demonstrated.6,7 In the case of EO devices, high-resistivity ZnTe is necessary. An n-type impurity is conventionally doped in ZnTe to obtain high-resistivity crystals.

To know the point defects in the single crystal, annealing is very important for vacancy defects. However, there are few reports on annealing in ZnTe.8,9 Therefore, in the previous paper,10 it was found that wafer annealing is very effective to control the stoichiometric composition of P-doped ZnTe single crystals under the condition where the relationship between zinc pressure and annealing temperature is

$P_{\text{Zn}} (\text{Pa}) = 9 \times 10^{11} \exp(-2.02 \text{ eV}/kT)$

where $P_{\text{Zn}} (\text{Pa})$ is zinc vapor pressure during the anneal, $k$ is Boltzmann’s constant, and $T$ (K) is the absolute temperature.

In this work, nondoped p-type ZnTe substrates were annealed under Zn atmosphere. Optical spectroscopy, such as photoluminescence (PL), was investigated at liquid helium temperature to study the point defects of the nondoped ZnTe substrates.

EXPERIMENTAL PROCEDURES

Nondoped ZnTe substrates were grown by the VGF method.3 Boron oxide (B2O3) was used to prevent the evaporation of Zn and Te during crystal growth. The substrates were polished and etched in a 1 vol.% Br2-methanol solution for 5 min to remove the damaged
surface layer. The etch pit density of the substrates were counted after a 1HF:2H2O2:2H2O solution. The mean dislocation density of the substrates was about 4,000–7,000 cm−2.

The nondoped ZnTe substrates were annealed at Zn atmosphere. The Zn vapor pressure could be changed from 0.77 Pa and 34 Pa. The horizontal annealing furnace, which has a two-zone temperature distribution for controlling the Zn vapor pressure during annealing, was used for the experiments.6

The PL measurements were carried out between liquid helium temperatures. The sample was excited by a He-Cd laser (325 nm and 441.6 nm). The PL spectra were measured by using a grating monochromator (Jovin Yvon (France) HR-1000) and a photomultiplier (Hamamatsu R2368).

RESULTS AND DISCUSSION

The PL and optical-reflection spectra in the band-edge region at 4.2 K of the high-quality nondoped ZnTe substrate (100) are shown in Fig. 1. The inset shows details of the band-edge region in the PL spectrum. One dip is clearly observed at 2.381 eV in the optical-reflection spectrum. On the other hand, in the PL spectrum, four kinds of peaks are present around 2.382 eV, 2.381 eV, 2.379 eV, and 2.375 eV in the band-edge region. Free exciton, associated with lower and upper polaritons (EXL and EXU) at 2.382 eV and 2.381 eV, respectively, were clearly observed.10 The other peaks at 2.379 eV and 2.375 eV are due to the radiative recombination of excitons bound to neutral donors (I2) and neutral acceptors (I1), respectively. Using Haynes’ rule,11 we can estimate the activation energies of donor and acceptor, which are 10 meV and 60 meV, respectively. A value of 10 meV is unknown to donor activation energy. On the other hand, a value of 60 meV is reported as the acceptor activation energy of Zn vacancy.12 Therefore, the I1 peak seems to be due to the Zn vacancy (VZn).

The PL spectrum also includes the radiative recombination of donor-to-acceptor pair (DAP) emission at 2.334 eV with longitudinal-optical phonon replicas and free-to-acceptor emission at 2.343 eV. Furthermore, unknown peaks are observed at 2.348 eV and 2.340 eV. It seems that these peaks originate from residual impurities, such as boron and silicon, by the glow discharge mass spectrometry. The I2 and I1 emissions indicate a doublet structure with an energy separation of about 2 meV, which originates from a JJ coupling. These observations demonstrate the high quality of the nondoped single crystal.

Figure 2 shows the dependence of the Zn vapor pressures in the PL spectra. From the previous paper.10 in this annealing condition (600°C, 40 h), the Zn vapor pressure around 2.8 Pa becomes a stoichiometric composition. On the other hand, the Zn vapor pressure more than and less than 2.8 Pa become Zn-rich and Zn-poor compositions, respectively.