한국표면공학회지
Journal of the Korean Institute of Surface Engineering
Vol. 35, No. 5,
Oct. 2002
<연구논문>

적외선 센서 재료로 사용되는 고순도 ZnTe 박막의 평가

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Evaluation of the High Purity ZnTe which is an Far-Infrared Sensor Material

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Abstract

Optical measurements have been used to study the biaxial tensile strain in heteroeptaxial ZnTe epilayers on the (100) GaAs substrate by hot wall epitaxy (HWE) with Zn reservoir. It is effect on the low-temperature photoluminescence spectrum of the material. Optimum growth condition has been determined by a four-crystal rocking curve (FCRC) and a low temperature photoluminescence measurement (PL). It was found that Zn partial pressure from Zn reservoir has a strong influence on the quality of grown films.

Under the determined optimum growth condition, ZnTe epitaxial films with thickness of 0.72~24.8μm were grown for studying the effect of the thickness on crystalline quality. The PL and FCRC results indicated that the quality of ZnTe films becomes higher rapidly with increase of thickness up to 6μm. The best value of the FWHM of the four crystal rocking curve, 66 arcsec, was obtained on the film with 12μm in thickness. The PL spectrum shows the splitted strong free exciton emissions and very weak deep band emissions. These results show the high quality of films.

Keywords : ZnTe, HWE, heteroepitaxy, free exciton, XRD, photoluminescence.

1. Introduction

Due to its wide, direct band gap of 2.26eV at room temperature, Zinc telluride is an attracted interest for potential applications to optical devices in the green spectral region$^{1)}$. For a practical application, high quality epitaxial layers should be grown. That is, if is introduces to application in detail, ZnTe has been identified as a very important sensing material for photonic applications such as laser generation, modulation, nuclear radiation sensing detection and devices which make use of novel optical nonlinearities[2]. Recently, various research works have been carried out to grow high quality ZnTe epilayers on GaAs substrates by means of molecular beam epitaxy[3], metal-organic chemical vapor deposition[4], atomic layer epitaxy[5] and hot wall epitaxy[6]. Among these epitaxial growth methods, hot wall epitaxy (HWE) has its own advantage[7]. For instance, all the steps, such as vaporization of source materials, transportation and growth, occur under the near-thermal equilibrium conditions, which allow us to grow high quality films. Actually, it has been found that the temperature of reservoir has strong influence on growth rate and film quality of CdTe epitaxial films[8]. Until now, in order to grow high quality ZnTe epilayers by HWE, the effect of substrate temperature, source temperature and preheating temperature has been examined[9], however, unfortunately the epitaxy has been performed without reservoir.

On the other hand, ZnTe/GaAs heterostructure has some problems[10] such as the out-diffusion of Ga and As from substrate, large lattice mismatch (8%) and different thermal expansion coefficients between the substrate and the grown film. Therefore, it has been very difficult to grow ZnTe films with a low defect density on GaAs substrate. Although the growth of thick ZnTe films can relax the strain caused by the lattice misfit at the epi/substrate interface, the large difference in thermal expansion coefficients will induce a large tensile strain even in the thick ZnTe layer during cooling after the growth.

The purpose of this study is evaluates an optimum condition using photoluminescence for growing a high quality ZnTe epitaxial layer on (100) GaAs substrate. In particular, I used a reservoir to improve the quality of ZnTe epitaxial layer. Furthermore, I examined the dependence of the epilayer thickness on crystallinity.

II. Experimental procedure

ZnTe epilayers were grown on semi-insulating (100) GaAs substrates, in HWE apparatus with a Zn reservoir[11]. In order to grow high quality ZnTe epitaxial layer, high purity source and reservoir materials were used in our experiment. The ZnTe poly-crystal, at first, synthesized in a quartz ampoule, using 6N-up Zn purified by vacuum distillation and overlap zone melting, and 6N-up Te provided by Osaka Asahi Metal Co. ZnTe polycrystals were further purified by sublimation method and subjected to a source for growing bulk single crystals by prior method. The ZnTe single crystals were cleaved to pieces, and put them into HWE source chamber.

Since the HWE growth depends on many factors such as the substrate temperature, the source temperature, the wall temperature and the reservoir temperature, their effects were clarified and the most suitable condition was determined.

The substrates were treated by ultrasonic cleaning with trichloroethylene, acetone, methanol and deionized water. Before starting growth, the substrates were heat-treated at 863K for 20 min under a vacuum of 2×10^{-4} Pa to remove the surface oxide layer. The vacuum was maintained below 2×10^{-4} Pa during the growth with a turbo molecular pump. The detail of growth condition, such as substrate temperature ($T_{sub.}$), source temperature ($T_{sou.}$), wall temperature ($T_{wall.}$), and reservoir temperature ($T_{res.}$), will be described later. As the wall temperature ($T_{wall.}$), $T_{sou.}+10K$

is adopted[7)].

The thickness and surface roughness of the ZnTe epilayers were measured by a surface profiler (DEKTAK^3). The surface morphology was observed with the SEM. The SEM observations have shown that all the surface of the present ZnTe epilayers have a smooth, mirror-like surface. To confirm the crystal orientation, X-ray diffraction was performed. Only the (400) peaks from GaAs substrate and ZnTe epilayer could be observed, which shows that the epilayers grow in the same (100) direction as the GaAs substrate orientation.

I also examined the crystallinity of the film by photoluminescence (PL) and four-crystal rocking curve (FCRC). PL was measured at 4.2K using ~ 390nm second harmonic wave of Ti : sapphire laser (10mW) as a exciting light source. I used two different gratings : 300 and 1200 grooves/nm which provide for wide range spectrum information and precise information about interesting peaks, respectively. The light from a halogen lamp was used for the reflectance measurement.

III. Result s and discussion

In the paper[12)] announced previously, growth parameter in which ZnTe was grown on GaAs (100) substrates using HWE equipment estimated the optimal condition in search of the optimum conditions using XRD. And I regard the optimum growth conditions of a ZnTe/GaAs thin film as the impurities relation of a thin film being authorized and carrying out comparison evaluation with a XRD result shortly using PL. At the beginning, I adopted the substrate temperature ($T_{sub.}=623K$) and source temperature ($T_{sou.}=743K$) reported for HWE of ZnTe/GaAs[9)].

In the paper[12)] previously, 463K is found to be optimum reservoir temperature with the change of the full-width at half-maximum (FWHM) with the reservoir temperature, which are measured on ZnTe epilayers with thickness of about 1.7μm. When the reservoir temperature is about 463K, FWHM shows a minimum value, and when it deviates from this temperature, FWHM value increases. This shows that more defects are introduced into the epilayers, as growth is carried out under a non-stoichiometric condition, and also that the reservoir plays an important role in the case of HWE.

The quality of ZnTe epilayers grown on GaAs substrate by HWE was evaluated by photoluminescence (PL). PL measurement, which is the representative technique of the optical measurement, provides basic physical parameters such as band gap, impurity level, defect and crystallinity. PL is the optical radiation, when the specimen is excited with light, and one of the most important basic research tools for studying II-VI compounds about impurity levels,[13)] defects[14)] and so on.

For the further optimization, effects of substrate temperature and reservoir temperature were re-examined using other conditions optimized in the previous steps. Then, PL spectrum was observed and seen, consulting the paper contributed previously, fixing $T_{sub.}=623K$ and $T_{res.}=463K$, and also changing Source Temperature . Firstly, PL spectra at low temperature were also measured. Fig. 1 shows the PL spectra of ZnTe films grown for 3h under the different source temperature. The spectrum of ZnTe film grown under the condition of $T_{sou.}=803K$ shows the strongest band edge emission and the weakest deep emissions. This result agrees with four-crystal XRD result in

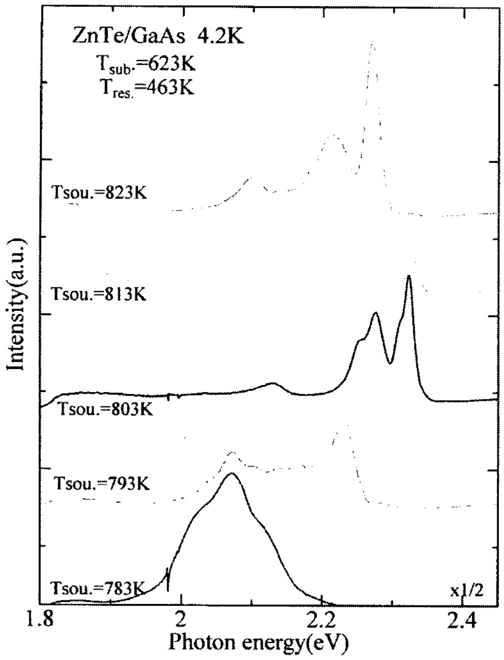

Fig. 1 Dependence of PL spectra on source temperature

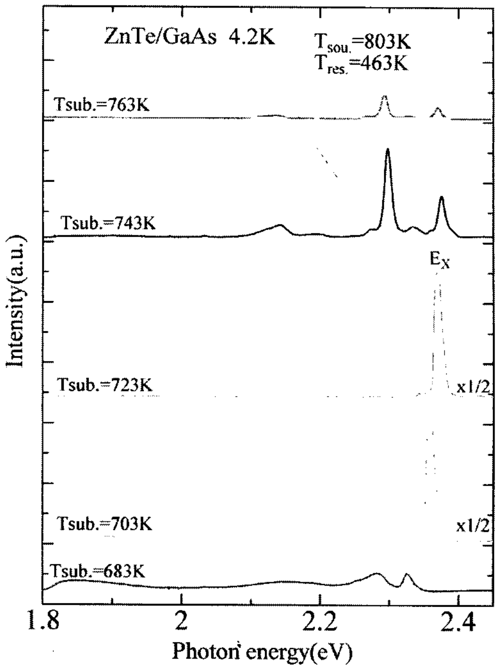

Fig. 2 Dependence of PL spectra on substrate temperatuer

the previous paper[12].

On the other hand, FWHM value depends on the substrate temperature, FWHM value decrease remarkably up to 723K, and then increase with substrate temperature. Consequently, it is found that 723K is the most suitable substrate temperature, which is higher than that adopted for the XRD result shown in the previous paper[12].

PL spectra shown in Fig. 2 also confirm this result. The ZnTe film grown at 723K shows the sharpest FE emission line and no deep emission, showing the highest quality with ZnTe epitaxial film. Therefore, $T_{sub.}$=723K is the most suitable growth temperature. This result agrees with the four-crystal XRD result shown in the previous paper[12].

PL was observed and seen, while substrate 723K and source temperature 803K are fixed and reservoir temperature carried out temperature change in the Fig. 3. Fig. 3 shows PL spectra of ZnTe epilayers grown at 723K with the different reservoir temperature of 443K~483K. The specimen grown under the optimum reservoir temperature (463K) shows the sharpest and strongest FE emission. On the other hand, deep emission becomes more remarkable when reservoir temperature is lower or higher than 463K. This indicates that the ZnTe epitaxial film grown under $T_{res.}$= 463K is the highest quality. Therefore, $T_{res.}$=463K was reconfirmed to be the most suitable temperature. This result indicates that the reservoir temperature is very important to support stoichiometric condition during the epitaxial growth. The optimized growth condition of ZnTe epilayer was summarized in the Table 1.

Effect of epilayer thickness on the crystallinity

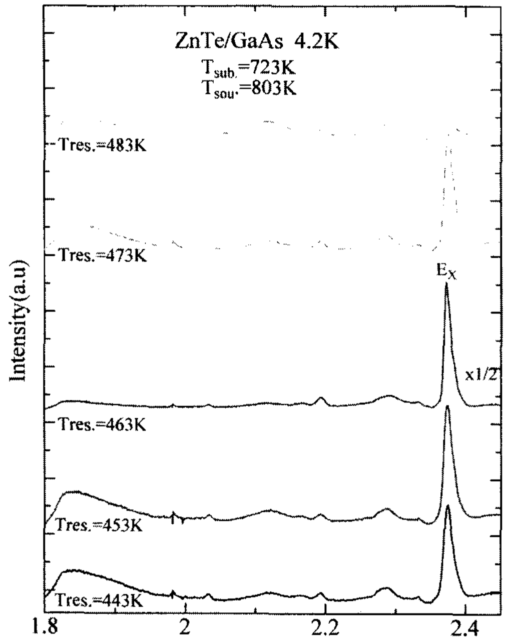

Fig. 3 PL spectra of ZnTe epilayers grown under the different reservior temperature

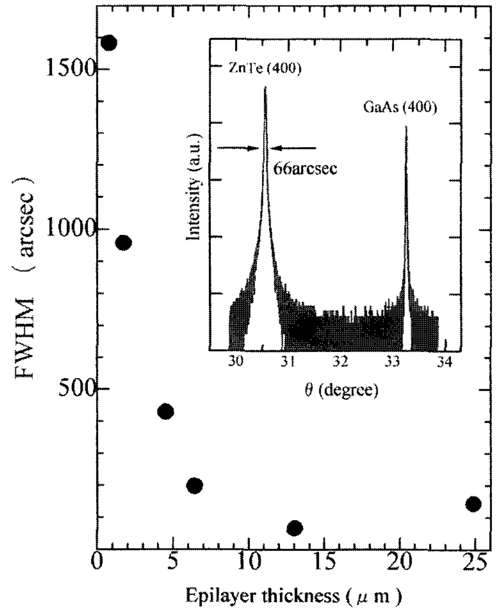

Fig. 4 The film thickness dependence of the FWHM. The insert is the four crytal rocking curves (FCRC) measured on the best of a good quality ZnTe epilayer

was investigated using the optimum growth condition. Fig. 4 shows the dependence of FWHM on the ZnTe epilayer thickness. The FWHM value shows a strong dependence on ZnTe epilayer thickness. For the films thinner than 6μm, the FWHM decreases very steeply as the thickness increases. For the film thicker than 6μm, it becomes an almost constant value. At the thickness of 12μm, the smallest value of 66 arcsec, which is the best value so far reported on ZnTe epilayers, was obtained.

PL spectrum measured on a 12μm thick epilayer using the grating of 300 grooves/nm is shown in Fig. 5(a). The excitonic emission peaks such as free-exciton (FE) and bound exciton (BE) peaks could be resolved clearly and intensity of the FE peak is extremely larger than that of the BE peaks. The other emissions, such as the donor-acceptor pair emission around 2.3eV[15] and Y-band emission are hardly observed in this specimen.

In the case of ZnTe/GaAs, the oxygen-bound-emission (OBE) band around (650nm) whose zero-phnon line locates at 1.986eV has been generally observed in so far reported PL spectra[16]. Our sample does not show such an emission line. These results indicate that the ZnTe epilayer grown in the present paper is of high quality.

Detailed spectrum in the band edge region of Fig. 5(a) was measured using 1200 grooves/nm grating and shown in Fig. 5(b). Emission lines in the PL spectrum was assigned by estimating their peak positions and also measuring the refraction spectra shown in the figure. The high resolution measurement makes the FE peak split clearly into 2 peaks. Furthermore, measured reflection spectra shows that the double peaks are related to free

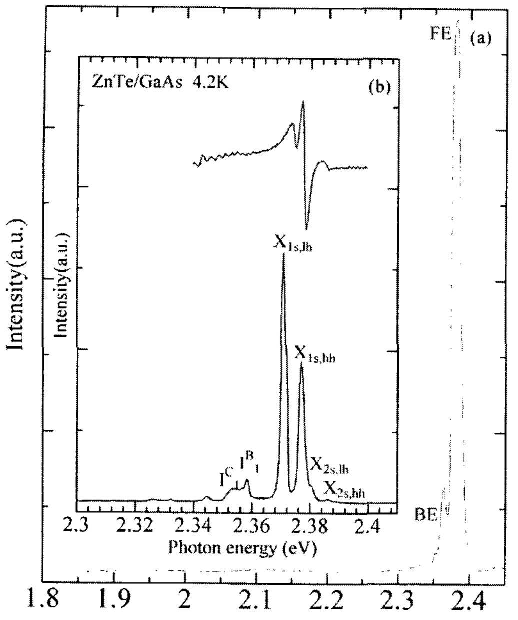

Fig. 5 Photoluminesence spectrum of ZnTe epilayer(a), and the detailed spectrum near the band edge and reflection spectrum(b)

exctions recombination. It is reported that the doublet peaks at 2.3787eV and 2.3768eV attribute to the recombination of ground state free excitons related to heavy hole (X1S,hh) and light hole (X1S,lh), respectively. The energy difference between X1S,hh and X1S,lh is about 5meV, which is known due to the residual strain in ZnTe film grown on GaAs substrate[17)]. For this reason, the doublet peaks seen in Fig. 5 (b) can be assigned as X1S, hh and X1S,lh ,respectively. In addition, the X2S,hh and X2S,lh peaks[9)] related to the first excited-state of X1S,hh and X1S,lh can be observed in Fig. 5(b). Their peak energies approximately correspond with other reported values[9 17)].

On the other hand, the IA1 at 2.3678 eV, IB1 at 2.3615 eV and IC1 at 2.3588 eV due to the radiative recombination of excitons bound to neutral acceptors have been reported on ZnTe epilayer[18)]. Especially, the IA1 peak, related to As atom diffused into from the substrate[19)], can not be observed in the present experiment. This indicates that As atoms do not diffuse into the epilayer under the present experimental condition. The IB1 emission might regard to an unknown impurity from the source material[9)]. The IC1 emission at 2.3579 eV is observed and has broader structure than IB1 emission. Kudlek et al[19)] reported that IC1 attributes to the extended defects at the ZnTe /GaAs hetero-interface cause by the lattice mismatch. In the case of our sample, the intensity of I1C emission decreases with increase in epilayer thickness and becomes the weakest at 12㎛, showing a good agreement with XRD results. For this reason, I1C emission should be related to extended defects of epilayer.

Ⅳ. Conclusions

ZnTe epilayers of high quality have been grown on GaAs substrates by hot wall epitaxy. In order to prepare high quality ZnTe epilayers, we have determined the most suitable growth condition. As the most suitable growth condition, source, substrate, and reservoir temperatures of 803K, 723K and 463K, respectively, are obtained. It was found that the epilayer quality strongly depends on the reservoir temperature.

The dependence of the crystallinity on the film thickness, indicated that the density of extended defects in ZnTe films decrease rapidly with the increase of thickness within 6㎛. High-quality ZnTe epitaxial films on GaAs can be obtained at the thickness of 12㎛. The best value of the FWHM assessed from the four crystal rocking curve, 66 arcsec, was obtained.

The PL spectrum shows that the FE emissions of X1S,hh , X1S,lh, are very sharp and strong, and the emission related to their excited states X2S,lh and X2S,hh emissions can be also detected. PL spectrum and FWHM value showed that the quality of the ZnTe epilayers is extremely high.

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accepted days : 2002. 9. 5
received days : 2002.10.28