한국공작기계학회논문집 Vol.11 No.6 2002. 12.
Transactions of the Korean Society of Machine Tool Engineers

Growth of high quality ZnTe epilayers used for an far-infrared sensor and radiation detector

B. J. Kim*

(논문접수일 2002 8. 16, 심사완료일 2002 10. 21)

Abstract

ZnTe epilayers have been successfully grown on (100) GaAs substrate by hot wall epitaxy (HWE) with Zn reservoir. Optimum growth condition has been determined by a four-crystal rocking curve (FCRC). 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 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. Until now, this result shows the best quality of ZnTe/GaAs films in reported.

Key Words : ZnTe, GaAs, HWE, Heteroepitaxy, XRD

1. Introduction

ZnTe has a direct band gap of 2.26eV at room temperature and, consequently, an attracted interest for potential applications to optical devices in the green spectral region and far-infrared sense detector(1). If it 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). For a practical application, high quality epitaxial layers should be grown. Recently, various research works have been carried out to grow high quality ZnTe epilayers on GaAs substrates by means of molecular beam epitaxy(3,4), metal-organic chemical vapor deposition (5,6), atomic layer epitaxy (7) and hot wall epitaxy(8,9). Among these epitaxial growth methods, hot wall epitaxy (HWE) has its own advantage(10). For instance, all the steps, such as vaporization of source materials, transportation and growth, occur

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* 주저자, Institute for Advanced Materials Processing, Tohoku University (jujahyun@hotmail.com)
주소: 1-1, 2-Chome Katahira, Aobaku, Sendai, 980-8577, Japan

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(11). 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(12,13), however, unfortunately the epitaxy has been performed without reservoir.

On the other hand, ZnTe/GaAs heterostructure has some problems(14) 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 to find an optimum condition for growing a high quality ZnTe epitaxial layer on (100) GaAs substrate. In particular, this study uses a reservoir to improve the quality of ZnTe epitaxial layer. Furthermore, this study examines the dependence of the epilayer thickness on crystallinity.

2. Experimental procedure

ZnTe epilayers were grown on semi-insulating (100) GaAs substrates, in HWE apparatus with a Zn reservoir (15). 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 (16), and 6N-up Te provided by Osaka Asahi Metal Co. ZnTe poly-crystals were further purified by sublimation method and subjected to a source for growing bulk single crystals by prior method(16). 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 (10).

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. This examination was concentrated upon the crystallinity of the film by four-crystal rocking curve (FCRC).

3. Results and discussion

ZnTe epilayers were grown on semi-insulating GaAs (100)substrates by HWE, and the growth parameter were varied to determine the optimum condition. At the beginning, we adopted the substrate temperature (Tsub.= 623K) and source temperature (Tsou.=743K) reported for HWE of ZnTe/GaAs(12,16).

As vapor pressure of Zn and Te is different, deviation from stoichiometric composition will occur in the

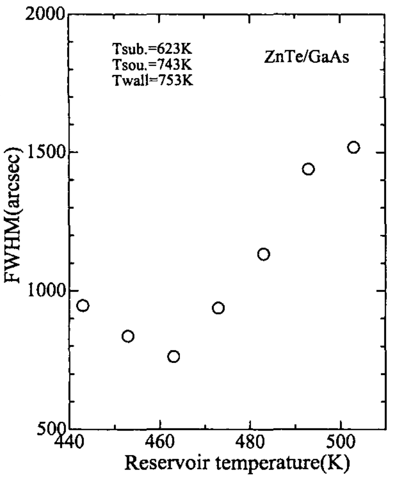

Fig. 1 Relation between reservoir temperature and FWHM value

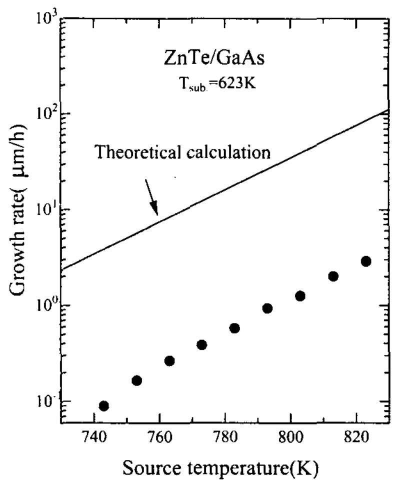

Fig. 2 Dependence of growth rate on source temperature

process of epitaxial growth. Therefore, the dependence of reservoir temperature on the epilayer quality was firstly examined, followed by the optimization of source temperature. Furthermore, the effect of substrate and reservoir temperatures was examined sequentially for wholly optimizing the growth condition.

Figure 1 shows 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. The other growth conditions shows in Fig.1. It is clearly seen in the figure that the reservoir temperature has a strong effect on epilayer quality, as reported on CdTe/GaAs (11). The quality of epitaxial films depends also on the layer thickness. To avoid this influence, FWHM was measured using the specimens having almost the same thickness. For this reason, the change of FWHM in Fig.1 is caused by the deviation from the stochiometric condition.

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. From this experiment, 463K is found to be optimum reservoir temperature when the other growth factors are set up as shown in Fig.1.

As source temperature has a great influence upon growth rate and quality of the films, the dependence of growth rate on the source temperature and the FWHM value was examined, fixing the reservoir temperature at 463K.

The relation between source temperature and growth rate is shown in Fig. 2. The solid line in Fig. 2 represents a theoretical transport rate calculated using Hertz-Knudsen-Langmuir eguation(17). Evaporation rate, J_v, from solid-state source can be written as following equation:

$$J_v = P(2\pi m kT)^{-2/1}, \qquad (1)$$

where P is a equilibrium vapor pressure, *m* a molecular mass, and *k* Boltzmann constant. Provided that all evaporated molecules are transported to substrate surface, the flux(J_d) of molecules deposited on the lattice can be expressed by the difference between the molecular number transported to surface ($J_{v(sou)}$) and that re-evaporated ($J_{v(sub)}$) at the surface.

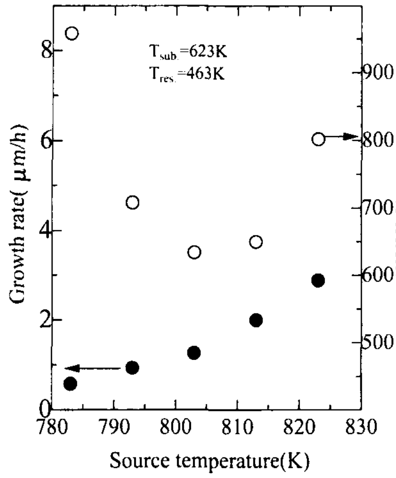

Fig. 3 Source temperature dependence of growth rate and FWHM

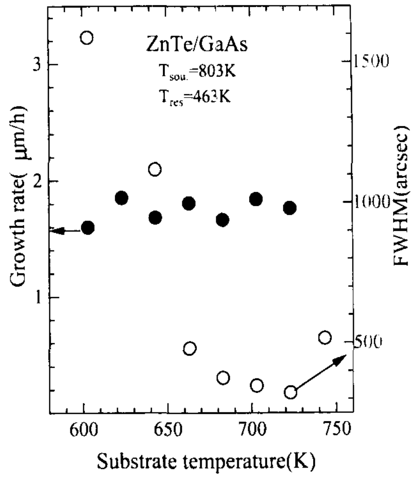

Fig. 4 Substrate temperature dependence of growth rate and FWHM

$$J_d = J_{v(sou)} - J_{v(sub)} = (P_{sou}\, T_{sou}^{-1/2} - P_{sub}\, T_{sub}^{-1/2}) (2\pi m\ k)^{-1/2} \qquad (2)$$

When substrate area is A, source density ρ, and molecular weight M, growth rate, R_d, can be written as follows:

$$R_d = J_d\, AMN^{1}\, \rho^{-1}\, A^{-1} = MN^{-1}\, \rho^{-1}\, J_d, \qquad (3)$$

where N is Avogadro's number.

The solid circles in Fig. 2 are the experimental results. It is found that experimental values are about one order smaller than the theoretical value, but the slopes are approximately equal and both of them increase exponentially with the increase of source temperature. This is consistent with the temperature dependence of ZnTe vapor pressure. The relation between theoretical growth rate (R_d) and experimental one (R_g) can be written as follows:

$$R_g = \gamma R_d. \qquad (4)$$

The proportional coefficient γ is estimated as 3.5×10^{-2}, which is larger than 1.3×10^{-2} reported on CdTe/GaAs grown at the same substrate temperature in the same apparatus(11). Although this value include some factors related to the growth condition and the apparatus, the difference of γ between ZnTe/GaAs and CdTe/GaAs should be caused by the difference of their sticking coefficient. The detailed study on γ is required for confirming the growth mechanism(18) of HWE and for the growth of solid solutions.

Figure 3 shows the source temperature dependence of FWHM value measured on the epilayer grown for 3h. When the source temperature increases, the FWHM values decrease up to 803K and then increase. In consequence, when the source temperature is 803K, FWHM shows a minimum value. Although the thicker samples were grown under the higher source temperature than 803K, FWHM value increases. This means that more defects are introduced into the epilayers, when growth rate is higher. This result shows that the optimum source temperature is 803K.

For the further optimization, effects of substrate temperature and reservoir temperature were re-examined using other conditions optimized in the previous steps. Figure 4 shows the substrate temperature dependence of the growth rate and FWHM value. The substrate temperature does not affect the growth rate. This indicates that the growth rate is directly dependent on

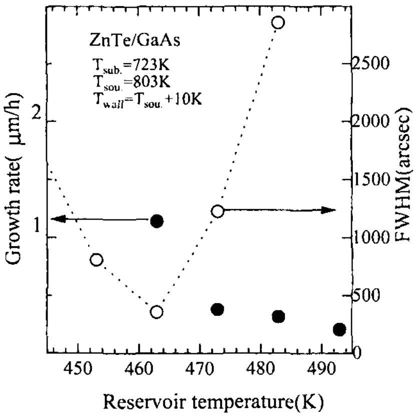

Fig. 5 Reservoir temperature dependence of growth rate and FWHM

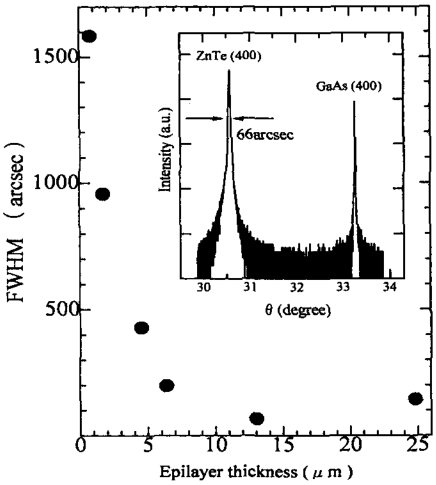

Fig. 6 The film thickness dependence of the FWHM. The insert is the four crystal rocking curves (FCRC) measured on the best of a good quality ZnTe epilayer

source temperature, and the re-evaporation can be neglected. 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 first experiment shown in Fig.1.

Therefore, Tsub.=723K is the most suitable growth temperature. This result agrees with the four-crystal XRD result shown in the Fig.4.

Figure 5 shows the reservoir temperature dependence of the growth rate and FWHM value. When the reservoir temperature increases, the FWHM value decreases up to 463K and then increases above 463K. When the reservoir temperature is about 463K, FWHM shows a minimum value. This reservoir temperature corresponds with that optimized at the first step (Fig.1), indicating that all the conditions have been fully optimized. Therefore, Tres.=463K was confirmed 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.

Table 1 The growth optimum condition of ZnTe epilayer by HWE

Substrate Temperature	Source Temperature	Reservoir Temperature
723K	803K	463K

Effect of epilayer thickness on the crystallinity was investigated using the optimum growth condition. Figure 6 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 6 μm, 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.

4. 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 6μm. High-quality ZnTe epitaxial films on GaAs can be obtained at the thickness of 12μm. The best value of the FWHM assessed from the four crystal rocking curve, 66 arcsec, was obtained. FWHM value showed that the quality of the ZnTe epilayers is extremely high.

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