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Growth of High Quality $Cd_{0.96}$-$Zn_{0.04}Te$ Epilayers Used for an Far-infrared Sensor and Radiation Detector

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Abstract

The high quality and a nearly stoichiometric growth of $Cd_{1-y}Zn_yTe$ (y=0.04) epilayers have been successfully grown on GaAs substrate by hot wall epitaxy (HWE) by optimizing the growth condition including the preheating treatment and Cd reservoir temperature. The relationship between quality and thickness was examined and best value of FWHM from X-ray rocking curve of 121 arcsec are obtained. Also, emission peaks related to the recombination of free excitons such as the ground state and the first excited state were observed in the PL spectrum at 4.2K. The (A^0,X) emission related to Cd vacancy and deep level emission was not measured. These results indicated that the grown CZT/GaAs epilayer was high quality and purity

Key Words : Cd ZnTe, HWE, Heteroepitaxy, Free exciton, XRD, Photoluminescence

1. Introduction

CdZnTe (CZT) is an important material for development of far-infrared detector and radiation detector[1,2]. CZT substrate is applied for HgCdTe (MCT), HgCdTe (MCZT) epitaxial growth. Particularly, lattice constant of $Cd_{1-y}Zn_yTe$ (y=0.04) is close to that of $Hg_{1-x}Cd_xTe$ (X=0.2), which has a band gap corresponding to about 10μm[3], CZT is also promising materials for X-ray and gamma-ray detector. CZT epilayer on GaAs has been focused on an interest as a substrate for the epitaxial growth of MCT and MCZT. However such a heteroepitaxy has a problem that a high density of defects are introduced resulting from the large lattice mismatch and the difference of their thermal expansion coefficient. In order to grow a high-quality CZT epilayer on GaAs substrate, much effort has been paid to solve this problem.

The CZT epilayers have been grown by many epitaxial growth methods such as molecular beam epitaxy[4], metalorganic chemical vapor deposition[5,6], metalorganic molecular beam epitaxy [7] and hot wall epitaxy[8]. Among

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these methods, HWE has its own advantage such as the reaction and growth in near-thermal equilibrium, simplicity, small loss of the source material and low cost for maintenance.

Koo et al.[8] investigated growth condition of $Cd_{1-y}Zn_yTe$ (y=0.045) epilayer on GaAs substrate using the same HWE apparatus as the present study. However, they did not examine optimum preheating temperature. Since quality of epitaxial layers strongly depends on the substrate condition[10], it is important to clarify the effect of preheating condition on the grown film.

In this paper, in order to grow high quality $Cd_{0.96}Zn_{0.04}Te$ epilayers on GaAs substrates by HWE, the effects of preheating temperature, Cd reservoir and other growth parameters upon growth rate, composition (y) and crystalline quality are examined, using PL spectra, electron probe micro analysis (EPMA) and four crystal X-ray rocking curves (FCRC). Under the determined optimum growth condition, CZT epilayers with different thickness are grown, and the relationship between quality and thickness is examined and compared with the results of CdTe[12] and $Cd_{0.955}Zn_{0.045}Te$[8].

2. Experimental procedure

The CZT epilayers were grown by HWE using a Cd reservoir. To provide Cd, Zn and Te_2 vapors for the CZT epitaxial growth, a high purity CZT source with y=0.2 was synthesized with the vertical Bridgman method using starting materials of 6NS-Zn and 6NS-Cd, purified by vacuum distillation and overlap zone melting [9], and 6N-Te. The grown single crystal was cleaved to pieces and loaded into the growth chamber.

The GaAs substrates were cleaned before chemical etching by an ultarasonically cleaner with trichloroethylene, acetone, and ethanol in sequence. The cleaned GaAs substrate was chemically etched with ($3H_2SO_4$: H_2O_2 : H_2O) for 90 s and finally, the substrate was rinsed with the deionzed water. After drying with N_2 gas, the substrate was put on the holder in the HWE apparatus. Prior to the growth, the GaAs substrate was preheated to remove the oxide layer and remaining impurity on the substrate surface. Preheating temperature was examined in the range from 823K to 913K. During the growth and preheating, the vacuum was maintained at 1-2 x 10^{-6} Torr.

The grown epilayers were characterized by several techniques[16]. The thickness of epilayers was measured by a surface profiler (ULVAC, DEKTAK^{3}ST). Electron probe microanalysis (EPMA) with the wave length dispersive X-ray spectroscopic mode was employed to determine the Zn composition (y). Crystalline quality was estimated by four crystal rocking curves (FCRC). Photoluminescence (PL) spectra were measured at 4.2K using the SGH-532nm line of an Nd:YAG (12mW) as a exciton light source. The 150W light from a halogen lamp was used for the reflectance measurement.

3. Results and discussion

Since the preheating temperature has a great influence upon film quality[10], the optimum preheating condition must be optimized in order to prepare a high quality CZT epilayer. At the beginning, the experiments were performed by fixing the growth time of 3hours, referring to the other factors reported previously for CZT/GaAs epilayer [8].

The FWHM value of the grown films was measured as a function of the preheating temperature from 823K to 913K and results are shown in Fig. 1.

Koo et al.[8] was adopted to 853K fixed with preheating temperature, which is not examine optimum preheating temperature. Source temperatures employed are 743K, 753K and 763K. The FWHM value is smallest at around 873K for all examined source temperatures. This indicated that the preheating temperature of 873K gives the best surface condition. For this reason, this temperature will be adopted hereafter.

The source temperature has strong influence on the quality and the composition of epilayers. Particularly, the growth rate plays a very important role in determining epilayer quality. Furthermore, the Cd reservoir is

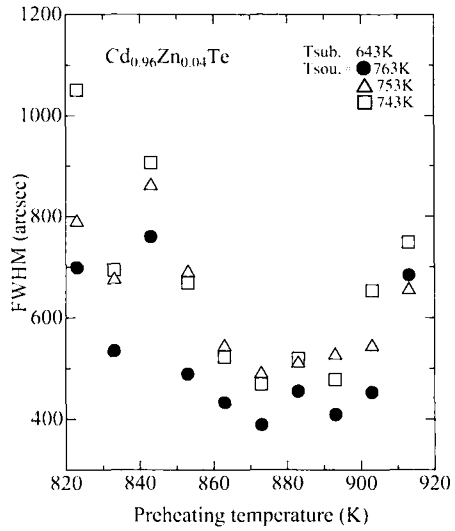

Fig. 1 Pre-heating temperature dependence of the FWHM with four crystal rocking curve

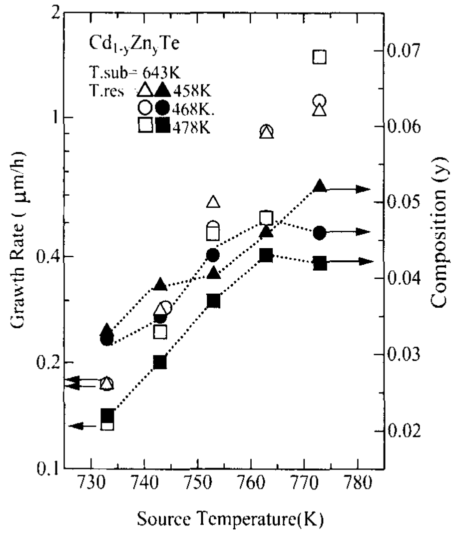

Fig. 2 CZT source temperature depend of growth rate and composition (y)

thought to change the composition in grown films. Figure 2 shows the dependence of the growth rate and the composition upon source temperature under the three different reservoir temperatures.

The growth rate increases exponentially with increase of source temperature. It is similar to the temperature dependence of ZnTe and CdTe vapor pressure [11]. On the other hand, the composition initially increases with increasing of source temperature up to 763K and thereafter decreases in the case of Tres.=468,478K. Similar results were also observed for CZT epilayer grown at the previous results [8]. In the case of Tres.=458K, the result is different. When the source temperature increases, the composition continuously increase up to 773K. This difference may be due to the relative change of Zn and Cd partial pressures supplied by the reservoir and source material. However, this behavior cannot be explained clearly.

Figure 3 shows source temperature dependence of FWHM value measured on CZT film grown under three different reservoir temperatures. As source temperature increases up to 763K, the FWHM value decreases with increasing the epilayer thickness. In spite of the largest layer thickness, the FWHM value increase at 773K. When the source temperature is fixed at 763K, the best value was obtained for all the case. These samples shows the similar concentration (y) which is desired in the present work. It can be concluded that the optimum source temperature is 763K.

Since the vapor pressures of Cd, Zn and Te are different, the composition and the deviation from stoichiometry depends on the reservoir temperature, although the effect of the reservoir temperature on the composition is not remarkable. The influence of the reservoir temperature on the composition of epilayers grown at source temperatures lower than 763K was examined more precisely as shown in Fig. 4. The composition (y) of the epilayer was varied between 0.02 and 0.07. Both the composition and the layer thickness decrease as the reservoir temperature (Cd vapor pressure) increase. These results show that the composition can be effectively controlled by the reservoir temperature during the epitaxial growth in the present HWE apparatus, when the source temperature is fixed.

In order to prepare optimum condition and high quality $Cd_{1-y}Zn_yTe$ epilayer with y=0.04, the dependence

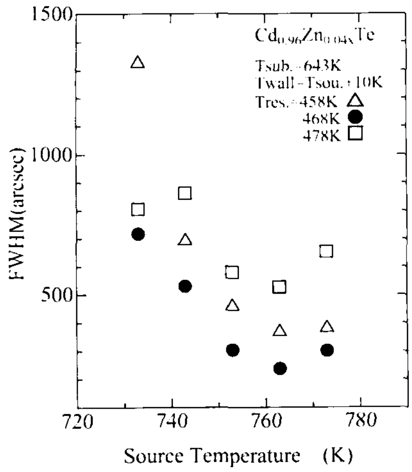

Fig. 3 Relationship between source temperature and FWHM estimated from X-ray rocking curve

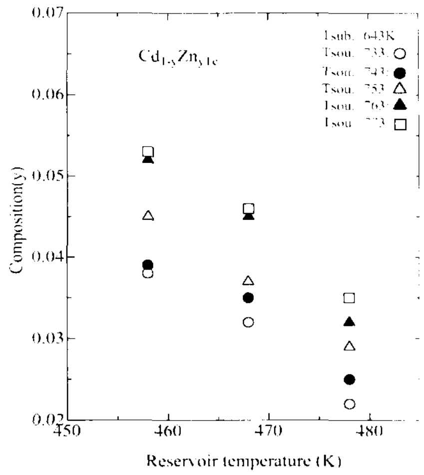

Fig. 4 Reservoir temperature dependence of the composition

of preheating, substrate, source and the reservoir temperature on the quality and the composition of grown films was investigated. As a result, the optimum condition for growth of $Cd_{1-y}Zn_yTe$ (y=0.04) epilayer is summarized in Table 1. The optimum substrate temperature is the same as the previous work[8].

The $Cd_{1-y}Zn_yTe$ (y=0.04) epilayers of about 0.3 ~ 35μm thickness were grown on (100) GaAs substrate under the above-determined optimum growth condition for studying the effect of epilayer thickness on crystalline quality.

Figure 5 shows the dependence of FWHM on the thickness of CZT epilayer, together with the results for CdTe [15] and CZT [8]. The composition of CZT samples in this present work is y=0.035 ~ 0.048. In all cases, the FWHM values abruptly decrease with the increase in thickness up to 6μm. These results indicate that the biaxial compressive stress in epilayer grown on GaAs substrates is significantly relaxed with increasing thickness. When the thickness of epilayer becomes larger than 6μm, FWHM value gradually decreases to 121 arcsec.

In the case of CdTe, crystallinity is remarkably improved by increasing the epilayer thickness to thicker than 5μm. Although a 14.6% lattice mismatch and a -26% thermal expansion coefficients mismatch exist at 300K between CdTe and GaAs, the smallest FWHM value of 90 arcsec is obtained at thickness exceeding 10 μm [12].

Despite of the smaller lattice mismatch (14.3%) of $Cd_{0.96}Zn_{0.04}Te$/GaAs than CdTe/GaAs, the results show that the FWHM of CZT epilayer is much larger than that of CdTe/GaAs, especially, at thickness smaller than 4μm. It should be noted that the FWHM value at the thickness from 5 to 12μm is extremely smaller than these in the previous data and the smallest value of 121 arcsec in so far reported values is obtained in the present work. This improvement should be due to the optimization of the preheating temperature.

Figure 6 shows typical PL spectra measured at 4.2K

Table 1 The optimum growth conditions of $Cd_{1-y}Zn_yTe$ (y=0.04) epilayer by HWE

Preheating Temperature	Substrate Temperature	Source Temperature	Reservoir Temperature
873K	643K	763K	468K

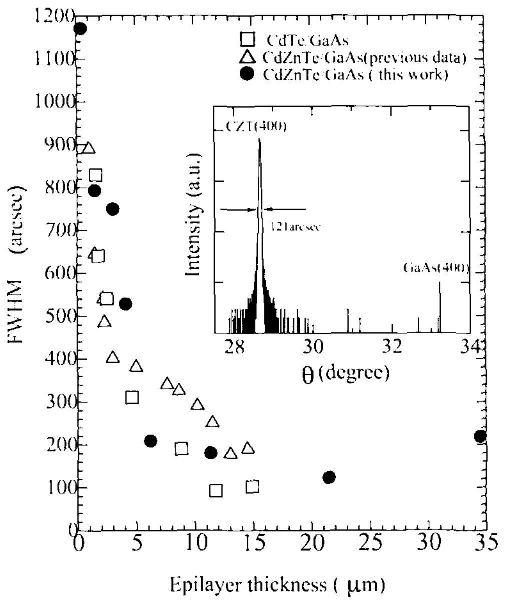

Fig. 5 The film thickness dependence of the FWHM of the FCRC. The inset is the FCRC of a good quality Cd ZnTe epilayer

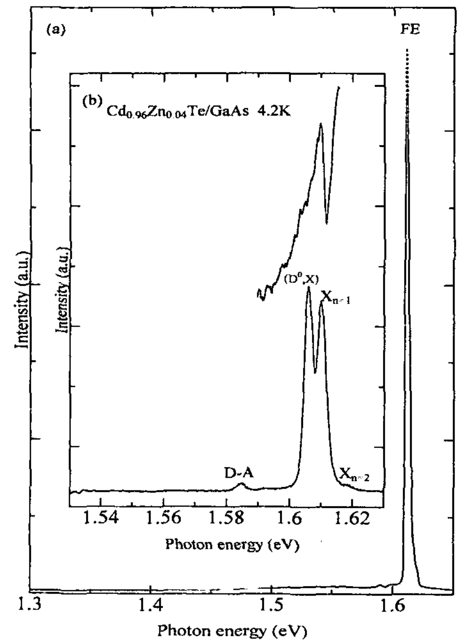

Fig. 6 Photoluminesence spectrum of CdZnTe epilayer(a), The detail spectrum near the band edge(b)

on $Cd_{1-y}Zn_yTe$ (y=0.043±5) with 20μm thickness. The grating of 300 grooves/mm provides a large range spectrum information (a). Figure 6 (a) can be divided into three regions : (a) the excitonic emission region at wavelength (λ) lower than about 776nm (1.597eV). (b) the free-to-bound and bound-to-bound emissions at intermediate λ, and (c) deep emission at λ> 820nm (1.512eV) associated with crystal imperfections and deep impurity levels [13]. In the first region (see also Fig. 6(b)), the excitonic emission peaks such as free- exciton (Ex) peak and bound exciton (BE) peaks could be observed clearly. An extremely weak DAP emission is found in the intermediate range. In the last region, any emission regarding deep impurities and crystal imperfections is hardly observed. This PL spectrum proves high quality CZT epitaxial layer.

Fig. 6(b) is the detailed spectrum (the 1200 grooves/mm provides accurate information) near band edge region of Fig. 6(a). Emission lines in the PL spectrum were assigned by estimating these peak positions and also measuring the reflection spectra shown in Fig. 6(b). This spectrum is shifted about 0.02eV to higher energy side than that of pure CdTe, because the energy gap of the $Cd_{1-y}Zn_yTe$ (y=0.048) single crystal film is larger than that of pure CdTe. The emission line due to the recombination of free excitons at 770.2nm (1.610eV), denoted by $X_{n=1}$ is clearly observed[13]. Also, the emission related to the first excited state of Ex has been reported[14] in CdTe epilayer at 774nm (1.601eV). In the present case, this emission appears at 765.8nm (1.619eV) as the peak denoted by $X_{n=2}$.

On the other hand, the bound exciton peak was identified and denoted to be (D^0,X) at 772.0nm (1.606eV). This assignment is based on the pure CdTe with (D^0,X) at 763.5nm (1.623eV). Generally, the PL spectrum of CdTe and CZT epitaxial layer show the (A^0,X) emission, which is related to the recombination of exctions bound to Cd vacancy complexes as reported by Seto et al [15].

Such an emission can not be observed in the present experiment , although the reason is not clear.

Especially, the broad peak around 885nm (1.4eV) is not found. It is therefore concluded that present $Cd_{1-y}Zn_yTe$ (y=0.04) epitaxial layer are high purity.

4. Conclusion

A detailed study on growing $Cd_{0.96}Zn_{0.04}Te$ epilayers on GaAs substrate was carried out. The optimum growth condition for growing high-quality $Cd_{0.96}Zn_{0.04}Te$ epilayers has been determined. The growth of high quality and nearly stoichometric $Cd_{0.96}Zn_{0.04}Te$ epilayers has been achieved using y=0.2 source and Cd reservoir. It was found that the epilayer quality strongly depends on the preheating and reservoir temperature.

Under the determined optimum growth condition, the effect of CZT epilayer thickness on crystalline quality was investigated. The FWHM value abruptly decreases with increasing thickness from 0.3 to 5μm. And the FWHM value of 121 arcsec was obtained at 20μm in the film thickness.

The PL spectrum was measured at 4.2K for the high quality film and the emission related to the recombination of free exctions, the ground state and also the first excited state, were observed. (A^0,X) emission with related to Cd vacancy and deep level emission was not detected. All the results indicate that the CZT/GaAs epilayer grown in the present study are high quality and purity.

Reference

(1) P. W. Kruse, in: "Semiconductors and Semimetals", Vol. 18,Eds. R.K. Willardson and A.C. Beer, Academic Press, New York, p.1, 1981.

(2) K. Zannio, in: "Semiconductors and Semimetals", Vol. 13,Eds. R.K. Willardson and A.C. Beer, Academic Press, New York, p.164, 1978.

(3) D.D. Edwall, E.R.Gertner and E.Tennant, "*Liquid phase epitaxial growth of large area Hg1-xCdxTe epitaxial layers*" J. Appl. Phys. 55, pp. 1453, 1984.

(4) R.D. Feldman, R.F.Austin, P.H. Dayem and E.H. Westerwick ; "*Growth of $Cd_{1-x}Zn_xTe$ by molecular beam epitaxy*", Appl. Phys. Lett. 49 797,1986.

(5) N.H. Karam, R.Sudharsanan, A.Mastrovito, M.M. Sanfacon, F.T. J. Smith, M. Leonard and N.A. El-Masry ; "*Large Area Deposition of Cd1-xZnxTe on GaAs and Si Substrates by Metalorganic Chemical Vapor Deposition*" J. Electron. Mater. 24. pp. 483, 1995.

(6) P.W. Sze, N.F. Wang, M.P. Houng, Y.H. Wang, Y.T. Cherng and H.Wang, "*Characteristics of ZnCdTe grown on (100) GaAs substrate by MOCVD*" J. Cryst. Growth, 169 pp. 27, 1996.

(7) D.Rajavel and J.J. Zinck, "*Growth Kinetics and Properties of Heteroepitaxial (Cd, Zn)Te Films Prepared by Metalorganic Molecular Beam Epitaxy*" J. Electron Mater. 22, pp. 803, 1993.

(8) B.H. Koo, J. Wang, Y. Ishikawa and M. Isshiki "Growth and Evaluation of Cd1-yZnyTe Epilayers on (100) GaAs Substrates by Hot Wall Epitaxy" Jpn. J. Appl. Phys. 37 pp5674, 1998.

(9) Y. Ishikawa, B. Yang, K. Mimura, T. Tomizono and M. Isshiki, "preparation of high purity cadmun by vacuum distillation and Zone-Melting Method" J. Mining& Mater. Process. Inst. Jpn 110, pp. 1175, 1994.

(10) S.N. Nam, J.K. Rhee, B.S. O, K.S. Lee, Y.D. Choi, G.N. Jeon and C.H. Lee, "*Characterization and growth of high quality ZnTe epilayers by hot-wall Epitaxy*" J. Crystal Growth, 180pp 47, 1997.

(11) I. Korneeva, A. V. Belsyser and A.V. Novoselova, Zh. Neorg. Khim., "Determination of the saturated vapor pressure of solid Zinc and Cadmum Tellurides" 5, pp. 1, 1960.

(12) J.F. Wang, K. KiKuchi, B.H. Koo, Y. Ishikawa, W. Uchida and M. Isshiki, "*HWE growth and evaluation of CdTe epitaxial films on GaAs*" J. Crystal Growth, 187, pp. 373, 1998.

(13) E.Cohen, R. A. street and A.Muraevich, "*Bound excitons and resonant Raman scattering in $Cd_xZn_{1-x}Te$ (0.9 <= x <= 1)*" Phys.Rev.B 28, pp. 7115, 1983.

(14) J.GonZalez-Hernadez, E.Lopez-cruz, and D.D.Allred

and W. Allred, "*Photoluminescence studies in ZnxCd1-xTe single crystals*" J. Vac.Sci.Technol. A8, pp. 3255, 1990.

(15) S.Seto, A.Tanaka, Y.Masa, S. Dairaku and M. Kawasima, "*Bound excitons and resonant Raman scattering in* $Cd_xZn_{1-x}Te$ *(0.9 <= x <= 1)*" Appl. Phys. Lett.53, pp. 1524, 1989.

(16) OK SAM. KiM "*Analysis of the Temperature Distribution at Micromachining Processes for Microaccelerometer Based on Tunneling Current Effect*" Journal of the Korean Society of Machine Tool Engineers 2000,10 v.9, n.5, pp. 105 ~ 111, 1226-8097.