ЖУРНАЛ ФІЗИЧНИХ ДОСЛІДЖЕНЬ
т. 15, № 3 (2011) 3701(4 с.)

JOURNAL OF PHYSICAL STUDIES
v. 15, No. 3 (2011) 3701(4 p.)

EFFECT OF H_2 HEAT TREATMENT ON CRYSTALLINITY OF CdTe FILMS GROWN ON GaAs SUBSTRATES

Chikara Onodera[1], Masaaki Yoshida[2]
[1] *Electronic Engineering Course, Aomori Prefectural Towada Technical Senior High School,*
215–1 Shimotai Sanbongi, Towada, Aomori 034–0001, Japan, ycd1ngt@yahoo.co.jp
[2] *Department of Electrical and Computer Engineering, Hachinohe National College of Technology,*
16–1 Uwanotai, Tamonoki, Hachinohe, Aomori 039–1192, Japan, yoshida-e@hachinohe-ct.ac.jp

(Received March 17, 2011)

We investigated the effect of H_2 heat treatment on CdTe films grown on GaAs substrates by using photoluminescence (PL) and reflectance spectra. We observed the changes in heavy- and light-hole free exciton (FE) emissions and reflectance spectra with heat-treatment temperature. The energy separation between heavy-hole and light-hole FE lines calculated using the bimetallic strip model is in good agreement (4.08 meV) with that estimated from the peak energies of the heavy- and light-hole FE lines (4.0 meV). By Lorentzian deconvolution of the heavy-hole and light-hole FE lines, their widths decrease with increasing H_2 heat treatment temperature. By fitting the theoretical reflectance spectra to the measured reflectance spectra, the associated broadenings of light-hole FEs decrease with increasing H_2 heat treatment temperature. The observations suggested that the crystallinity of CdTe films is improved by H_2 heat treatment.

Key words: cadmium telluride, free exciton, photoluminescence, reflectance, heat treatment.

PACS number(s): 78.55.Et, 81.05.Dz

I. INTRODUCTION

CdTe has attracted considerable attention as an optoelectronic material for various applications such as solar cells and gamma-ray detectors. Extensive efforts have been devoted to growing high-quality and large-area CdTe films that can be used as buffer layers in the fabrication of HgCdTe for the application in infrared detectors. CdTe is a favorable buffer layer for the growth of HgCdTe owing to the close lattice match between them. Currently, the wafer size of CdTe is limited to a small area. Although there is a high lattice mismatch between GaAs and CdTe, the crystal quality of epitaxial CdTe grown on GaAs via several growth techniques is comparable with that of the bulk CdTe [1–3]. CdTe epitaxial films grown on GaAs substrates suffer from a biaxial compressive stress due to a large-thermal expansion difference [4].

We reported that no aditional strain was induced in CdTe films grown on GaAs after post-growth annealing in a H_2 atomosphere [5]. Moreover, the surface quality of CdTe films after heat-treatment remained excellent because of the appearance of free exciton (FE) lines [5]. However, we did not report the effect of H_2 heat treatment on CdTe crystallinity in detail [5]. To characterize CdTe film quality after post-growth annealing in a H_2 atomosphere, we analyzed the photoluminescence (PL) and reflectance spectra of CdTe films grown on GaAs substrates at 4.2 K.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

(100) CdTe films were grown on (100) GaAs substrates via low-pressure metal organic chemical vapor deposition (MOCVD). Dimethylcadmium (DMCd) was used as a metal-organic Cd source, whereas dimethyltelluride (DMTe) or diethyltelluride (DETe) was used as a metal-organic Te source. The substrates were cleaned with a solvent, etched in H_2SO_4:H_2O_2:H_2O(5:1:1), rinsed with de-ionized H_2O, and boiled in HCl solution. Immediately prior to growth, the substrates were heated in the chamber at 550°C under a H_2 atomosphere. The detailed procedures have been described elsewhere [5].

The PL spectra were measured at 4.2 K under He–Cd laser (441.6 nm, 50 mW) excitation, and they were analyzed using a single-grating monochromator(1 m; Jobin Yvon). The signal was detected using a conventional lock-in detection system. We obtained reflectance spectra at 4.2 K, with light from a halogen lamp normally incident on the sample surface.

In the same MOCVD chamber, isochromal heat treatment was carried out for 30 min in the temperature range of 250 to 450°C under a H_2 gas atmosphere.

III. RESULTS AND DISCUSSION

Figure 1 shows the both PL and reflectance spectra of CdTe films grown on GaAs substrates at 4.2 K, obtained before and after the H_2 heat treatment. Heavy- and light-hole free exciton (FE) lines can be observed at the high-energy shoulder of the (D^0, X) peak.

In order to distinguish FE transitions from the (D^0, X) peak, we measured reflectance spectra in the band-edge energy range. In the reflectance spectra shown in Fig. 1 (upper trace), two distinct dips are observed, and their energy positions are in good agreement with the two peaks at the high-energy shoulder of the (D^0, X) line in the PL spectra. There is a biaxial compressive strain in the CdTe films, which splits the valence band into two bands, i. e., heavy- and light-hole bands [4, 5]. Thus, the low- and the high-energy emission peaks are the heavyand light-hole FE transitions, respectively. The FE line is a direct indication of a high-quality crystal because exciton binding results from the long-range Coulomb interaction between an electron and a hole.

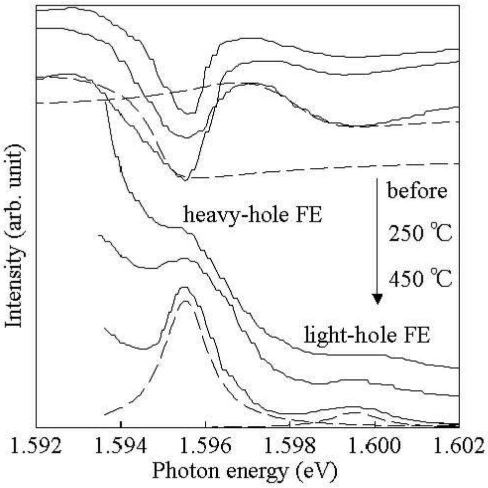

Fig. 1. High resolution heavy-hole and light-hole free exciton emission spectra (lower trace) and reflectance spectra (upper trace) of a CdTe film grown on a GaAs substrate, measured at 4.2 K. The broken lines denote the Lorentzian deconvolved emission line shapes of band-edge emissions (lower trace) and calculated reflectance spectra of heavy- and light-hole FE transitions (upper trace).

In order to estimate heavy-hole and light-hole FE peak energies, we carried out a Lorentzian deconvolution of the PL spectra. The peak energy positions of the heavy-hole and light-hole FE lines before H_2 heat-treatment are 1.5955 and 1.5995 eV, respectively. The energy separation between the heavy-hole and light-hole FEs is estimated to be 4.0 meV. The energy separation between the heavy- and light-hole FE lines in a CdTe film on a GaAs substrate can be analytically calculated on the basis of a bimetallic strip model [4].

The strain at the surface of the CdTe film is given by [4]

$$\epsilon = T_s/K_{\mathrm{CdTe}}, \tag{1}$$

where

$$T_s = P/d_{\mathrm{CdTe}} - K_{\mathrm{CdTe}} d_{\mathrm{CdTe}}/2R, \tag{2}$$

$$\frac{1}{R} = \frac{6(\alpha_{\mathrm{GaAs}} - \alpha_{\mathrm{CdTe}})(T - T_0)(1+m)^2}{h[3(1+m)^2 + (1+nm)(m^2 + 1/mn)]}, \tag{3}$$

$$m = d_{\mathrm{GaAs}}/d_{\mathrm{CdTe}}, \tag{4}$$

$$n = K_{\mathrm{GaAs}}/K_{\mathrm{CdTe}}, \tag{5}$$

$$P = 2(K_{\mathrm{GaAs}} I_{\mathrm{GaAs}} + K_{\mathrm{CdTe}} I_{\mathrm{CdTe}})/hR, \tag{6}$$

$$I_{\mathrm{GaAs}} = d^3_{\mathrm{GaAs}}/12, \tag{7}$$

$$I_{\mathrm{CdTe}} = d^3_{\mathrm{CdTe}}/12, \tag{8}$$

$$h = d_{\mathrm{GaAs}} + d_{\mathrm{CdTe}}, \tag{9}$$

$$K_{\mathrm{GaAs\ or\ CdTe}} = (C_{11} - C_{12})(C_{11} + 2C_{12})/C_{11}. \tag{10}$$

In the equations stated above, α_{GaAs} and α_{CdTe} denote the thermal expansion coefficients of GaAs and CdTe, respectively, d_{GaAs} and d_{CdTe} denote the thicknesses of the GaAs substrate and CdTe film, respectively, and C_{11} and C_{12} are the elastic stiffness constants. We assume that the thermal expansion coefficients are not temperature dependent. The energy separation between the heavy- and light-hole FE lines is given by [5]

$$E_{\mathrm{split}} = 2b\frac{C_{11} + C_{12}}{C_{11}}\epsilon, \tag{11}$$

where b is the shear deformation potential. The physical parameters used in the calculation are listed in Table 1. T_0 denotes room temperature (300 K), and T denotes the temperature at which the PL and reflectance spectra are measured (4.2 K). Using the bimetallic strip model, the energy separation between the heavy- and light-hole FE lines is calculated to be 4.08 meV. The energy separation calculated using the bimetallic strip model is larger than that estimated from the peak energies of the heavy- and light-hole FE lines. However, the difference is very small.

	CdTe	GaAs
Hydrostatic deformation potential a (eV)	−3.3 [7]	
Shear deformation potential b (eV)	−1.4 [7]	
Elastic stiffness constant C_{11} (GPa)	53.3 [8]	119.0 [9]
Elastic stiffness constant C_{12} (GPa)	36.5 [8]	53.8 [9]
Thermal expansion coefficient α ($\times 10^{-6}$ K^{-1})	5.1 [8]	7.2 [10]
Thickness (μm)	3.4	500

Table 1. Physical parameters used in the calculation.

As the H_2 heat treatment temprature increases, there is no change in the dip and peak positions. The widths of the heavy-hole and light-hole FE lines decrease gradually as the H_2 heat treatment temprature increases.

We carried out Lorentzian decomvolution of the heavy-hole and light-hole FE lines after H_2 heat treatment in order to estimate the change in their widths with H_2 heat treatment. The deconvolved heavy-hole and light-hole FE lines at the H_2 heat treatment temperature of 450°C are plotted as broken lines (lower trace) in Fig. 1.

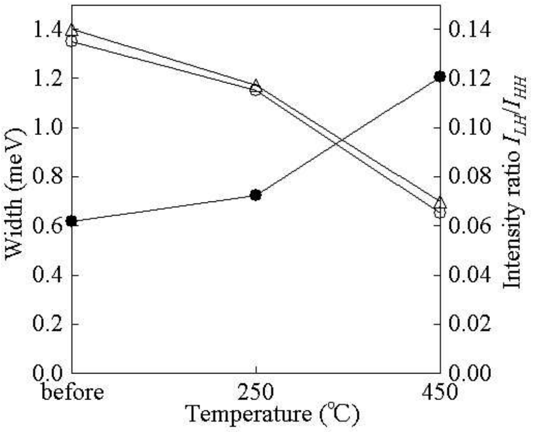

Fig. 2. Widths of heavy-hole (open circles) and light-hole (open triangles) FE lines plotted against H_2 heat treatment temperature. Intensity ratios of light-hole FEs to heavy-hole FEs (closed circles) plotted against H_2 heat treatment temperature. The solid lines are eye guides.

In Fig. 2, the widths of the heavy-hole and light-hole FE lines are plotted against H_2 heat treatment temperature. The widths of the heavy-hole and light-hole FE lines decrease with increasing H_2 heat treatment temperature. The decrease in the widths of the FE lines are indicative of low level impurity scattering. This suggests that the H_2 heat treatment improves the CdTe film quality. We also estimate the intensity ratios of light-hole FEs (I_{LH}) to heavy-hole FEs (I_{HH}), i.e., $I_{\mathrm{LH}}/I_{\mathrm{HH}}$. $I_{\mathrm{LH}}/I_{\mathrm{HH}}$ is plotted against the H_2 heat treatment temperature in Fig. 2. The values of I_{HH} and I_{LH} are also estimated via Lorentzian deconvolution. $I_{\mathrm{LH}}/I_{\mathrm{HH}}$ increases with increasing H_2 heat treatment temperature. The increase in the emission intensity of the light-hole FE line suggests that the crystallinity of the CdTe film is improved via H_2 heat treatment.

In order to clearly observe the effect of H_2 heat treatment on the reflectance spectra, we carried out a theoretical fitting of the reflectance spectra. Theoretical reflectance spectra were calculated using a double-layer model [6]. The polarizabilities and broadenings of the heavy- and light-hole FE transitions were obtained from these spectra by using a fit function. The theoretical reflectance spectrum was calculated by using the equation [6]

$$\varepsilon(\omega) = \varepsilon_{\mathrm{H}} + \frac{A_n \omega_n^2}{\omega_n^2 - \omega^2 - i\omega\Gamma_n}, \tag{12}$$

where ε_{H} is the background dielectric constant, $\omega_n = (E_g - E_n)/\hbar$ is the corresponding circular frequency associated with the heavy-hole (n = hh) or light-hole (n = lh) FE transition, A_n is the polarizability, and Γ_n is the associated broadening. In this calculation, we use ε_{H} = 7.1 [11]. The theoretical reflectance spectra of light-hole and heavy-hole FE transitions at the H_2 heat treatment temperature of 450°C are shown as broken lines (upper trace) in Fig. 1.

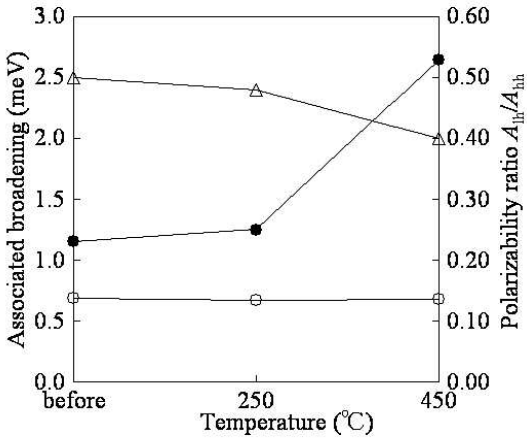

Fig. 3. Associated broadenings of the heavy-hole (open circles) and light-hole FE (open triangles) transitins plotted against H_2 heat treatment temperature. Polarizability ratios of light-hole FEs to heavy-hole FEs (closed circles) plotted against H_2 heat treatment temperature. The solid lines are eye guides.

Figure 3 shows associated broadenings of the heavy-hole (Γ_{hh}) and light-hole FE (Γ_{lh}) transitions plotted against the H_2 heat treatment temperature. Γ_{lh} decreases with increasing H_2 heat treatment temperature, whereas Γ_{hh} remains virtually constant. The decrease in Γ_{lh} is a indication of improved CdTe crystallinity because the damping parameter is attributed to the dislocation density resulting from layer relaxation. [12] We also estimate the ratios of A_{lh} (light-hole FE) to A_{hh} (heavy-hole FE), i.e., $A_{\mathrm{lh}}/A_{\mathrm{hh}}$. $A_{\mathrm{lh}}/A_{\mathrm{hh}}$ is plotted against the H_2 heat treatment temperature in Fig. 3; it increases with increasing H_2 heat treatment temperature. The increase in the polarizabilities of light-hole FEs suggests that the crystallinity of CdTe is improved by H_2 heat treatment.

IV. SUMMARY

We analyzed the PL and reflectance spectra of CdTe films grown on GaAs substrates in order to chracterize the effect of H_2 heat treatment on these films.

By Lorentzian deconvolution of the heavy-hole and light-hole FE lines, their widths decrease with increasing H_2 heat treatment temperature. The intensity of the light-hole FE line increases with increasing H_2 heat treatment temperature. By fitting the theoretical reflectance spectra to the measured reflectance spectra,

$\Gamma_{\rm lh}$ decreases with increasing H_2 heat treatment temperature, whereas $\Gamma_{\rm hh}$ remains virtually constant. The polarizabilities of light-hole FEs increase with increasing H_2 heat treatment temperature.

The results mentioned above suggest that the crystallinity of CdTe films is improved by H_2 heat treatment.

---

[1] N. Otsuka, L. A. Kolodziejski, R. L. Gunshor, S. Datta, R. N. Bicknell, J. F. Schetzina, Appl. Phys. Lett. **46**, 860 (1985).

[2] D. J. Olego, J. Petruzzelo, S. K. Ghandhi, N. R. Taskar, I. B. Bhat, Appl. Phys. Lett. **51**, 127 (1987).

[3] H. Sitter, K. Lischka, W. Faschinger, J. Wolfrum, H. Pascher, J. L. Pautrat, J. Cryst. Growth **86**, 377 (1988).

[4] H. Tatsuoka, H. Kuwabara, Y. Nakanishi, H. Fujiyasu, J. Appl. Phys. **67**, 6860 (1990).

[5] C. Onodera, M. Ekawa, T. Taguchi, J. Cryst. Growth **99**, 459 (1990).

[6] R. Pässler, E. Griebl, H. Riepl, G. Lautner, S. Bauer, H. Preis, W. Gebhardt, B. Buda, D. J. As, D. Schikora, K. Lischka, K. Papagelis, S. Ves, J. Appl. Phys. **86**, 4403 (1999).

[7] H. Mathieu, J. Allegre, A. Chatt, P. Lefebvre, J. P. Faurie, Phys. Rev. B **38**, 7740 (1988).

[8] T. Schwarzl, E. Kaufmann, G. Springholz, K. Koike, T. Hotei, M. Yano, W. Heiss, Phys. Rev. B **78**, 165320 (2008).

[9] *Semiconductors – Basic Data, 2nd rev. ed.*, edited by O. Madelung (Springer, Berlin, 1996), p. 105.

[10] V. Kumar, B. S. R. Sastry, Cryst. Res. Technol. **36**, 565 (2001).

[11] *Semiconductors – Basic Data, 2nd rev. ed.*, edited by O. Madelung (Springer, Berlin, 1996), p. 186.

[12] A. Abounadi, M. Di Blasio, D. Bouchara, J. Calas, M. Averous, O. Briot, N. Briot, T. Cloitre, R. L. Aulombard, B. Gil, Phys. Rev. B **50**, 11677 (1994).

ВПЛИВ ТЕРМООБРОБКИ МОЛЕКУЛЯРНИМ ВОДНЕМ НА КРИСТАЛІЧНІСТЬ ПЛІВОК CdTe, ВИРОЩЕНИХ НА СУБСТРАТАХ GaAs

Чікара Онодера[1], Масаакі Йошіда[2]

[1] *Вища технічна школа Товади, префектура Аоморі, Японія*

[2] *Національний технологічний коледж Гачінобе, префектура Аоморі, Японія*

Вивчено вплив термообробки молекулярним воднем H_2 на плівки CdTe, вирощені на субстратах GaAs, з використанням спектрів фотолюмінесценції та відбивання. Було виявлено залежність спектрів спектрів емісії та відбивання важко- та легкодіркових вільних екситонів (ВЕ) від температури термообробки. Енерґетична відстань між лініями важко- та легкодіркових ВЕ, розрахована в межах біметалічної смугової моделі (4.08 meV), добре узгоджується з оцінкою, отриманою з енерґетичних піків відповідних ліній (4.0 meV). Через лоренцівську деконволюцію ліній важко- та легкодіркових ВЕ значення їхньої ширини зменшуються зі зростанням температури термообробки. Узгодження теоретичних і виміряних спектрів відбивання знижує розширення ліній легкодіркових ВЕ зі зростанням температури термообробки. Спостереження показують, що кристалічність плівок CdTe поліпшується термообробкою молекулярним воднем H_2.