

Raman scattering and temperature-dependent photoluminescence properties of CdS/GaAs epilayers grown by hot-wall epitaxy

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Hexagonal-structured CdS/GaAs epilayers were grown by the hot-wall epitaxy method. From the Raman spectrum, we found that the exciton-phonon coupling is deeply related to the dimensionality. The optical properties attributed to the thermal quenching phenomenon of CdS were studied through photoluminescence (PL) measurements as a function of temperature. With an increase in the temperature, PL intensities of free excitons were exponentially reduced and their spectral width showed a tendency to broaden. This tendency is related to the phonons generated by the lattice vibration of the host material in CdS. These findings led us to conclude that the phonons may be participating in the quenching process. Also, the temperature dependence of the band gap energy of CdS was well interpreted by $E_g(T) = 2.5684 - (5.4 \times 10^{-4})T^2/(258.8 + T)$.

Key words: CdS, Hot-wall epitaxy, Photoluminescence, Raman Scattering.

Introduction

The energy band gap of cadmium sulfide (CdS) at room temperature is about 2.42 eV [1]. Therefore, CdS is used in optoelectronic devices applicable to the visible region because the energy of its band gap is in the visible region. But, a portion of the photo-generated carriers in CdS for these applications disturbs the photocurrent generation due to the radiative and non-radiative recombination. Some of these will contribute to the photocurrent loss of solar cell devices due to optical absorption in the CdS window layer. Such disturbing defects originate from the stoichiometric deviation of the CdS generated during the growth or an additional thermal treatment. This stoichiometric deviation occurs because the vapor pressure of sulfur is higher than that of the cadmium during the growth. In order to research these defects, the photoluminescence (PL) measurements have been intensively investigated for bulk CdS crystals [2, 3]. Thus, the properties of the CdS material are deeply related to the native defects because they have a high self-compensation with comparable densities of shallow donor and deep acceptor states. Therefore, the PL performance is able to explore optically-active recombination centers in CdS. Furthermore, observation of the low temperature PL can allow us to obtain valuable information about the electronic

structure and the structural quality of CdS. Generally, it has been shown that a low temperature growth could reduce the native defects of CdS. Therefore, hot-wall epitaxy (HWE) is suitable for growing a high-purity CdS layer since HWE is one of the low-temperature growth technologies and it is possible to grow layers under a condition of the near thermodynamics equilibrium [4, 5].

In this paper, the CdS/GaAs epilayers were grown at low temperature by the HWE method. Also, Raman and PL experiments were conducted. Based on these results, the intensity, the linewidth, and the position of the free exciton emission on the PL spectra are discussed as a function of the temperature dependence.

Experimental Procedure

CdS epilayers were grown on semi-insulating (100)GaAs by the HWE method. The semi-insulating GaAs (100) substrates were cleaned ultrasonically for 1 minute in successive baths of trichloroethylene, acetone, methanol, and 2-propanol and etched for 1 minute in a solution of H₂SO₄ : H₂O₂ : H₂O (5 : 1 : 1). The substrates were degreased in organic solvents, and rinsed with deionized water (18.2 MΩ). After the substrates were dried, they were immediately loaded onto the substrate holder in the HWE. The GaAs substrates were annealed at 580 °C for 20 minutes to remove the residual oxide on the surface of them. To obtain the optimum growth condition, the CdS/GaAs layers were analyzed by double crystal X-ray diffraction. The optimum temperatures of the GaAs substrate and the source containing the CdS powder were found out to be 350 and 600 °C, respectively. The

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thickness of the grown CdS/GaAs layers measured by a profilometer (Tencor, α -step 200) was 1 μm . The crystal structure of the grown layers was investigated by X-ray diffraction (XRD). The room temperature Raman spectrum was obtained using a Jasco micro-Raman system (NRS-2100). As an excitation source, the 514.5 nm line from an Ar^+ laser was used. The laser power was 27 mW, and the exposure time was 20 s. The Raman signal was detected by a CCD camera. Also, the PL measurements were carried out at various temperatures from 13 to 300 K (room temperature) using a cryogenic helium refrigerator (AP, CSA-202B). The samples mounted on the cold finger of a cryostat were focused using the 325 nm line of a He-Cd laser (Nippon, 40 mW). The emitted light was then detected by a photomultiplier tube through a monochromator. The detected signal was amplified by a lock-in amplifier and recorded on an x - y plotter.

Results and Discussion

Fig. 1 shows the rocking curve of CdS/GaAs layer obtained by the XRD experiment. Two peaks relating to the CdS pattern curve were observed. As shown in Fig. 1, these peaks correspond to the diffraction peaks of (0002) and (0004) of CdS. The intensity of the CdS (0002) peak located at a two theta of 26.35° is very sharp and dominant. This indicates that the layer is strongly oriented to the c -axis of the hexagonal structure and also crystallized under constraints created by the substrate. Therefore, this means that the CdS layer is epitaxially crystallized although the lattice mismatch between CdS and GaAs is 0.188. At this time, the full width at half maximum (FWHM) value of the epilayer was 381 arcsec.

Fig. 2 presents the micro-Raman spectrum of the CdS/GaAs epilayer measured at room temperature. The

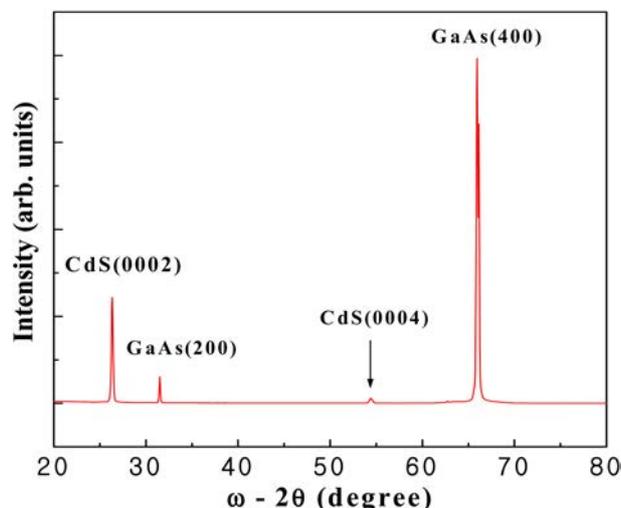


Fig. 1. Rocking curve of CdS/GaAs epilayer obtained by the XRD experiment.

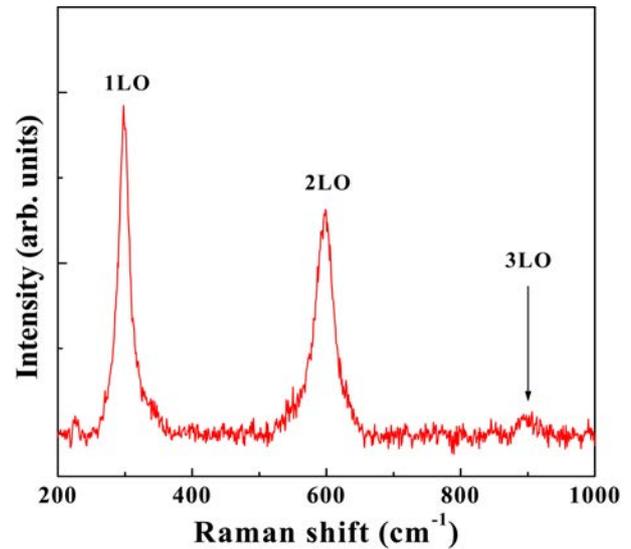
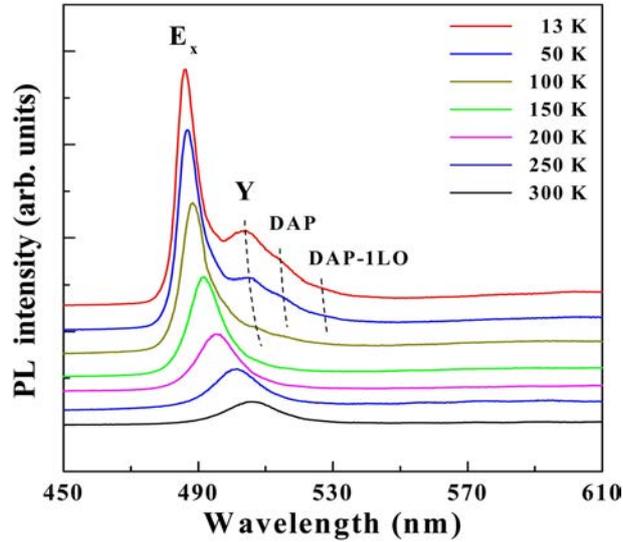


Fig. 2. The micro-Raman spectrum of the CdS/GaAs epilayer measured at room temperature.

hexagonal wurtzite-structured CdS belongs to the space group $C_{6v}^4(P6_3mc)$ with two formula units per primitive cell where all atoms occupying C_{3v} . The zone center optical phonons predicted by group theory are $A_1 + 2B_1 + E_1 + 2E_2$ [6]. Here, the A_1 , E_1 , and E_2 are Raman active modes, whereas B_1 is a forbidden mode. Also, A_1 and E_1 modes are polar and split into the transverse optical (TO) and longitudinal optical (LO) phonons. The E_2 mode consists of two modes of low and high frequency. Thus, the phonons of the LO mode only appear from a (100) surface and those of the TO mode from a (110) surface, and both LO and TO modes from a (111) surface [7]. These phenomena apply for ideal crystals and surfaces. As shown in Fig. 2, a typical Raman peak of the CdS/GaAs epilayer was observed intensively at 298.2 cm^{-1} . This peak corresponds to the vibration mode of the LO (1LO) phonon and its FWHM value is estimated to be 17.4 cm^{-1} . This peak showed a blue shift of 0.56 cm^{-1} in comparison with that of a bulk crystal of 297.64 cm^{-1} [8]. This suggests that it is caused by the strain due to the lattice mismatch between the substrate and epilayer in the heteroepilayer growth. Therefore, the observation of the 1LO phonon peak suggests that the CdS/GaAs epilayer is of high quality, which is consistent with the XRD result. If not, the selection rules in the (0002) plane must be broken down due to disordered or polycrystalline material. Thus, two peaks corresponding to the 1LO phonon replicas were observed at 600.1 cm^{-1} and 900.6 cm^{-1} . These replicas are the vibration phonon modes of 2LO and 3LO, respectively. At this time, the strength of the exciton-phonon coupling can be defined by the ratio I_{2LO}/I_{1LO} , which was 0.68 [8, 9]. Table 1 shows the ratio of I_{2LO}/I_{1LO} compared with several dimensions [10]. As Table 1 shows, the ratio of I_{2LO}/I_{1LO} decreased with a reducing number of dimensions. It was estimated that

Table 1. Ratio of I_{ILO}/I_{LO} compared with several dimensions in Ref. 10

Sphere	Rod	Epilayer (This work)	Bulk
0.42	0.40	0.68	0.88

**Fig. 3.** Typical PL spectra obtained in the temperature range from 13 to 300 K.

the relative intensities of the overtones in the resonance Raman spectrum of CdS depended on the number of dimension. Therefore, this indicates that the exciton-phonon coupling is deeply related to the dimensionality.

Fig. 3 shows typical PL spectra obtained in the temperature range from 13 to 300 K. Several peaks in the PL spectrum at 13 K were observed at 486.1 (2.5506 eV), 503.92 (2.4604 eV), 515.31 (2.406 eV), and 524.37 nm (2.3645 eV). The peak at 2.5506 eV showed a strong intensity, which is believed to correspond to the free exciton, E_x , whereas it was a broad FWHM. This peak position is in close agreement with the value of 486 nm measured at 10 K by Lovergine *et al.* from a CdS epilayer grown on a CdTe substrate [11]. Also, this value is in a reasonable coincidence in comparison to the value of the exciton A obtained by Seto from a CdS epilayer on a Si(111) substrate [12]. Thus, the observation of the free exciton suggests that the CdS/GaAs epilayer is of high quality, because the emission peak of the exciton can only be observed when an interaction of the long range Coulomb coupling between the electron and the hole exists. A low intensity peak was observed at 2.4604 eV, suggesting that it is caused by the Y band. This emission disappeared at a temperature above 100 K. Ordinarily, CdS layers formed structural defects at the interface during heteroepitaxial growth. Therefore, these structural defects strongly influence the optical properties of the layers. This suggests that the Y band emission originates from the radiative recombination of the excitons localized at extended structural defects such as dislocations at the

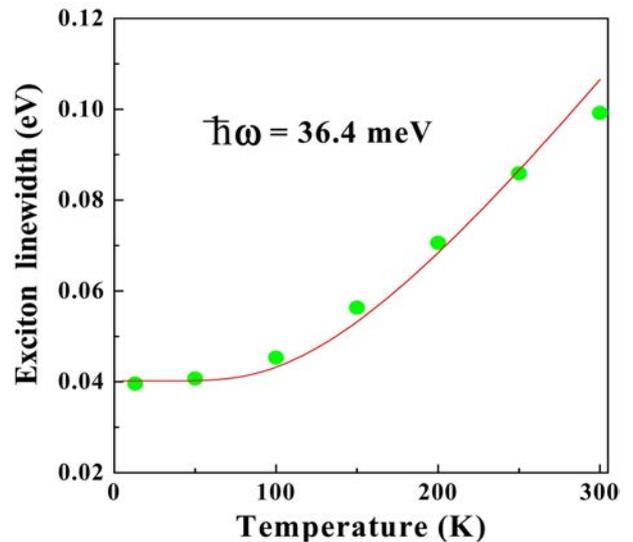
interface [12]. On the other hand, two peaks of low intensity toward the low energy region of the Y band were observed at 2.406 and 2.3645 eV [13]. Also, the energy difference between these peaks is similar to the LO phonon energy of 0.037 eV obtained from the Raman spectrum. These emissions are believed to be donor-acceptor pairs (DAP) and its LO phonon replica, respectively. When the temperature was increased to 100 K, these peaks disappeared.

As shown in Fig. 3, the PL spectra show that the position of the free excitons tend to shift to shorter wavelength regions with a decrease in the temperature, and its intensity continues to decrease with an increase in the temperature. Also, the FWHM of the free excitons broadened with an increase in the temperature. Generally, an exciton is thermally dissociated when the thermal energy exceeds the exciton binding energy of E_x^b . So, an exciton is only observed when the measurement temperature satisfies the relation $T \geq E_x^b/k$. In addition, the lifetime of an exciton reduces with an increase in the temperature and the linewidth of its energy broadens according to the uncertainty principle of $\Delta E = \hbar/\Delta\tau$, where $\Delta\tau$ is the exciton lifetime. Conversely, the linewidth of the exciton peak tends to be narrower due to a reduction of the impurity scattering in the crystal with a decrease in the temperature. Thus, the exciton linewidth can be determined by measuring the exciton lifetime broadening.

Fig. 4 presents the exciton linewidth on the PL emissions as a function of the measurement temperature. However, the temperature dependent linewidth of the FWHM of an exciton can be expressed by Toyozawa theory [14], which is given by:

$$Y = A/\{\exp(\hbar\omega/kT) - 1\} + C \quad (1)$$

Here, $\hbar\omega$ is the average energy of the phonon participating

**Fig. 4.** Exciton linewidth on the PL emissions as a function of measurement.

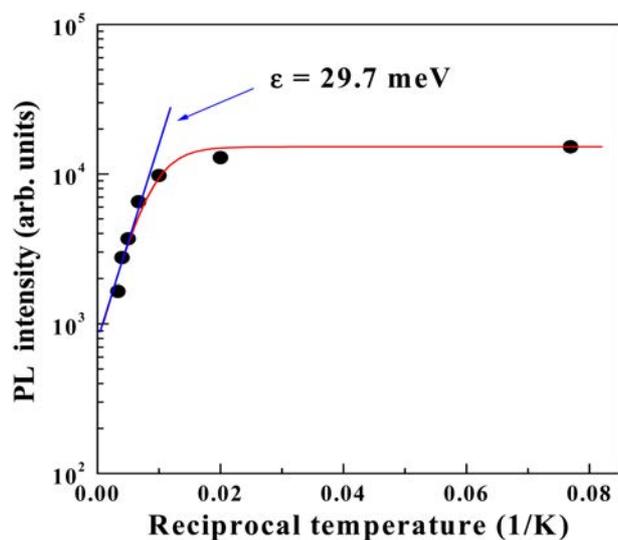


Fig. 5. Temperature dependence of the PL intensity of free excitons in the temperature range from 13 to 300 K.

in the quenching process and C is a constant linewidth at low temperature. As shown in Fig. 4, the solid line fitted by Eq. (1) is consistent with the data of the exciton linewidth obtained in this experiment. At this time, the ω value given by Eq. (1) was 36.4 meV. This value is nearly equal to the LO phonon of 37 meV obtained from Raman spectroscopy. Therefore, this fact provides the cause of the FWHM reduction with a decrease in the temperature. So, the FWHM quenching suggests that the vibration mode of the LO phonon participates in the quenching process of a free exciton.

Fig. 5 shows the temperature dependence of the PL intensity of free excitons in the temperature range from 13 to 300 K. As Fig. 5 shows, the PL intensity is exponentially reduced in the higher temperature region. This is mainly related to the thermally-activated non-radiative recombination. The temperature dependence of the PL intensity can be expressed by the equation [15]:

$$I = I_0 / \{1 + C \exp(-\varepsilon/kT)\} \quad (2)$$

where C is the fitting parameter and ε is the activation energy. Therefore, the change of luminescent intensity can be attributed to a partial dissociation of excitons. From the fitting curve with Eq. (2), we obtained $\varepsilon = 29.7$ meV from the curvature of the high temperature region. This luminescence quenching creates a relatively high activation energy. This activation energy corresponds with the thermal dissociation energy of the free exciton at the ground state and is also in good agreement with the binding energy, 29.4 meV, of a free exciton [1].

Fig. 6 illustrates the energy band gap and the PL peak position as a function of temperature. Here, the energy band gap of CdS was added to the exciton binding energy of 29.4 meV that was experimentally determined irrespective of the temperature dependence. As Fig. 6

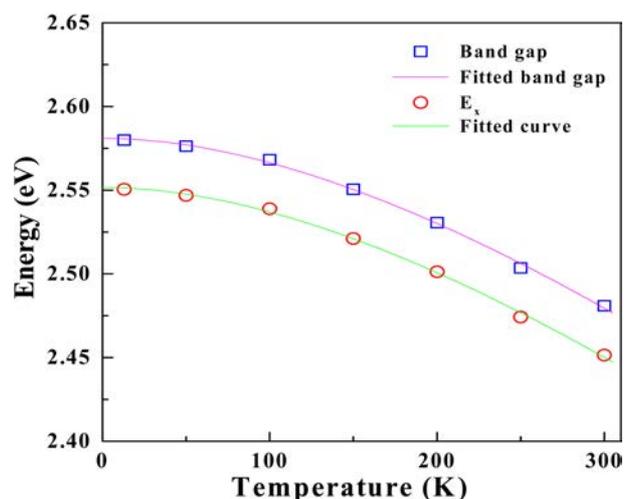


Fig. 6. Energy band gap and the PL peak position as a function of temperature.

shows, the exciton peak energy shows a nonlinear relationship and tends to a shift towards the red side with an increase in the temperature. At this time, the temperature dependence of the exciton peak position is related to the relative position variation between the conduction and valence bands due to the temperature-dependence dilatation of the lattice and the temperature-dependent electron-lattice interaction [16]. The variance of the energy band gap, $E_g(T)$, as a function of temperature is given by [17]:

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T) \quad (3)$$

where α is a constant and β is approximately the Debye temperature. Also, $E_g(0)$ is the energy band gap at 0 K. When α and β are given to be 5.4×10^{-4} eV K⁻¹ and 258.8 K, respectively, $E_g(0)$ is extracted out to be 2.5684 eV. The curve plotted by Eq. (3) is closely matched with the experimentally-measured values as shown in Fig. 6. However, $E_g(0)$ and α are nearly consistent with the values obtained by Ray [1]. Also, the Debye temperature of CdS was found to be 219.3 K and is in reasonable agreement with our result [18].

Conclusions

Hexagonal-structured CdS epilayers on GaAs substrates were grown using the HWE method. From the micro-Raman measurements, the LO phonon mode of an epilayer was observed to shift towards a higher energy than that of bulk. This blue shift suggests that the cause was the strain due to the lattice mismatch between the substrate and layer in the heteroepilayer growth. Also, we found that the exciton-phonon coupling, which are the relative intensities of the overtones in the resonance Raman spectrum of CdS, are deeply related to the dimensionality. The optical properties attributed by the thermal quenching phenomenon of CdS were studied

by PL measurements as a function of temperature. The peak position of the free exciton emission shifted to a shorter wavelength region with a decrease in the temperature. With an increase in the temperature, PL intensities were exponentially reduced and their spectral width showed a tendency of broadening. Consequently, the FWHM quenching suggests that the vibration mode of the LO phonon participates in the quenching process of a free exciton. At this time, the average energy of the phonon that was part of the quenching process was found out to be 36.4 meV. These findings led us to suggest that the phonons may have participated in the quenching process. Thus, the change of luminescent intensity can surely be attributed to the partial dissociation of excitons. The extracted activation energy of $\varepsilon = 29.7$ meV corresponding to the thermal dissociation energy of the free exciton at the ground state was in good agreement with the binding energy of the free exciton of 29.4 meV. The temperature dependence of the free exciton was well interpreted using Varshni's relation. Thus, the energy band gap of $E_g(T)$ as a function of temperature was derived to be expressed by $E_g(T) = 2.5684 - (5.4 \times 10^{-4})T^2/(258.8 + T)$.

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