

Temperature dependence of excitonic emission in cubic CdSe thin film

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Abstract

A detailed photoluminescence investigation of the thermal redshift and broadening of the excitonic line of cubic CdSe film grown by molecular beam epitaxy is presented. Free excitonic emission from the cubic CdSe film was observed at low temperature. Temperature-dependent measurement was performed to obtain material parameters related to exciton–phonon interaction by fitting the experimental data to the phenomenological model. The relative contribution of both acoustic and optical phonon to the band gap shrinkage and exciton linewidth broadening are discussed. Exciton binding energy of 16 ± 1.5 meV was determined from the Arrhenius analysis.

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1. Introduction

Nanostructures of CdSe have been demonstrated to be a promising II–VI semiconductor material for optoelectronic devices [1]. Bulk CdSe is a prototype of a hexagonal wurtzite semiconductor [2], and its optical properties [3] and band structures have been extensively studied [4]. After the successful growth of epitaxial zinc-blende CdSe on GaAs substrate by Samarth et al. [5], several optical spectra of zinc-blende CdSe were reported [6,7]. Nevertheless, optical quality of cubic CdSe epilayer is degraded by the large lattice mismatch between CdSe and GaAs substrate. Therefore, the photoluminescence (PL) of the cubic CdSe epilayer is mainly characterized by deep level emission [6,7]. The band edge emission is weak in this case. A closely lattice-matched ZnTe buffer was then adopted for the growth of cubic CdSe epilayer and an enhancement of band edge emission intensity was reported [8]. However,

there is still less reports on temperature (T) dependence of emission from cubic CdSe thin film, especially the investigation of excitonic properties.

In this work, we report the evolution of PL as a function of T for the cubic CdSe epilayer grown on GaAs substrate with ZnSe buffer by molecular beam epitaxy. Signature of free exciton emerges from low T , and this enables us to elucidate the T dependence of exciton parameter, i.e., the exciton–phonon coupling strength. Furthermore, exciton binding energy of 16 ± 1.5 meV for the cubic CdSe epilayer is experimentally determined from the Arrhenius plot.

2. Experimental details

The CdSe epilayer was grown on a (001) GaAs substrate by using Veeco Applied EPI 620 molecular beam epitaxy system. The EPI 40 cm³ low-temperature cells were utilized for the evaporation of Cd and Se elements. Before the growth, the substrates were etched in H₂O:NH₄OH:H₂O₂ solution and then flushed with deionized water for 2 min. Substrate temperature of 300°C was adopted during the growth. Six monolayers of ZnSe were first fabricated using

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the migration enhanced epitaxy technique [9], and then a 100-nm-thick ZnSe buffer was deposited. Cell temperatures of the Cd and Se sources were set at 200 and 178 °C, respectively. The growth condition is Se-rich. The zinc-blende crystal structure of the grown CdSe thin film is confirmed by X-ray diffraction measurement. A closed cycle refrigerator is used to cool down the sample for the low- T optical measurement. Typical tungsten halogen lamp is the light source for the reflectivity (R) measurement. The reflected beam from the samples were dispersed in a SPEX 1403 double-grating spectrometer and detected by a thermoelectrically cooled photo-multiplier tube, using photon-counting technique. For the PL measurement, we use the 325 nm line of HeCd laser, which corresponds to an energy well above the band gap of cubic CdSe [10], as an excitation source.

3. Results and discussion

Fig. 1 shows the low- T PL (solid curve) and reflectivity (dot curve) of the cubic CdSe epilayer. Despite of significant interference fringes in the reflectivity spectrum, a characteristic reflection feature of exciton is observed. The dip energy of the excitonic feature is 1.745 eV, which is very close to free exciton energy determined from piezomodulated reflectivity measurement [5]. According to the polariton model [11], the dip energy in the exciton reflection feature is equal to the longitudinal exciton energy. However, the transverse–longitudinal splitting of exciton in cubic CdSe is not available at the moment. Therefore, we ascribe the sharp emission line to free exciton

with peak energy of 1.741 eV, in view of its proximity to the excitonic feature in the reflectivity spectrum. The full-width at half-maximum (FWHM) of the excitonic line is about 7 meV. A small emission band (1.718 eV) lies at lower energy side of the excitonic emission is probably due to the recombination of impurity-bound exciton or LO-phonon (26 meV) [12] sideband of the exciton line. Besides, a radiative transition involving deep levels (1.5–1.7 eV) due to impurities and structural defects, characterizes the PL at low T . In order to clarify the extrinsic nature of this broad emission band, we performed an excitation density dependence of PL at low T . The excitation power was varied from 10 to 140 mW. Fig. 2 shows the normalized (by exciton peak intensity) PL of the CdSe thin film. Comparison with the excitonic emission intensity, the deep level emission intensity increases slowly against the excitation power and tends to saturate at high excitation power. This indicates the limited density of states for the recombination involving localized centers in the energy gap. Besides, different lineshape of the deep level emission from that of Fig. 1 suggests a local dependence of this emission, implying an extrinsic nature of the emission. Therefore, the deep level emission is likely originated from the impurities or structural defects, which are mainly due to the lattice mismatch between CdSe and ZnSe buffer.

Evolution of PL as a function of T is shown in Fig. 3. The deep level emission diminishes rapidly as T increases. No new emission line emerges at energy above the sharp emission line as T increases, supporting the assignment of

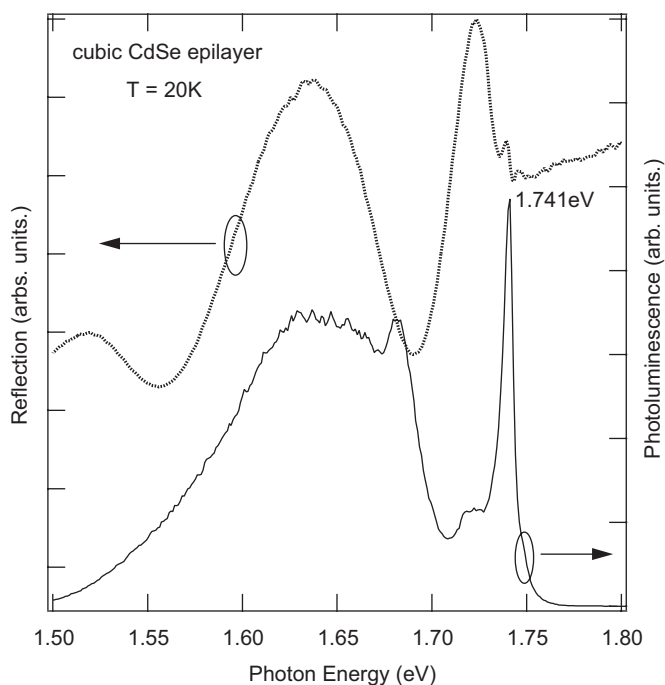


Fig. 1. Low- T reflectivity (dot curve) and PL (solid curve) spectra of cubic CdSe epilayer. The excitonic features in the spectra are located at energy about 1.741 eV.

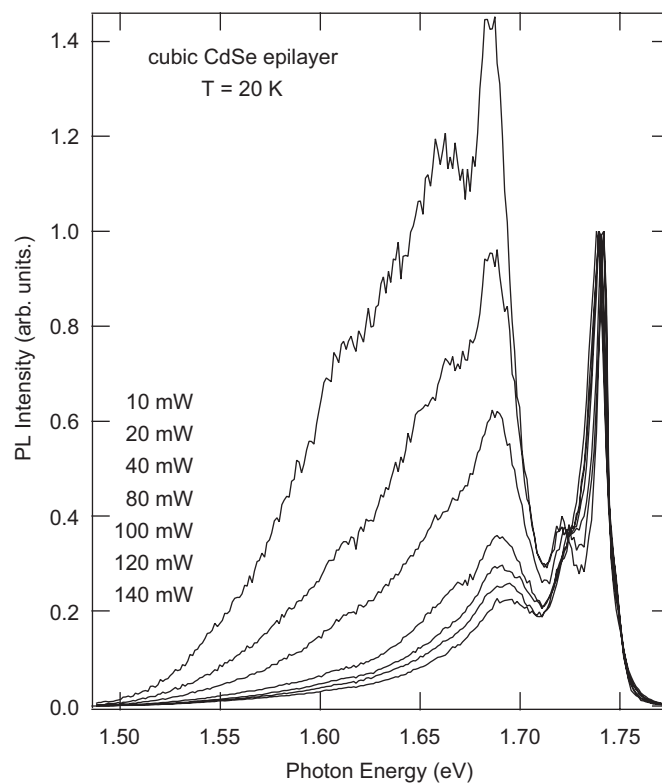


Fig. 2. Normalized low- T PL spectra of cubic CdSe epilayer as a function of excitation power. The excitonic emission peak intensity is normalized.

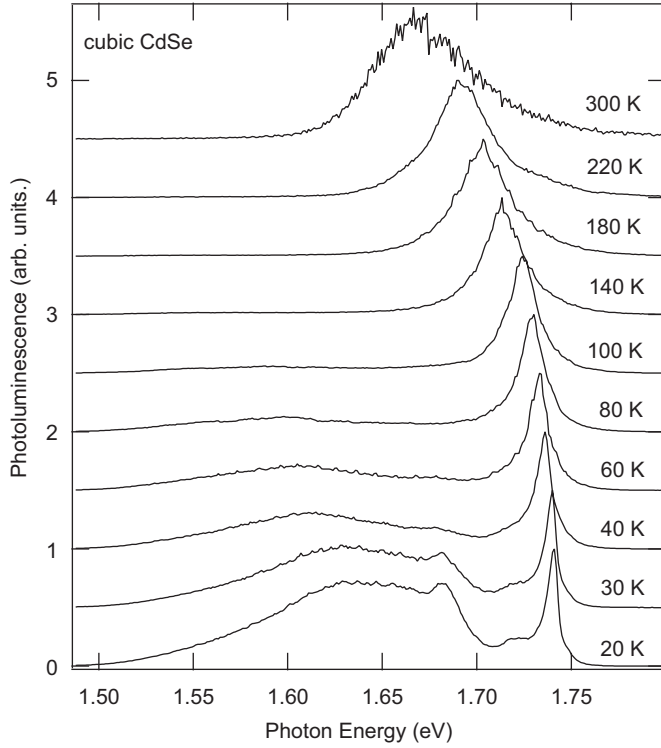


Fig. 3. T -evolution of PL spectra of cubic CdSe epilayer. The corresponding T is written at the right part of graph. Deep level emission is rapidly quenched as T increases.

free excitonic nature of the sharp emission line. The redshift (close squares) and broadening (open circles) of the excitonic emission line is summarized in Fig. 4. If we assume a constant exciton binding energy against T , the redshift of excitonic emission line is the consequence of thermal expansion of the lattice and electron–phonon interaction [13]. The former effect is important only at higher temperature, whereas the latter effect induces the relative shifts of conduction band and valence band which leads to a quadratic variation of the fundamental energy gap at low T and to a linear one at high T . Both effects cause the shrinkage of band gap, thus, redshift of the emission line. In general, the experimental values of energy gap of a semiconductor as a function of T are well fitted to the following phenomenological Varshni's model [13]:

$$E_{\text{ex}}(T) = E_{\text{ex}}(0) - [\alpha T^2 / (\beta + T)], \quad (1)$$

where $E_{\text{ex}}(0)$ is the transition energy at 0 K; α and β are the material-dependent parameters, known as Varshni's coefficients. In particular, α represents the linear shift of $E_{\text{ex}}(T)$ at high T and plays the role of $T \rightarrow \infty$ limit of the gap entropy [14], while β accounts for the quadratic variation of $E_{\text{ex}}(T)$ at low T and should be related to the Debye temperature (Θ_{D}) after the correction due to the thermal expansion effect of the lattice [15]. According to Refs. [7,10], the exciton binding energy of cubic CdSe is about 13 meV. Therefore, dissociation of excitons is expected at high T , thus, an emission component due to band-to-band recombination should appear at higher

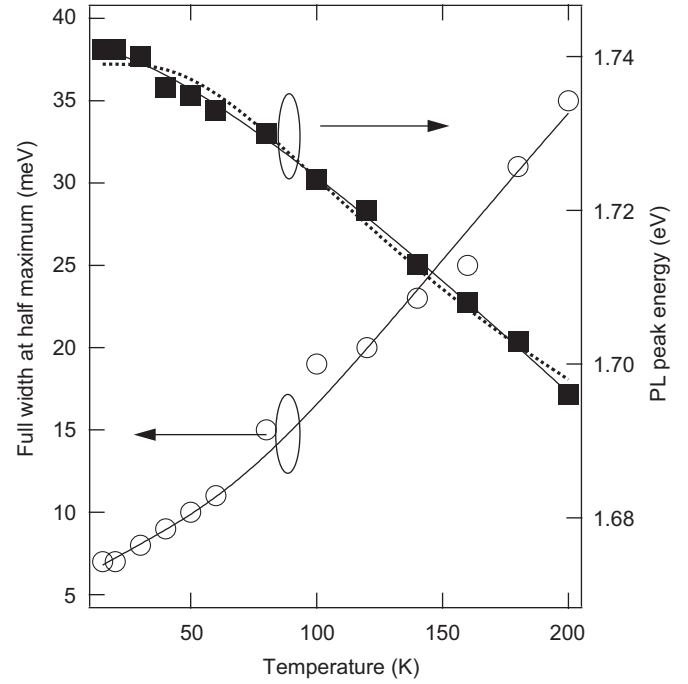


Fig. 4. T -dependence of excitonic peak energy (close squares) and FWHM (open circles) for cubic CdSe epilayer. The solid line and dash line fitted to the excitonic peak energy correspond to Eqs. (1) and (2), respectively, whereas the solid line fitted to data of FWHM correspond to Eq. (3).

energy wing of the PL band [16]. In order to exclude the effect of the free carrier recombination, we fitted the PL peak energy at $T < 200$ K [17]. The Varshni's fit (solid line in Fig. 4) yields $E_{\text{ex}}(0) = 1.742$ eV, $\alpha = 0.33$ meV/K and $\beta = 83$ K. The value of α is in reasonable agreement with those reported, $\alpha = 0.37$ meV/K and $\beta = 150$ K in Ref. [12], whereas there is a considerable discrepancy between our fitting parameters and those reported, $E_{\text{g}}(0) = 1.766$ eV, $\alpha = 0.70$ meV/K and $\beta = 281$ K in Ref. [10]. Adding exciton binding energy of 13 meV [10] to the obtained $E_{\text{ex}}(0)$ value, we found that the fundamental band gap energy (1.755 eV) is comparable to their reported value of energy gap. However, the Varshni's thermal coefficients are fairly smaller. It is very common that Varshni parameters fall in a broad range for the same material. This could be attributed to the empirical origin of Varshni relation [18,19]. Manoogian and Woolley [15] have suggested that after removing the contribution of the thermal expansion of lattice, the β parameter follows the relation $\beta = (3/8)\Theta_{\text{D}}$. The β parameter obtained in Ref. [10] is unreasonably larger than the Θ_{D} (182 K) [12] of CdSe. We obtained a smaller value of β parameter compared to the Θ_{D} of CdSe. This is usually valid for the Varshni's fit of other semiconductors [20,21].

Another empirical model describing the T redshift of the band gap based on the electron–phonon interaction is represented by the following expression [22]:

$$E_{\text{ex}}(T) = E_{\text{ex}}(0) - 2a_{\text{B}} \left[\exp\left(\frac{\theta}{T}\right) - 1 \right]^{-1}, \quad (2)$$

where a_B is the strength of the electron–average phonon interaction, $[\exp(\theta/T)-1]^{-1}$ is the Bose–Einstein statistical factor for phonon emission and absorption, θ is a T corresponding to an average phonon energy. The best fit (dash line in Fig. 4) yields $E_{ex}(0) = 1.739$ eV, $a_B = 21$ meV and $\theta = 203$ K. The main difference between Eq. (1) and Eq. (2) comes from the dependence of energy gap at low- T range: the quadratic dependence in Varshni’s model is replaced by an exponential dependence in Eq. (2). The two fitting curves are quite coincident, except for low- T range, where the difference in energy is about 3 meV. Indeed, the θ value possesses information about the contribution of the acoustic phonons to the redshift of band gap: the lower the θ value with respect to the LO-phonon energy, the larger the contribution of the acoustic phonons to the band gap shrinkage due to electron–phonon interaction. The estimated average phonon temperature θ in the sample is lower than the LO phonon temperature (about 305 K) of cubic CdSe [12], indicating that acoustic phonons as well as optical phonons contribute to the redshift of the emission energy. The electron–average phonon interaction strength a_B , is slightly smaller than that of hexagonal CdSe (36 meV) [22]. This could be partially attributed to the stronger electron–LO-phonon interaction in the hexagonal CdSe, which will be identified later.

The T dependence of excitonic line broadening can give important information of exciton–phonon interaction. In general, the linewidth of excitonic emission has two contributions: the homogeneous broadening due to the phonon scattering process, i.e., the dissociation of exciton by means of collision with phonons and the inhomogeneous broadening due to extrinsic effects such as dislocation, interface roughness and impurities. In particular, the large lattice mismatch between CdSe and ZnSe buffer induces strain effects at the interface that broadening the exciton line. At low- T range, the exciton–acoustic phonon interaction is the dominant mechanism since their density is relatively high. On the contrary, the contribution of optical phonon, whose population follows the Bose–Einstein statistics, becomes important at high T . Based on the above description, the FWHM of excitonic line can be expressed by the following equations [22]:

$$\Gamma(T) = \Gamma_0 + \Gamma_{ac}T + \Gamma_{LO}/(\exp(E_{LO}/k_B T) - 1), \quad (3)$$

where Γ_0 is the zero broadening parameter, Γ_{ac} is the coupling strength of exciton–acoustic phonon interaction, Γ_{LO} is the coupling strength of exciton–LO phonon interaction, E_{LO} is the LO-phonon energy and k_B is the Boltzmann constant. The parameters Γ_0 , Γ_{ac} and Γ_{LO} were obtained through the fitting to the T dependence of FWHM. The LO-phonon energy was set at 305 K. The Γ_0 and Γ_{ac} parameters were first determined from the fitting at $T < 40$ K. The best fit yields $\Gamma_0 = 5.5$ meV, $\Gamma_{ac} = 84$ μ eV/K and $\Gamma_{LO} = 20$ meV. It is interesting to compare the exciton–LO phonon interaction strength with other semiconductors, since this parameter related to the stability of exciton at high T . In comparison with the

hexagonal CdSe (49 meV) [23], the exciton–LO phonon coupling of the cubic CdSe is weaker, consistent with the results discussed above. Nevertheless, a study of exciton PL linewidth as a function of T for wurzite and zinc-blende GaN shows a reverse result [24], where the Γ_{LO} of cubic GaN is larger than that of the hexagonal one. The authors have suggested that the result is due to the larger LO-phonon energy and relatively smaller exciton binding energy of cubic GaN. In our case, the comparable exciton binding energy of the cubic CdSe, as will be determined later, may only have little contribution to the variation of the Γ_{LO} . The structural orders due to the misfit dislocations are likely large in the CdSe epilayer on a lattice-mismatched ZnSe buffer, and originate a strong damping of optical phonons. Therefore, a dumping of optical phonons by structural disorder in the cubic CdSe could be a reason responsible for the smaller coupling strength of exciton–LO phonon interaction [19].

It is well known that the so-called Fröhlich interaction, which is a Coulomb interaction between excitons and the longitudinal electric field produced by LO phonons, dominates the exciton–LO phonon interaction. Therefore, in general, the larger LO phonon energy favors stronger Fröhlich interaction and, thus, a larger coupling strength of Γ_{LO} . The Γ_{LO} is also compared with other semiconductors. We found that it is comparable to that of CdTe (17 meV) [25], smaller than that of CdS (41 meV) [25], ZnSe (81 meV) [26], ZnO (876 meV) [27] and GaN (525 meV) [28]. It was found that the measured magnitude of Γ_{LO} ’s have correlation with LO phonon energy. Cubic CdSe possesses LO phonon energy of 26 meV, which is comparable to that of CdTe (21 meV), but smaller than that of CdS (38 meV), ZnSe (31 meV), ZnO (72 meV) and GaN (92 meV) [12].

In order to estimate the exciton binding energy, Arrhenius plot of the integrated excitonic PL intensity is shown in Fig. 5. The most possible mechanism for the quenching of the PL intensity is the dissociation of free excitons into the continuum states and trapped by the nonradiative centers. Therefore, accounting for one recombination process, the T dependence of the integrated excitonic PL intensity can be fitted by the following equation [29]:

$$I(T) = \frac{I(0)}{[1 + C \exp(-E_a/k_B T)]}, \quad (4)$$

where $I(T)$ and $I(0)$ are the integrated PL intensities at temperature T and 0 K, respectively. C is a fitting constant related to the ratio of radiative lifetime to nonradiative lifetime [29] and k_B is the Boltzmann constant. E_a is the activation energy, which is equal to the exciton binding energy for the bulk structure case. Indeed, the T dependence of the exciton PL intensity is not well produced by only one E_a . However, if T is considered only in the range $0 < T < 200$ K is adopted, we obtained an activation energy of approximately 16 ± 1.5 meV, which is comparable to that of hexagonal CdSe. It is reasonable since the

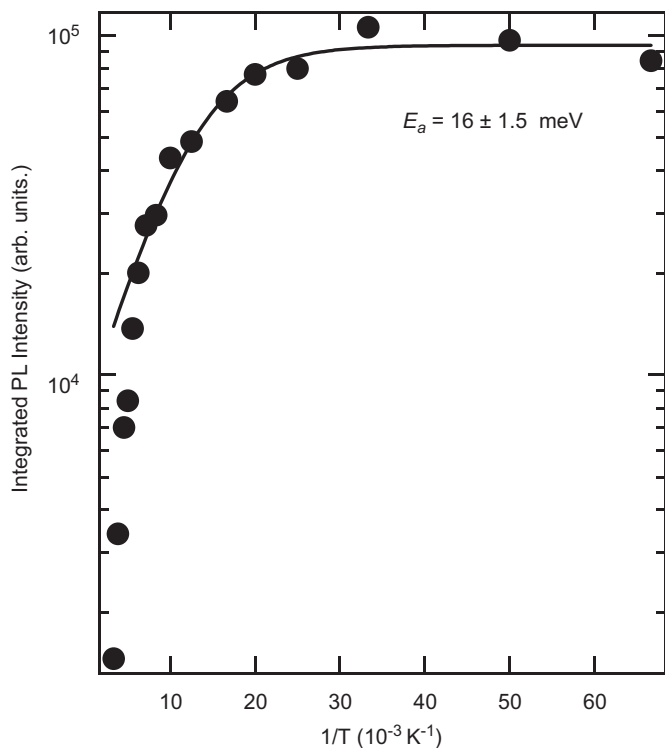


Fig. 5. Arrhenius plot of integrated excitonic PL intensity versus the reverse of T . The best fit for the data at T range of $0 < T < 200$ K yields activation energy of 16 ± 1.5 meV.

excitonic emission should almost vanish as $T > 200$ K (thermal energy of 17 meV). The exciton binding energy obtained is somewhat larger than the calculated value reported in Ref. [7], but comparable to that obtained experimentally (15 meV) [30]. We reevaluate the exciton binding energy by employing the simple hydrogen-like model, used by the authors [7]. The values of effective electron mass, heavy hole mass and static dielectric constant are $0.12m_0$, $0.9m_0$ and 9.2 [12]; or $0.11m_0$, $0.45m_0$ and 9.6 [30], selected for cubic CdSe. Those material parameter sets result in exciton binding energies of 17 and 13 meV, respectively. The discrepancy in the calculated exciton binding energy comes mainly from the heavy hole mass. An accurate determination of the material parameters for cubic CdSe is necessary to clarify the difference between the calculated and the experimentally determined exciton binding energy.

4. Conclusion

The thermal redshift and broadening of the excitonic PL line of a cubic CdSe film grown by molecular beam epitaxy are investigated. Free exciton features from the cubic CdSe film were observed by the low-temperature photoluminescence. Temperature-dependent measurements were performed to obtain material parameters related to exciton–phonon interaction by fitting the experimental data to a phenomenological model. The relative contribution of

both acoustic and optical phonons to the band gap shrinkage and exciton linewidth broadening are discussed. The exciton binding energy obtained from the Arrhenius analysis is 16 ± 1.5 meV.

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