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Temperature dependence of the fundamental band gap parameters in cadmium-rich $Zn_xCd_{1-x}Se$ using photoluminescence spectroscopy

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Abstract. Thin films of ternary $Zn_xCd_{1-x}Se$ were deposited on GaAs (100) substrate using metal-organic-chemical-vapour-deposition (MOCVD) technique. Temperature dependence of the near-band-edge emission from these Cd-rich $Zn_xCd_{1-x}Se$ (for $x = 0.025$, 0.045) films has been studied using photoluminescence spectroscopy. Relevant parameters that describe temperature variation of the energy and broadening of the fundamental band gap have been evaluated using various models including the two-oscillator model, the Bose–Einstein model and the Varshni model. While all these models suffice to explain spectra at higher temperatures, the two-oscillator model not only explains low temperature spectra adequately but also provides additional information concerning phonon dispersion in these materials.

Keywords. Photoluminescence; semiconductors; band gap.

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1. Introduction

In recent years, several theoretical and experimental studies have focused on the electronic properties of ternary II–VI semiconductor alloys and their multilayer heterostructures, largely motivated by the potential applications of these materials in opto-electronic devices, particularly blue–green lasers [1–6]. ZnSe-based quantum well devices using ternary $Zn_xCd_{1-x}Se$ alloys as quantum well materials are used as the active medium for blue–green lasers. While some parameters of the quantum well devices can be optimized by an appropriate choice of structural parameters, a detailed knowledge concerning the temperature dependence of the near-band-edge transitions would be useful for optimizing other crucial parameters including the operating temperatures of these devices.

The crystal structure of $Zn_xCd_{1-x}Se$ depends both on the alloy composition (x) and whether the material is in bulk or thin-film form. Growth of $Zn_xCd_{1-x}Se$ on GaAs substrates leads to a zinc blende structure over the entire composition range [7]. In spite of a 7% lattice mismatch between the substrate and the epilayer, high quality films have been successfully grown. The optical and electronic properties of a semiconductor depend on its

energy band gap, which among other factors, is related to the crystal structure. While the energy band gap parameters in the Zn-rich alloys have been well investigated, relatively less work is reported for the Cd-rich alloys.

Significantly important information concerning electron–phonon interactions, excitonic effects etc. could be obtained from the temperature dependence of the electronic inter-band transitions [8–11]. Temperature dependence of the fundamental band gap parameters of $Zn_xCd_{1-x}Se$ has been investigated by photoluminescence spectroscopy, reflection spectroscopy, ellipsometry and electroreflectance [7,12–16]. Most of the experimental results were analysed using the Varshni equation or its modifications [17] and could properly describe the temperature dependence of the band gap in a variety of group IV, III–V and II–VI semiconductors.

Another popular model that is used to describe the temperature dependence of the energy band gap is the Bose–Einstein model [8]. Melikova *et al* [16] studied temperature dependence of the energy gap $E(T)$ and the broadening parameter $\Gamma(T)$ for the direct gap of $Zn_{0.56}Cd_{0.44}Se$, grown on InP substrate, by employing the electro-reflectance technique. The experimental data were fitted using the well-known Varshni's model as well as the Bose–Einstein model. However, both these models are semi-empirical and consider only the average phonon energy involving no information concerning phonon dispersion. Recently, Passler *et al* ([18,19] and references therein) have developed an analytical model called the two-oscillator model that accounts for phonon energy dispersions and was shown to be useful for materials which fall in the category of moderate or high dispersion range. This model was shown to fit the temperature dependence of the fundamental band gap of some binary III–V and II–VI semiconductors and could also be a reasonable model for ternary semiconducting materials.

In this paper we report a temperature dependent study of the photoluminescent near-band-gap emission in Cd-rich $Zn_xCd_{1-x}Se$ films as a means of determining the temperature variation of the fundamental energy band gap parameters. Photoluminescence is a simple non-destructive tool for studying the near-band-edge emission. Availability of high quality samples and good spectroscopic instrumentation allow precise observation of room temperature PL emissions and determination of the fundamental energy gap parameters with great accuracy. In this study, PL measurements, as a function of temperature, are analysed using three different models mentioned above, namely: (1) the Varshni model, (2) the Bose–Einstein model and (3) the two-oscillator model, so as to obtain the temperature-dependent band gap parameters. These parameters are presented in tables 1, 2 and 3 for the three models. A comparison between the different models shows that the two-oscillator model, which includes the effect of phonon dispersion, best describes the data in the low temperature region.

2. Experiment

Thin films of Cd-rich $Zn_xCd_{1-x}Se$ ($x = 0.025$, 0.045) were grown on GaAs (100) substrates by the metal organic chemical vapor deposition (MOCVD) technique. The thickness of the films was nearly 1.5 μm. Thin films grown by the MOCVD technique are known to have the zinc blende structure over the entire alloy composition range. The PL emission was excited using 2.41 eV excitation energy from an argon-ion laser (Coherent, Innova 90-5) with nearly 5 mW incident laser power and a focused laser spot diameter of

$\sim$100 μm. The scattered signal was collected in a backscattering geometry and analysed by employing a double monochromator (Ramanor HG2S) followed by a cooled photomultiplier tube (Hamamatsu R943-02) and associated photon-counting electronics. Low temperatures (down to 25 K) were attained by employing a closed-cycle liquid-helium refrigeration system (Air Product Displex). It consists of a helium-compressor (model IR02A) and expander (model CS-202), a DME-M/E interface which include a shroud and a microprocessor-based digital temperature controller (SC Instruments Inc., Model 9600-5). The temperature was monitored with a gold-chromel thermocouple. The temperature stability during each spectrum run was better than $\pm$0.5 K.

3. Results and discussions

The photoluminescence spectra were obtained in the energy range 1.6 eV to 1.8 eV, which covers the near-band-edge region for the $Zn_xCd_{1-x}Se$ ($x = 0.045$ and 0.025) samples. Figure 1 shows the PL spectra at various temperatures for the $Zn_{0.045}Cd_{0.955}Se$ film. For the temperature range 100 K to 300 K, a single prominent peak appears and this is labeled as 'A' in the figure. When the temperature is lowered to 75 K, an additional peak, labeled as 'M', appears on the lower energy side. As the temperature is further lowered from 75 K to 25 K, several additional peaks are observed and these are attributed to phonon replica modes [20]. They are assumed to be associated with some shallow energy levels whose exact origin is still not clear.

The band parameters of interest, for the peak 'A', are the temperature variations of (a) peak energy position, (b) width of the band and (c) its line shape. This luminescent band is due to direct electronic transition from the conduction to the valence band and is used to characterize the fundamental band gap. It exhibits a blue shift in energy and becomes narrower with decreasing temperature. The peak position shifts from 1.666 eV at 300 K to 1.756 eV at 75 K. Similar qualitative features are also observed in the temperature-dependent PL spectra of the film for the other alloy composition, $Zn_{0.025}Cd_{0.975}Se$. Its room temperature PL peak position occurs at 1.660 eV.

It may be noted that the PL peak position is governed by different contributions in the low and high temperature regimes. The peak position (within the error limit of the peak width) of the PL band gives a good estimate of the band gap energy. The band gap energy thus obtained at various temperatures from this data, was analysed numerically using the various models.

According to the two-oscillator model, the temperature dependence of band gap can be given by [18]

$$E(T) = E(0) - \frac{\alpha}{k}\int \mathrm{d}\varepsilon \frac{w(\varepsilon)\varepsilon}{\exp(\varepsilon/k) - 1}, \tag{3.1}$$

where α denotes the limiting magnitude of the slope of the $E(T)$ curve at $T \to \infty$, $w(\varepsilon)$ is a normalizing weightage function and k is the Boltzmann constant. Finding the exact dependence of $w(\varepsilon)$ on ε in a given material is complicated. Assuming that this function can be represented as a finite sequence of discrete peaks located at certain phonon energies $\varepsilon_i = \hbar\omega_i = \Theta_i$, $i = 1, 2, 3, \ldots, N$ (where Θ_i are the associated phonon temperatures), one can obtain from eq. (3.1) the following expression for the $E(T)$ dependence:

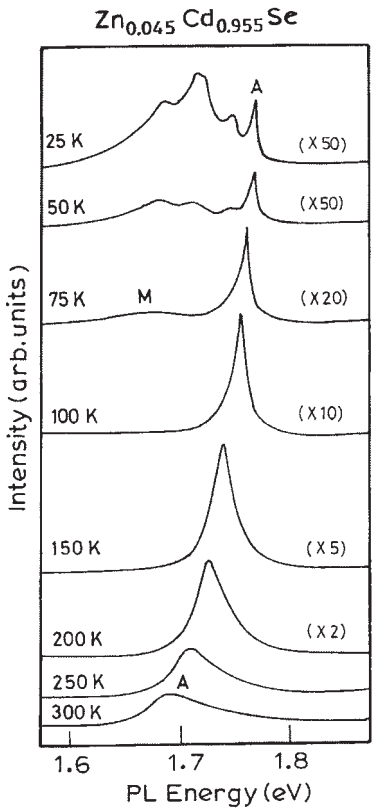

Figure 1. PL spectra of $Zn_xCd_{1-x}Se$ ($x = 0.045$) at indicated temperatures showing band edge luminescence (numbers in brackets indicate the intensity magnification).

$$E(T) = E(0) - \alpha \sum_{i}^{N} \frac{w_i \Theta_i}{\exp(\Theta_i/T) - 1}. \tag{3.2}$$

A reasonable estimate of the dispersion can be achieved by considering a two-oscillator model i.e. $N = 2$ in eq. (3.2). Two different phonon temperature values Θ_1 and Θ_2 can be associated with the acoustical and optical phonon branches. In our fitting, the low-energy oscillator was fixed in the vicinity of the dominant TA peak $k\Theta_1 \approx k\theta_{\mathrm{TA(max)}}$ and the high energy oscillator Θ_2, located within the energy region $\varepsilon_{\mathrm{LA(max)}} \leq k\theta_2 \leq \varepsilon_{\mathrm{LO(TO)}}$, and was taken as an adjustable parameter. The weighing parameter W_1 was also found from the fitting and the parameter W_2 gets automatically fixed by the normalization condition $W_1 + W_2 = 1$. The effective phonon temperature Θ can be given by $\Theta = W_1\Theta_1 + W_2\Theta_2$ and the dispersion coefficient (Δ) is given by

$$\Delta = \frac{1}{\Theta}\sqrt{(\Theta_2 - \Theta)(\Theta - \Theta_1)}. \tag{3.3}$$

The simplest version of the oscillator model with $N = 1$ corresponded to the limiting case of the vanishing phonon dispersion, where the effective phonon temperature $\Theta = \langle\varepsilon\rangle/k_{\mathrm{B}}$,

is in coincidence with the phonon temperature associated with the single oscillator in consideration. The $E(T)$ dependence thus reduces to the familiar model of Bose–Einstein [8]

$$E(T) = E'(0) - \frac{2a_B}{\exp(\theta_B/T) - 1}, \tag{3.4}$$

where a_B represents the strength of the e^- (exciton)–phonon interaction and θ_B is the average phonon energy. In this model, the frequency of the oscillator considered here does not normally correspond to the frequencies of any of the prominent peaks visible in the phonon spectrum of the given material and is a 'ghost' frequency. Consequently this model gives no information about phonon dispersion and may not be applicable to those semiconductors which have a significant disperison between the optical and acoustic phonon frequencies.

Our data has also been analysed using Varshni model. In this model the temperature dependence of the band gap energy follows the equation:

$$E(T) = E''(0) - \frac{\alpha' T^2}{\beta + T}. \tag{3.5}$$

Here the parameter α' is the $T \to \infty$ limit of the gap entropy and β is expected to be comparable with the Debye temperature θ_D in a given material. In the high temperature limit, it predicts a linear variation. The equation predicts a linear fit in the high temperature regime and a quadratic dependence in the low temperature regime both due to cumulative effects of lattice expansion and the electron–phonon contribution. However, several experimental data show discrepancies with this model in the low temperature range and hence, it has to be treated with caution.

The results of fitting the PL peak energy as a function of temperature using eqs (3.2), (3.4) and (3.5) are shown in figure 2 for the composition $x = 0.045$. The various parameters used for the fittings are listed in table 1 for eq. (3.2) and table 2 for eqs (3.4) and (3.5). From figure 2, it is clear that both the Bose–Einstein and two-oscillator models give better fittings for the experimental data as compared to the Varshni formula, specifically in the low temperature range (below 100 K). The differences in the low temperature region for the three curves can be seen more clearly in the inset. It can be readily seen from tables 1 and 2 that the zero gap energy and coupling strength increase with increase in the Zn concentration. The values of the dispersion-related parameter Δ (ninth column of table 1) show that ZnCdSe falls in the region of moderate dispersion. This is due to a comparatively smaller contribution of the low-energy acoustic phonon as compared to that from the higher energy optical phonons $(W_1 = 0.14, W_2 = 0.86)$ and justifies the need to include phonon dispersion in the calculations. From the last two columns of table 1, we see that the effective position of the high energy oscillator $k\Theta_2$, is located in the vicinity of optical phonon branch indicating the dominance of the optical phonon contribution. The values of effective phonon temperature Θ (column 8 of table 1), obtained from the two-oscillator model is slightly higher than the average phonon temperature θ_B (column 3 of table 2) obtained using the Bose–Einstein model. The temperature variation of the fundamental band gap is due to thermal lattice expansion as well as electron–phonon interactions. According to the existing theories, this leads to a value θ_B which is significantly smaller than θ_{LO}. Our observation, as tabulated in tables 1 and 2 are in good agreement with this theoretical consideration. The fitting parameter β is also found to be of the order of the Debye temperature (last two columns of table 2). Comparing the values of parameter α (two-oscillator

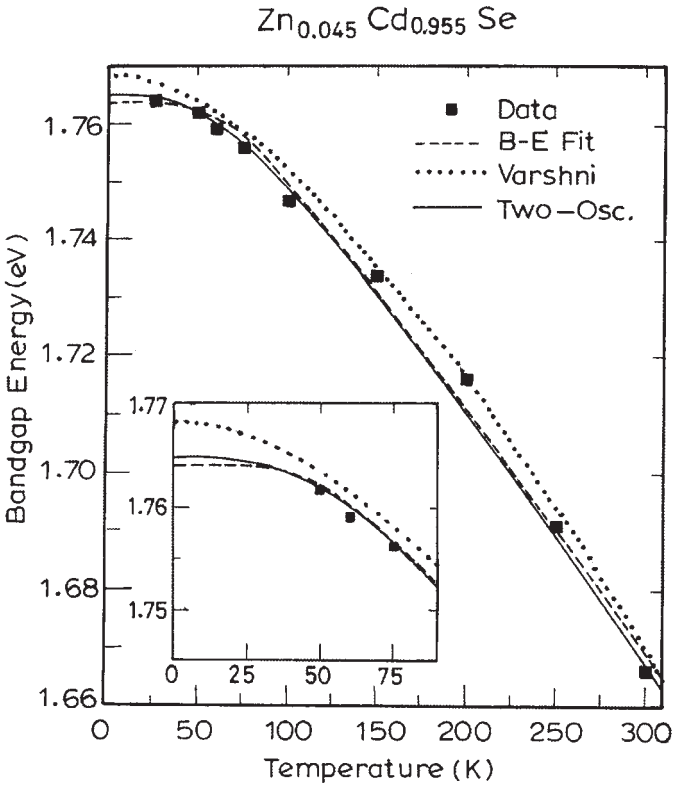

Figure 2. Temperature dependence of the band gap energy in $Zn_xCd_{1-x}Se$ ($x = 0.045$). Solid squares show the experimental points, dashed line (- - -) shows the fit to the Bose–Einstein model, dotted line ($\cdots$) shows the fit to the Varshni model and solid line (——) shows the fit to the two-oscillator model.

model), α' (Varshni model) and a_B (Bose–Einstein model) which shows the strength of electron–phonon coupling, it is seen that the values obtained by the Varshni model does not match with those obtained by the Bose–Einstein model and the two-oscillator model, which are in mutual agreement. Thus the Varshni model does not give a good fit in the low temperature region.

The single-oscillator Bose–Einstein model, which takes into account the average phonon energies, better describes the temperature dependence of the band gap. However, its shortcoming lies in the very-low-temperature region $0 < T < 50$ K [18] where it does not fit the experimentally observed low temperature regime of $E(T)$ in several semiconductors. Another disadvantage of this model is that it does not give any information on the degree of dispersion.

Figure 1 also clearly shows that the luminescence band due to direct band-to-band transitions shows a broadening with increasing temperatures. The width of the band is due to electron–phonon interactions as shown in the literature. The temperature dependence of the half-width at half-maximum (HWHM) of the PL peak for a zinc blende type semiconductor can be expressed as [21]

Table 1. Fitting parameters for the temperature dependence of band gap energy used in the two-oscillator model (eq. (3.2)).

	$E(0)$	Θ_1^* (K)	Θ_2 (K)	α (eV/K)			Θ		$k_B\Theta_2$	$\varepsilon_{LO(TO)}^{**}$
x	(eV)	(meV)	(meV)	$\times 10^{-4}$	W_1	W_2	(K)	Δ	(meV)	(meV)
0.025	1.745	50.88	212	4.0	0.14	0.86	189.3	0.298	18.2	26(20)
		4.39	18.28							
0.045	1.765	51.58	215	4.5	0.15	0.85	190.5	0.306	18.5	26(20)
		4.45	18.54							

*These parameters were used as fixed quantities; **taken from refs [18,21,22].

Table 2. Fitting parameters in temperature dependence of band gap energies used in the Bose–Einstein and Varshni models (eqs (3.4) and (3.5)).

	Bose–Einstein model			Varshni model			
x	$E'(0)$ (eV)	a_B (meV)	θ_B (K)	$E''(0)$ (eV)	α' (eV/K)$\times 10^{-4}$	β (K)	θ_D^* (K)
0.025	1.742	32.6	180	1.746	6.45	289	301.0
0.045	1.764	44.7	185	1.768	6.42	284	301.8

*Taken from refs [18,21,22].

$$\Gamma_0(T) = \Gamma_0(0) + \gamma_{AC}T + \frac{\Gamma_{LO}}{\exp(\theta_{LO}/T) - 1}, \tag{3.6}$$

where the first term of eq. (3.6) is due to intrinsic effects, while the second term corresponds to lifetime broadening due to electron (exciton)–acoustical phonon interaction and the third term is caused by the electron (exciton)–LO phonon interaction. The quantity Γ_{LO} represents the strength of the electron (exciton)–LO phonon coupling while θ_{LO} is the LO phonon temperature.

The measured HWHM were fitted using eq. (3.6). The parameters γ_{AC} is the acoustical phonon coupling constant and θ_{LO} was fixed (calculated using linear interpolation between ZnSe and CdSe) in order to obtain two significant quantities $\Gamma_0(0)$ and Γ_{LO} by means of a least square fit. The results are shown in figure 3. The values obtained along with the other parameters are listed in table 3. Figure 3 shows that eq. (3.6) fits the observed peak widths fairly well for $x = 0.045$. Our values for Γ_{LO} and θ_{LO} are consistent with the values reported in the literature [16]. The smaller values of the acoustical phonon coupling constant, γ_{AC} in comparison with the acoustical-LO phonon coupling, Γ_{LO} reveals the dominance of LO phonon interaction in the decay process.

The room temperature PL emission (see figure 1) exhibits high energy tails which extend well beyond the band gap energy. This high energy contribution is due to electron–hole recombination. With increasing temperature, states deeper in the conduction band fills up, permitting emission at higher energies and thus resulting in the high energy tail. The band-to-band contribution to the PL intensity can be expressed as [23].

Table 3. Fitting parameters for the peak width (HWHM) (eq. (3.6)).

x	$\Gamma_0(0)$ (meV)	$\Gamma_{\rm LO}$ (meV)	$\theta^*_{\rm LO}$ (K)	$\gamma^*_{\rm AC}$ (μeV/K)
0.025	8.0	24.7	301	0.03
0.045	5.0	24.8	302	0.04

*These parameters were used as fixed quantities.

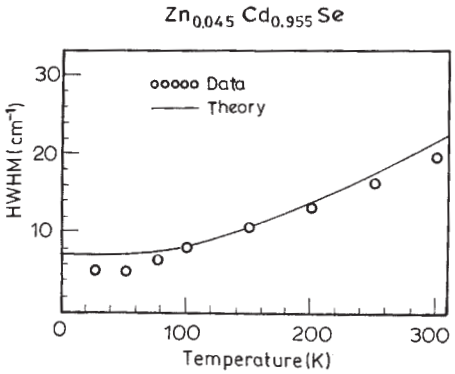

Figure 3. Temperature dependence of the broadening parameter (HWHM) of the fundamental gap in PL spectra of $Zn_xCd_{1-x}Se$ ($x = 0.045$).

$$I_{\rm PL}(h\nu) = A(h\nu - E_g)^{1/2}\left[\frac{1}{[\exp(h\nu - E_g)/kT]}\right] \quad \text{for } h\nu > E_g. \tag{3.7}$$

Thus e^-–h recombination will result in an emission peak $1/2kT$ above the band gap. In the ideal model, the PL intensity should rapidly drop to zero on the low energy side. However, as observed in figure 1, there is an emission below the band gap. This arises from localized band tail states, which are either due to disorder or localized defects or localized bound excitons. Hence, an exponential decaying line shape is used to describe its density of states [24].

At lower temperature the tail at high energy side vanishes and one observes more symmetry in the band. For low temperatures, an asymmetry is observed in the low energy side. The details of this analysis will be published elsewhere.

4. Conclusions

We have reported a study of the temperature dependence of the near-band-edge photoluminescent band gap in MOCVD-grown $Zn_xCd_{1-x}Se$ thin films grown on GaAs (100) substrate using PL. The temperature variation was investigated within the purview of the Varshnil, the Bose–Einstein and the two-oscillator models. At higher temperatures (>200 K), all the three models show an almost linear decrease of the PL peak energy with temperature. In the low temperature region, Varshni formula fails completely to explain

the data. Both the Bose–Einstein and two-oscillator models fit the experimental data reasonably well in the temperature region below 100 K. The value of phonon dispersion for the ternary $Zn_xCd_{1-x}Se$ alloy ($x = 0.025, 0.045$) lies in the moderate phonon dispersion range $(0 \leq \Delta < 0.55)$. Such a study is useful for obtaining band gap parameters, which are of significant importance in designing opto-electronic devices.

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