CONTACTLESS ELECTROREFLECTANCE STUDY OF TEMPERATURE DEPENDENCE OF FUNDAMENTAL BAND GAP OF ZnSe*

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We report a systematic study of the temperature variation of the energy $[E_0(T)]$ and broadening parameter $[\Gamma_0(T)]$ of the fundamental band gap of ZnSe in the range 27 K $< T <$ 370 K using contactless electroreflectance. The obtained values of $E_0(T)$ and $\Gamma_0(T)$ have been fit to various semi-empirical expressions to obtain information about the exciton–phonon coupling in this system. The experimentally determined $E_0(T)$ also is of significance for technological applications since it can be used to determine the operating temperature of ZnSe-based devices such as quantum well lasers.

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The semiconductor ZnSe is an important material from both fundamental and applied perspectives. ZnSe-based semiconductors are becoming increasingly attractive due to their potential application in the fabrication of visible light emitters. The only blue semiconductor lasers reported to date are based on these materials [1]. In spite of this fact very little work has been done on the temperature dependence of the fundamental band gap, E_0 [2]. In this paper we report a study of the temperature dependence of the energy $E_0(T)$ and broadening parameter, $\Gamma_0(T)$, of a ZnSe/GaAs epilayer in the range 27 K$< T <$ 370 K using contactless electroreflectance (CER) [3]. We have fit the experimentally determined values of $E_0(T)$ to both semi-empirical Bose–Einstein type [4] and Varshni [5]

expressions. In order to obtain parameters directly related to exciton–phonon coupling effects we have eliminated the temperature shift of E_0 due to the thermal expansion (ΔE_{th}) [6]. The broadening parameter, $\Gamma_0(T)$, has been fitted by a Bose–Einstein-type expression containing an exciton–optical phonon coupling constant [3, 6].

A ZnSe layer of thickness 1.0 μm was grown by molecular beam epitaxy (MBE) on GaAs (100) substrate. For this thickness the ZnSe is not pseudomorphic. Desorption of the native oxide on the substrate was carried out under an As flux. Growth was performed using elemental solid sources, under excess group VI flux, at a temperature of 270°C.

The CER apparatus [3] and the heater arrangement [6] were similar to those already described in the literature. The ac modulating voltage (1 kV peak-to-peak) was applied in a capacitor-like arrangement at frequency 200 Hz. The temperature was measured by a thermocouple in contact with the sample surface.
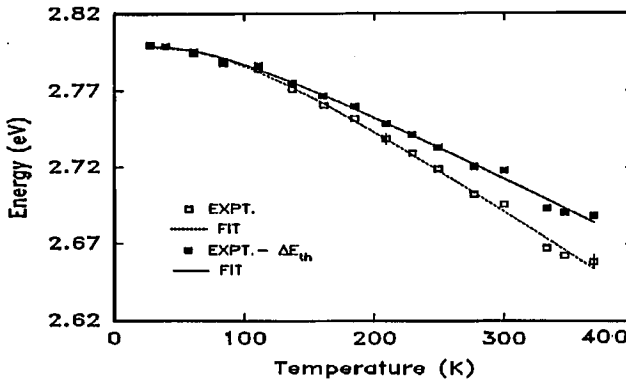

Fig. 1. Shown by the open and solid squares are the values of $E_0(T)$ and $E_0(T) - \Delta E_{th}(T)$, respectively. The dashed and solid lines are fits to Eqs. (1a) and (3a), respectively. Representative error bars are shown.

Plotted by the open squares in Fig. 1 is the temperature variations of $E_0(T)$. These energy positions were obtained from the CER spectra by the Aspnes three-point method for an excitonic transition [7]. Representative error bars are shown. The dotted line is a least squares fit to a Bose–Einstein type expression involving exciton coupling to an average phonon (optical and acoustical) [4]:

$$E_0(T) = E_0(0) - A_{ap}/[\exp(\theta_{ap}/T) - 1], \tag{1a}$$

where $E_0(0)$ is the gap at $T = 0$, while A_{ap} and θ_{ap} are average phonon coupling constant and phonon temperature, respectively. The data has also been fit to the semi-empirical Varshni expression which has been used extensively in the past [5]:

$$E_0(T) = E_0(0) - \alpha T^2/(\beta + T) \tag{1b}$$

where α and β are the Varshni coefficients.

The obtained values of the relevant parameters for fits to both equations are listed in Table.

TABLE

Values of the various parameters which describe
$E_0(T)$ and $\Gamma_0(T)$ for ZnSe and In$_{0.15}$Ga$_{0.85}$As [6].

Material	ZnSe	In$_{0.15}$Ga$_{0.85}$As
$E_0(0)$ [eV]	2.800 ± 0.005	1.285 ± 0.005
A'_{ap} [meV]	94 ± 6	78 ± 16
θ'_{ap} [K]	220 ± 10	300 ± 50
A_{ap} [meV]	146 ± 7	106 ± 20
θ_{ap} [K]	259 ± 10	238 ± 50
α' [10^{-4} eV/K]	5.0 ± 0.4	2.6 ± 0.4
β' [K]	206 ± 35	150 ± 40
α [10^{-4} eV/K]	7.3 ± 0.4	5.0 ± 0.4
β [K]	295 ± 35	231 ± 40
$\Gamma_0(0)$ [meV]	6.1 ± 2.5	10.5 ± 0.5
$\Gamma_{\mathrm{LO}}(0)$ [meV]	21 ± 8 $(30)^a$	23 ± 6
θ_{LO} [K]	360^b	380 ± 120

^{a}Ref. [9]. ^{b}Fixed and taken from Ref. [2].

The temperature shift of $E_0(T)$ contains contributions from both thermal expansion and exciton–phonon coupling effects. Therefore, in order to obtain parameters directly related to the latter influence, it is necessary to eliminate the influence of the former. The energy shift (ΔE_{th}) due to the thermal expansion term is given by [6]:

$$\Delta E_{\mathrm{th}}(T) = 3a \int_0^T \alpha_{\mathrm{th}} dT, \qquad (2)$$

where a is the hydrostatic pressure coefficient [2] and $\alpha_{\mathrm{th}}(T)$ is the thermal expansion coefficient [2].

Equations (1a) and (1b) can be rewritten as

$$E_0(T) - \Delta E_{\mathrm{th}}(T) = E_0(0) - A'_{\mathrm{ap}}/[\exp(\theta'_{\mathrm{ap}}/T) - 1], \qquad (3a)$$

$$E_0(T) - \Delta E_{\mathrm{th}}(T) = E_0(0) - \alpha'T^2/(\beta' + T). \qquad (3b)$$

Plotted by the solid squares in Fig. 1 is the data after subtraction of ΔE_{th} from the experimental values of $E_0(T)$. The solid line is a least squares fit to Eq. (3a). A fit to Eq. (3b) also has been performed. The obtained values of the various parameters are presented in Table.

For comparison purposes we have also included in Table previously published data from a systematic study of a representative III–V material, In$_{0.15}$Ga$_{0.85}$As [6].

Displayed by the open circles in Fig. 2 is the experimentally determined temperature dependence of the linewidth $\Gamma_0(T)$ [half width at half maximum (HWHM)]. Representative error bars are shown. The behaviour of $\Gamma_0(T)$ can be expressed as [4]:

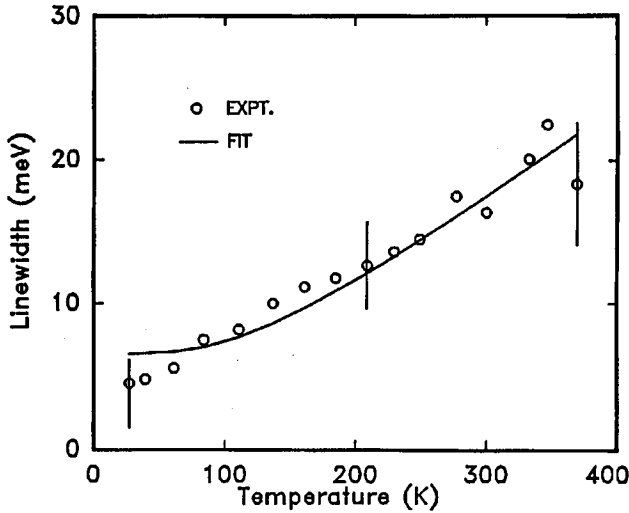$$\Gamma_0(T) = \Gamma_0(0) + \gamma T + \Gamma_{\mathrm{LO}}/[\exp(\theta_{\mathrm{LO}}/T) - 1], \qquad (4)$$

Fig. 2. The open circles are the temperature variation of the linewidth (HWHM) $\Gamma_0(T)$. The solid line is a least squares fit to Eq. (4). Representative error bars are shown.

where $\Gamma_0(0)$ is the intrinsic linewidth at $T = 0$, γ and Γ_{LO} are the acoustical and exciton–longitudinal optical (LO) phonon coupling constants, respectively, and θ_{LO} is the LO phonon temperature. Plotted by the solid line in Fig. 2 is a least squares fit to Eq. (4) with $\gamma = 7$ μV/K [8] and $\theta_{LO} = 360$ K [2]. The obtained values of $\Gamma_0(0)$ and Γ_{LO} are listed in Table.

Our experiment is the first systematic evaluation of $E_0(T)$ and $\Gamma_0(T)$ for the direct gap of ZnSe. The value of $E_0(0) = 2.800$ eV for the excitonic transition is in good agreement with other measurements [2]. It has been suggested [6] that $\beta' = (3/8)\theta_D$, where θ_D is the Debye temperature (339 K) [2]. We find reasonable agreement with this relationship. The behavior of $E_0(T)$ is of significance for comparison with theoretical calculations (corrected for ΔE_{th}) as well as for the evaluation of the operating temperature of ZnSe-based devices such as quantum well lasers. Our value of the coupling constant Γ_{LO} is in reasonable agreement with a number (30 meV in terms of HWHM) listed by Pelekanos et al. [9] who presented no data to support their result. Based on a theoretical calculation Rudin et al. [10] have reported $\Gamma_{LO}(ZnSe)/\Gamma_{LO}(GaAs) = 1.67$. Within experimental error our results are not inconsistent with this ratio.

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