

Photoacoustic Spectroscopic Study of Optical Band Gap of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ Semiconductors¹

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Using the photoacoustic spectroscopic (PAS) technique for the first time, the composition-dependent optical absorption coefficient and band gap of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ semiconductors (with $x=0.0-0.25$) have been measured at room temperature. The band gap E_0 estimated from the PAS spectra varies nonlinearly with Be concentration. The exchange interaction of electrons in conduction and valence bands, effects of polytypes, microstructures, and the mixed crystallization (zinc-blend and wurtzite structures) effect are considered for the analysis of the data. The observed exponential edge (Urbach's edge) can be considered as an internal Franz-Keldish effect arising from the charged impurity generated and "frozen-in" optical phonon-generated fields. The phonon-assisted indirect transition at the band tail regions for some samples is also observed in the present studies.

KEY WORDS: indirect transition; photoacoustic spectroscopy; semiconductor; Zn-Be-Se.

1. INTRODUCTION

During the past decade a great deal of attention has been devoted to the study of semiconducting alloys of technological importance for several reasons. Semiconducting and structural properties, such as energy gap, the lattice parameter, etc. of these alloys can be varied in a controlled fashion by changing appropriately the mole fraction of the magnetic ions in the alloys as in non-magnetic semiconductors, e.g., Zn-Se-Te, etc. This

¹Paper presented at the Fifteenth Symposium on Thermophysical Properties, June 22–27, 2003, Boulder, Colorado, U.S.A.

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aspect is particularly important in the use of monolithic semiconductor heterostructures where lattice matching is of obvious importance. Secondly, these materials are also of interest for their magnetic properties, e.g., spin-glass transition [1], antiferromagnetic cluster formation [2], magnon excitations [3] and other magnetic effects of current interest. Thirdly, the presence of magnetic ions in the lattice leads to spin–spin exchange interactions between the localized magnetic moments and the band electrons [4]. This interaction affects the energy band and impurity level parameters of these materials (e.g., by exchanging electronic g -factors), resulting in a new physical effect. Such novel and potentially important phenomena as the magnetic field-induced overlap between valence and conduction bands occurring in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ [5], extremely large Faraday rotation in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ [6], giant magnetoresistance associated with hopping conduction in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ [7], and the magnetic polaron observed in $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ [8] are all consequences of the spin–spin exchange interaction.

To the best of our knowledge, no photoacoustic (PAS) investigations of the energy band structure, optical absorption coefficient, etc. of many technologically important semiconducting materials have been made. These materials are very important for many of their applications in optical and electronic devices [9]. The need to fine tune the band gaps of semiconducting alloys in various device applications like light emitting diodes, low loss optical fibers, heterojunction lasers, infrared detectors, solar cells, etc., has provoked interest in understanding the band gap variation in terms of properties of the constituent composition in the semiconducting alloy. Here we have studied the optical response of a typical semiconducting alloy viz., $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ by photoacoustic spectroscopy, which is a highly sophisticated and very sensitive technique for the nondestructive characterization of semiconductors and other materials [10]. The nonradiative transition processes which are associated with the band structure, defect related energy loss mechanism, etc. can be obtained directly and very accurately from the analysis of PAS spectra [11–13]. In this study, the main objective is to find out the effect of Be substitution on the optical absorption and band gap [14] at room temperature.

2. EXPERIMENTAL

For the preparation of the samples $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ ($x = 0.0, 0.086, 0.17, 0.26$), ZnSe and metallic Be (each of purity 99.99%) are used as starting materials. The desired amounts of the mixture are ground to powder and pressed into thin pellets. These pellets are sealed in an evacuated quartz tube and placed inside a furnace at about 1400–1500 °C for several

days. The ampoules were then furnace cooled at room temperature. The samples thus prepared were crystalline in nature, and their composition and structure were tested by X-ray powder diffraction (Phillips: Model PW 1710) studies with $CuK\alpha$. The energy dispersive X-ray (EDX) experiment (Kevex: Model 3600-0388, California) confirms the ratio of the constituent atoms within $\pm 2\%$.

The single beam photoacoustic spectrometer used in the present investigation consists of a PA cell containing the sensitive microphone, a 1000 W Xe lamp with a power supply (Muller, type SVX 1000, Germany), a monochromator (Oriel 77250), and a mechanical chopper (SR540) discussed elsewhere [13,15]. The PA signal is detected by a sensitive microphone (Bruel and Kjaer 4147) and processed by using a preamplifier and a lock-in amplifier (SR530). To minimize light scattering, very thin (~ 3 – 4 mm dia and ~ 0.3 mm thick) samples were used for the PAS studies. All spectra were recorded at room temperature using a chopping frequency of 120 Hz. The optical band gap is determined by measuring the variation of the normalized PA signal intensity with the wavelength of the incident light. The PA spectrum obtained from highly absorbing carbon black powder was used to normalize the spectrum of the samples.

3. RESULTS AND DISCUSSION

The normalized PA spectra of $Zn_{1-x}Be_xSe$ ($0 \leq x \leq 0.3$) as a function of incident wavelength are shown in Fig. 1. The optical absorption coefficient α for thermally thick samples is calculated from the relation [16],

$$\alpha = (1/\mu_S)[q^2 + q(2 - q^2)^{1/2}]/(1 - q^2) \quad (1)$$

where q is the normalized PA amplitude and μ_S is the thermal diffusion length ($\sim 6.52 \times 10^{-3}$ cm). The variation of the absorption coefficient of the samples with the incident photon energy is shown in Fig. 2. The absorption spectrum of the Zn–Be–Se system consists of three distinct regions, viz., the high absorption region [$h\nu > E_o$ ($\alpha > 10^3 \text{ cm}^{-1}$)], the exponential region, and the weak absorption tail. Here h is Planck's constant, ν is the frequency of the incident radiation, and E_o is the band gap. The absorption spectra show that the transition is allowed and direct in nature in a quantum mechanical sense. In the high absorption region, the absorption coefficient α for the direct transition is governed by [17,18]

$$\alpha h\nu = A(h\nu - E_o)^{1/2} \quad (2)$$

where A is a constant. The direct transition in this system is confirmed from the plot of $(\alpha h\nu)^2$ versus $h\nu$ for various compositions as shown in

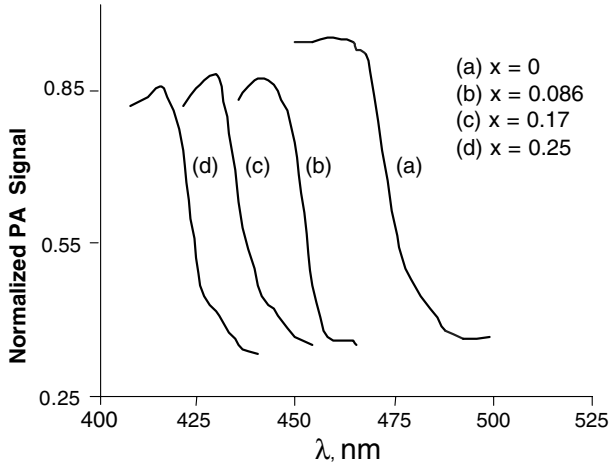


Fig. 1. Normalized photoacoustic (PA) spectra of four typical $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ systems with (a) $x = 0.0$, (b) $x = 0.086$, (c) $x = 0.17$, and (d) $x = 0.26$ as a function of wavelength of incident light.

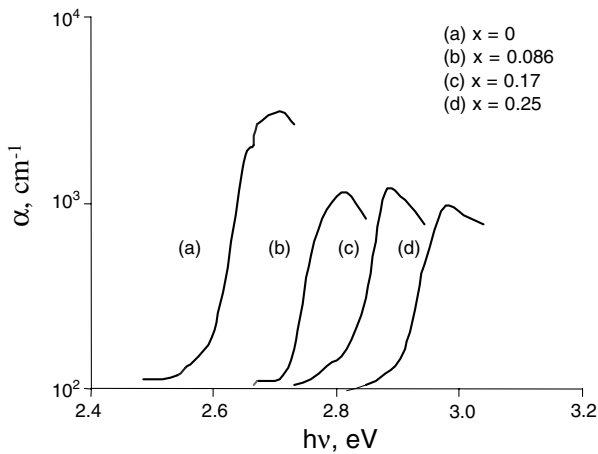


Fig. 2. Variation of absorption coefficient of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ as a function of incident photon energy with (a) $x = 0.0$, (b) $x = 0.086$, (c) $x = 0.17$, and (d) $x = 0.26$.

Fig. 3a–d. The values of the corresponding optical band gap (E_o) are estimated (where the dotted lines meet the abscissa). It is found that the variation of E_o with composition (x) is nonlinear in nature (Fig. 4) and obeys the relation $E_o(x) = 3.314x^2 + 0.67x + 2.618$ (Fig. 4). The variation is not very sharp, and this might be due to the fact that mixed $\text{Zn}_{1-x}\text{Be}_x\text{Se}$

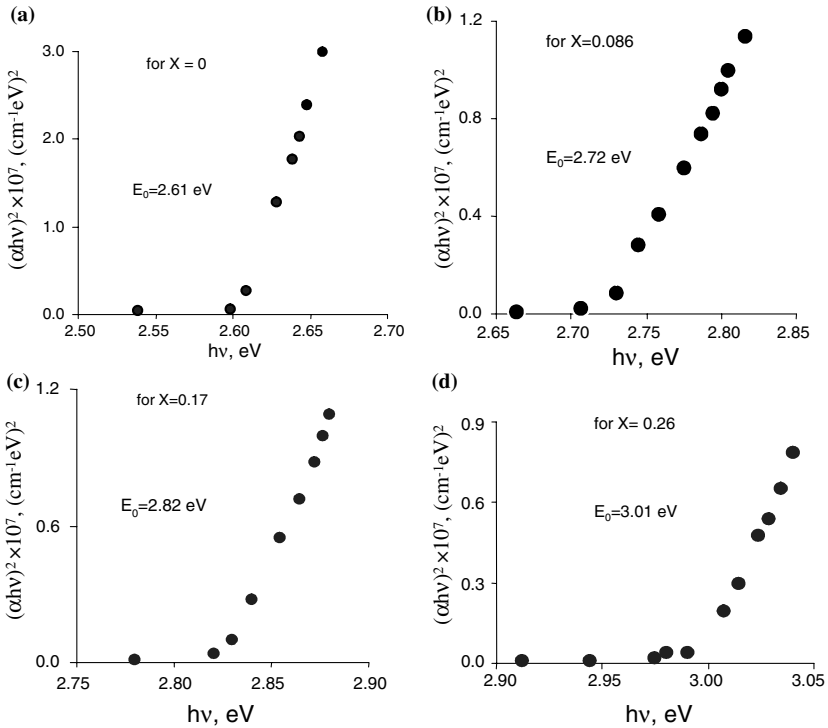


Fig. 3. (a) Plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0.0$; (b) plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0.086$; (c) plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0.17$; and (d) plot of $(\alpha h\nu)^2$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0.26$.

crystals crystallize [18] in a zinc-blend structure for $x \leq 0.19$, and in a mixture of zinc-blend and wurtzite structure for $0.19 \leq x \leq 0.3$. From reflectivity experiments [19], the band gaps of $Zn_{1-x}Be_xSe$ have been measured as 2.86 and 3.85 eV for $x = 0.03$ and 0.45, respectively. This result is nearly comparable with that in our experiment. a variation of band gap with alloy composition, with II–VI materials has also been reported in the literature [20]. The variation is also consistent with our result. From the variation of the absorption coefficient α with incident photon energy $h\nu$, the exponential edge (Urbach’s edge) is also observed. The absorption coefficient in this region can be written as [17]

$$\alpha = \alpha_0 \exp[\gamma\{h\eta - E_0(T)\}/(k_\beta T^*)] \quad \text{for } h\nu < E_0(T) \quad (3)$$

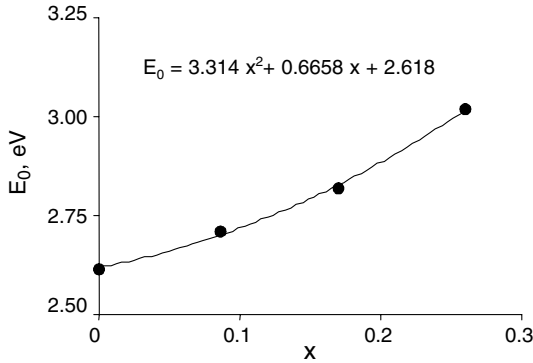


Fig. 4. Variation of energy gap (estimated from Fig. 3a-d) as a function of concentration (x).

where α_0 and γ (order of magnitude is unity) are constants, $E_0(T)$ is the temperature dependent band gap, and T^* is the effective temperature [21] which is almost constant below a critical value T_0 and is proportional to T in the higher temperature region (above T_0). From Eq. (3) one also finds Urbach's rule, viz., $d(\ln \alpha)/d(h\nu) = \gamma/(k_B T^*)$, which suggests that the sharp absorption edge becomes broader as the temperature rises above T_0 . This region is strongly related to the structural properties of the sample and can be correlated with the impurity concentration of the sample [17]. Recently it has been shown [22–24] that $\gamma/(k_B T^*)$ is independent of temperature for polycrystalline materials.

The perturbation of the band edge may arise from intrinsic charged impurities as well as from the frozen-in optical phonon [25]. Such a perturbation may produce a local electric field [17,25] which may be very large, $\sim 10^5 \text{ V cm}^{-1}$. The relation between the local internal field and the Franz–Keldysh effect was shown by Redfield [26] and Dow and Redfield [27,28]. They proposed that the fluctuation of the internal field is responsible for the exponential edge as observed in the present studies.

The tail in the absorption spectrum close to the band edge investigated from the PAS experiment (Fig. 1) is associated with various factors such as a phonon-assisted transition, purity and thermal history [29], and also on the thickness of the sample [26]. In this region ($h\nu < E_0$), the dependence of α on $h\nu$ obeys the following relation [25]:

$$\alpha = B(h\nu - E_{oi} + E_p)^2 / \exp(E_p/k_B T - 1), \quad (4)$$

where B is a constant nearly independent of photon energy, T is the absolute temperature, and k_B is the Boltzmann constant, E_p and E_{oi} are,

respectively, the phonon energy and optical energy gap for the indirect transition (E_p obtained from the extrapolation of the linear portion of $\alpha^{1/2}$ versus $h\nu$ plot to the energy axis where $\alpha=0$) (as shown in Fig. 5a,b). The value of the phonon energy E_p is obtained from the above relation (Eq. (4)) following $E_p=(E_{oi}-h\nu)$ at $a=0$. For ZnSe, the phonon energies (E_p) are 75, 130, and 180 meV, which correspond to the optical phonon wave numbers 601, 1040, and 1440 cm^{-1} . For $Zn_{0.83}Be_{0.17}Se$ these phonon wave numbers are 201, 482, and 803 cm^{-1} . For other samples of our present investigation, no phonon-assisted transition was observed.

4. Conclusion

From the PAS studies of the semiconducting alloys $Zn_{1-x}Be_xSe$, a direct band-to-band transition is observed for absorption coefficient

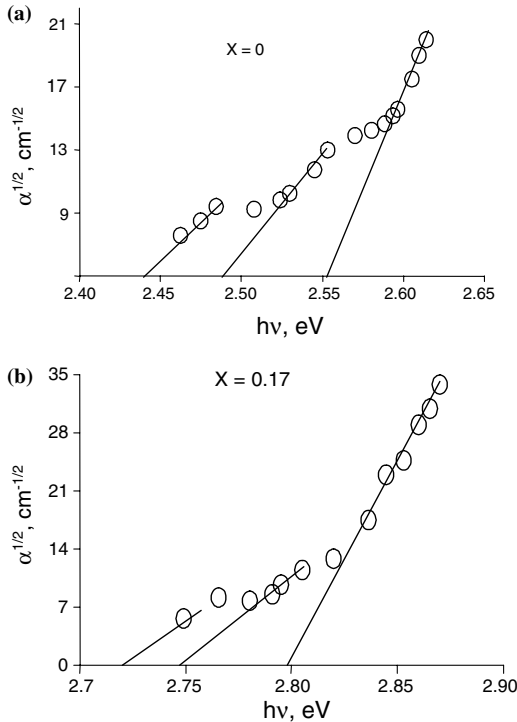


Fig. 5. (a) Plot of $\alpha^{1/2}$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0$ and (b) plot of $\alpha^{1/2}$ versus $h\nu$ for $Zn_{1-x}Be_xSe$ sample with $x = 0.17$.

values greater than 10^3 cm^{-1} . The feature of the PAS data enabled us to determine values of the fundamental band gap as a function of Be mole fraction x . The dependence of E_0 on x is nonlinear which might be due to the exchange interaction of electrons in conduction and valence bands with the s-electrons of Be ion interactions, the effect of polytypes, microstructures and mixed crystallization (zinc-blend and wurtzite structures). These effects are yet to be clearly explained. PAS is a direct and nondestructive method of determination of the band gap and optical absorption of semiconductors in the form of bulk, film, or single crystal.

ACKNOWLEDGMENT

This work was supported by the Department of Science and Technology, India.

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