Observation of free-to-acceptor-type photoluminescence in chlorine-doped Zn(Be)Se

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Abstract

We present photoluminescence (PL) studies of Cl-doped $Zn_{1-x}Be_xSe$ ($x = 0$–0.029) alloys performed in wide ranges of temperature (10–296 K) and of excitation intensities. We show that the high-temperature PL is characterized by a free-to-acceptor-type transition, involving shallow state of the localized holes. We shall show that similar transitions are also present in comparable undoped samples, but the PL intensity is substantially lower. Finally, we show that the ionization energy of the relevant acceptor-like species increases with Be concentration, suggesting an effective mass type defect.

1. Introduction

ZnSe has been of great interest for fabricating light emitting devices in the blue–green–yellow spectral regions. These are of interest for various devices; in particular, the use of green solid-state lasers with plastic optical fibers is emerging as one of the most important applications. However, such devices still suffer from limited lifetime; one of the reasons is the relative weakness of the ZnSe lattice against defect formation. The use of the

$Zn_{1-x}Be_xSe$ ternary alloy system has been suggested [1] for improving the lattice hardness and, as a result, the device lifetime. Therefore, recently many investigations were performed on this alloy material (e.g. [2,3]).

For fabrication of such light emitting devices, both n- and p-type ZnBeSe are required; however, few studies are available on n-type ZnBeSe. In this paper, we discuss photoluminescence (PL) results for our n-type $Zn_{1-x}Be_xSe$: Cl and, for comparison, also PL from undoped $Zn_{1-x}Be_xSe$ and ZnSe. We show that at low temperatures the dominant PL is, as expected, due to neutral donor bound excitons, but at high temperatures the dominant PL is due to free-to-bound (FB)

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radiative recombination, which, in our case, is believed to be due to the recombination of free electrons and holes localized at acceptors. It is further important that the activation energy of such acceptors is lower than that of standard acceptors in these materials. We shall also discuss the change of impurity activation energies as a function of Be composition.

2. Experimental

All our samples (thickness of about 0.8–1.0 μm) were grown by molecular beam epitaxy (MBE) on (0 0 1) GaAs substrates. Most of the samples had ZnBeSe buffer layers grown before the film deposition. All the Cl-doped samples have free electron concentration in the range from 10^{16} cm^{-3} to mid-10^{17} cm^{-3} as measured by Hall effect at room temperature (RT). PL measurements were performed at temperatures between 10 and 296 K, using a closed cycle refrigerator system. Samples were excited by the 325 nm emission from a He–Cd laser with 10 mW maximum power (the power intensity is estimated to be 28 W/cm^2). The PL was recorded with a $\frac{3}{4}$ m monochromator, a thermoelectrically cooled GaAs photomultiplier tube, and a photon counter.

3. Results and discussion

Results of low-temperature ($T = 10$ K) PL measurements for our Cl-doped $Zn_{1-x}Be_xSe$ samples with x between 0 and 2.9 are shown in Fig. 1. The spectra are all dominated by a strong, fairly sharp, peak in the band edge region. Specifically, for the sample with $x = 0$ (ZnSe:Cl), the peak is at 2.797 eV with a full-width at half-maxima (FWHM) of about 4.9 meV. This dominant PL has been attributed to the recombination of neutral donor (Cl) bound excitons (usually denoted as I_2 line) (e.g. Ref. [4]). We believe that is also the case for the present ZnBeSe:Cl since the PL peak positions can be easily corrected with the change of the band gap energy due to the addition of Be.
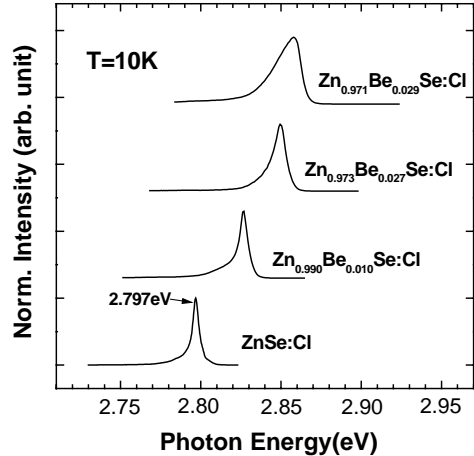

Fig. 1. PL spectra of Cl-doped $Zn_{1-x}Be_xSe$ with $x = 0$ to 2.9%.

Next we would like to discuss the line shape of this dominant I_2 line, which exhibits a long low-energy tail. This type of asymmetric broadening has been previously observed in ZnSe:Cl (e.g. Ref. [5]) and was ascribed to the Stark effect due to the interaction between charged impurities and bound excitons [6]. From Fig. 1, however, it also is obvious that such broadening increases with increasing Be concentration; thus, we suggest that in ZnBeSe:Cl, in addition to the Stark effect, the alloy composition fluctuations (e.g. Ref. [7]) also contribute to the broadening.

Furthermore, in addition to the dominant PL, we can also observe some other lines, two on the high-energy side of the dominant line for the ZnSe:Cl sample. Specifically, from the inset of Fig. 2(a), one can see that they are at about 2.800 and 2.803 eV; we attribute these to the light and heavy holes free exciton transitions, respectively [8].

Additionally, there is a peak,[1] of relatively low intensity, at the low-energy side of the dominant peak in all the samples, which is plotted in Figs. 2(a) and (b) for ZnSe:Cl and $Zn_{0.973}Be_{0.027}Se$: Cl, respectively. This small peak

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[1] It can be noted that in the ZnBeSe sample, where this peak is of relatively higher intensity than in the ZnSe sample, there is a second, smaller, peak which is presumably a phonon replica, being about 32 meV lower in energy.
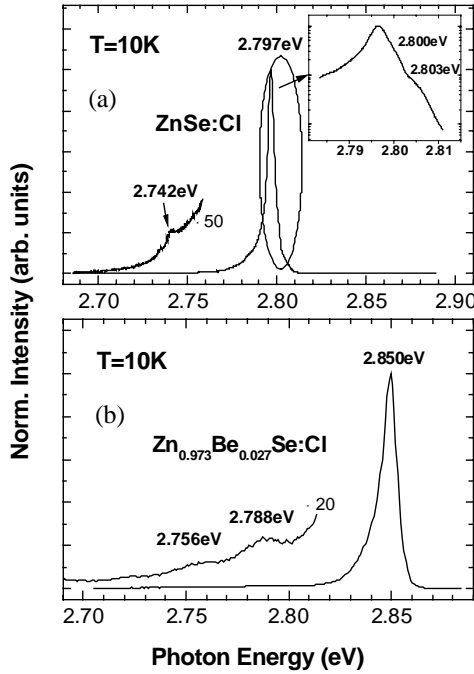
Fig. 2. PL spectra of ZnSe:Cl (a) and $Zn_{0.973}Be_{0.027}Se$:Cl (b) at $T = 10$ K. In the inset of (a), the spectrum is magnified to show the fine structure.

shifts weakly to the red with decreasing excitation intensity, indicative of a donor–acceptor-pair (DAP)-like behavior. We note that for ZnSe:Cl, the peak position is at 2.742 eV at high excitation intensity, and it coincides with the DAP emission observed earlier by Sakakibara et al. [5]. In view of this, we believe that a DAP transition is indeed the most plausible explanation. Using [9],

$$hv = E_G - (E_D + E_A) + e^2/\varepsilon R, \qquad (1)$$

where hv is the emitted photon energy, E_G is the band gap energy, $e^2/\varepsilon R$ represents the Coloumb energy between charged donors and acceptors (e is the electronic charge, ε is the dielectric constant of the material, and R is the average distance between a donor and an acceptor), and E_D (E_A) is the donor (acceptor) activation energy, and assuming Cl as the donor ($E_D = 27$ meV [10]), we can calculate, for any $e^2/\varepsilon R$, the activation energy (E_A) of the acceptor. Assuming that there is no preferential paring see e.g. Ref. [34], and assuming
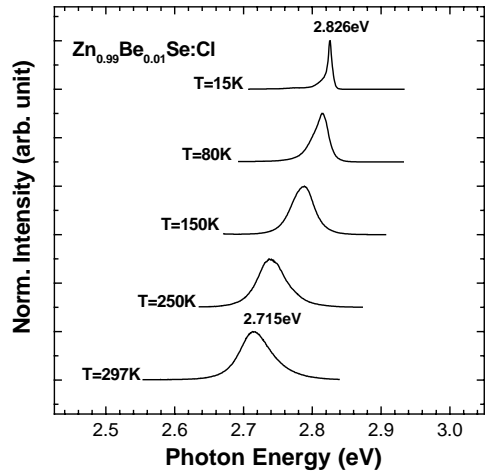

Fig. 3. Temperature evolution of PL spectra of $Zn_{0.99}Be_{0.01}Se$:Cl.

a Coloumb energy of 10 ± 5 meV,[2] the result is E_A of 63 ± 5 meV.

We next consider evolution of the PL spectra with temperature. We use the PL spectra from the $Zn_{0.99}Be_{0.01}Se$: Cl as an example (Fig. 3). It is clear that as the temperature increases, the dominant peak becomes broader and, at first, more symmetric until at $T \approx 180$ K it becomes asymmetric again, with a tail on the high-energy side of the spectrum. At room temperatures ($T \geqslant 294$ K), the peak still maintains a relatively high intensity with a FWHM of about 54 meV. We plotted the integrated PL intensity of the dominant peak as a function of excitation intensity at different temperatures in Fig. 4; one can clearly observe a single slope close to unity at $T = 10$ K, which is expected for a single excitonic transition [13], while at an intermediate temperature

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[2] It is well known that the Coulomb shift depends on impurity concentration, impurity Bohr radii, and excitation intensity. However, as shown for instance by G. F. Neumark et al. [11], the primary dependence is on the Bohr radius of the shallower impurity (a_D) and on the excitation intensity; thus, at low-intensity, the shift is proportional to $N_{maj}^{1/3}$ (Eq. (9)) and to a_D at high intensity (Eq. (10)). We estimate from our laser power (10 mW) and from the optical losses in our systems that we are in the low-intensity region. We also estimate a Bohr radius of about 30 Å for Cl, from scaled effective mass theory (as presented for instance in Ref. [12]). This leads to our estimated shift of 10 ± 5 meV.
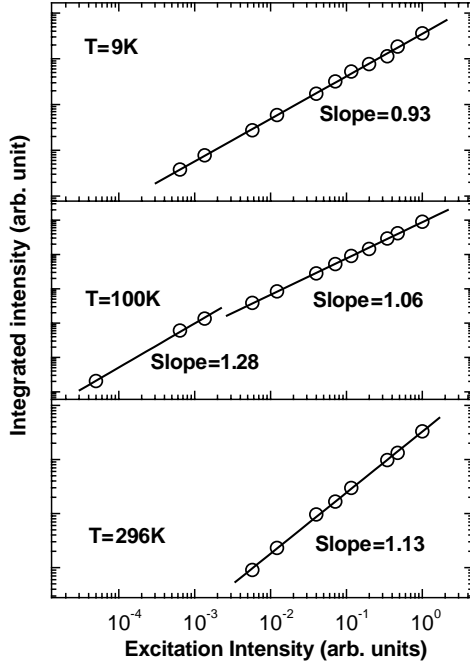
Fig. 4. Integrated PL intensity as a function laser excitation intensity for $Zn_{0.99}Be_{0.01}Se:Cl$ at $T = 9$ K, 100 K and 296 K.

($T \sim 100$ K), there are two distinct slopes, indicating two types of transitions [14]. Therefore, we suggest that, in addition to the I_2 line, there is another transition beginning to emerge at some intermediate temperature, which then becomes dominant at $T > 180$ K. It is also interesting that the peak energy of the observed PL closely follows the band gap with the temperature, so that we cannot resolve these two transitions; moreover, the broadening of the PL spectra as the temperature increases also contributes to our difficulties in resolving these two peaks. Finally, at RT the plot shows a single slope again, indicating only one dominant transition. (Note that due to the power limit of our laser, we could only measure the PL at RT with excitation intensity varying over less than three orders of magnitude.) This peak shows no energy shift with changes in excitation intensity, which excludes a donor–acceptor pair origin. We note that since the energy of the exciton bound to Cl in ZnSe is relatively small (~ 4 meV) [11], the Cl-bound excitonic transition would not be expected to survive at such high temperatures.

Furthermore, a transition due to an exciton bound to some accidental center deeper than Cl also seems unlikely based on the line shape and FWHM of the spectra.

Having excluded bound excitonic PL, we further exclude free excitonic recombination since free excitons are usually observed only in high-purity semiconductors at relatively low temperatures (see e.g. Ref. [15]); moreover, the energy separation between the peak position and the band gap is somewhat large—38 meV for ZnSe:Cl (using the band gap value from Ref. [16])—compared to 20 meV, which is the typical free exciton binding energy in ZnSe [17], and at high temperatures is expected to be even lower due to screening effects.

Thus, we suggest, based on the line shape (see Fig. 3) and the discussion above, that this high-temperature transition is FB, where it is generally assumed that the line shape is given by [18]

$$I(hv) \propto (hv)^2 \frac{\sqrt{\gamma[(hv - E_G(T) + E_I)/E_I]}}{[1 + \gamma(hv - E_G(T) + E_I)/E_I]^4}$$
$$\times \exp\left[-\frac{hv - E_G(T) + E_I}{k_B T}\right], \qquad (2)$$

where I is the PL intensity, hv is the emitted photon energy, γ is defined as m_c/m_v for the free-to-acceptor (FA) transition, and as m_v/m_c for the free-to-donor (FD) transition (here m_c and m_v are the electron and hole effective masses, respectively), k_B is the Boltzmann constant, and $E_G(T)$ and E_I are the band gap energy as a function of the temperature and the impurity activation energy, respectively.

Before using this line shape function to fit our experimental data, first we should point out that T is, strictly, the electron temperature rather than the lattice temperature. However, we use the lattice temperature values for T since it approaches the lattice temperature at high temperatures [19]. Moreover, from Fig. 5, one can infer that the slope of the high-energy tail of all our spectra at $T > 180$ K matches the corresponding value of $k_B T$ almost exactly if T is taken as the lattice temperature. Secondly, for fitting to ZnBeSe:Cl, the appropriate E_G is required. This, so far, has not been well established, especially at low Be concentrations ($<4\%$), despite several reports, e.g.
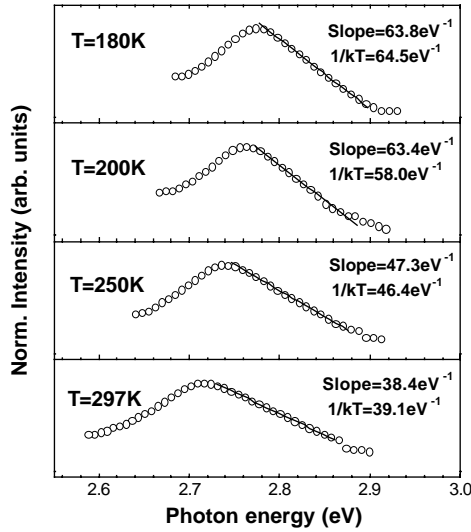
Fig. 5. PL of one typical sample (circles) at various temperatures with solid line representing the corresponding $1/kT$ values (shown in the figure). The intensity in the figure is plotted in natural log scale.

Table 1
Fitting parameters for samples with various Be compositions

Be (%)	$E_1{}^{\text{a}}$ (meV)	$E_1{}^{\text{b}}$ (meV)	γ
0	48	48	0.20
1	52	40	0.10
2.5	70	52	0.17
2.7	71	51	0.13
2.9	70	51	0.10

[a] Using band gap values given by Kuskovsky et al. [20].
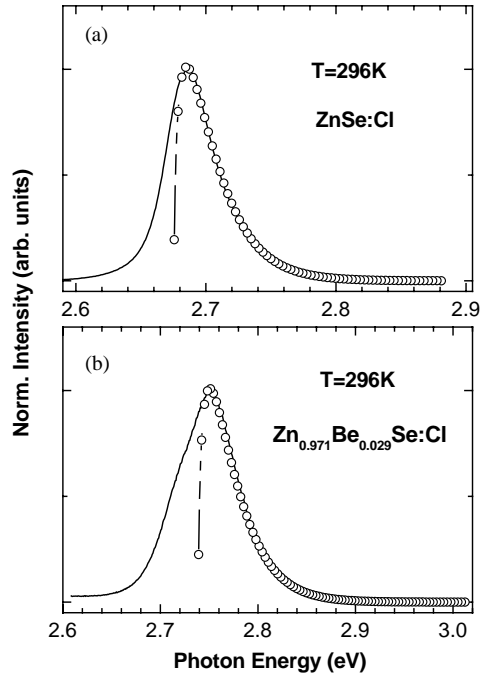[b] Using band gap values given by Chauvet et al. [21].

Fig. 6. Fitting of experimental PL spectra (solid line) at $T = 296$ K with the function (circle) given by Eq. (2): (a) ZnSe:Cl; (b) $Zn_{0.971}Be_{0.029}Se$:Cl.

Refs. [20–23]. In Ref. [22] the direct band gap values were obtained at RT via absorption, but with only four data points. In other literature the excitonic band gap values were obtained (We note that in Ref. [21] the data are referred to as the direct band gap; however, by extrapolating the curve, one obtains 2.80 eV for ZnSe, which clearly suggests that, in fact, the excitonic band gap was obtained). Since Refs. [22,23] pertain to bulk crystals, for our purpose we shall use values from Refs. [20,21] corrected for the binding energy of the ZnSe free exciton (~ 20 meV). We note that only Kuskovsky et al. [20] have given more than two data points in the range of Be concentrations below 5%. For the temperature dependence of the band gap, we assumed the relation for ZnBeSe to follow that of pure ZnSe, which is given by Passler et al. [16], since the Be compositions in our samples are relatively low.

The resultant fit, with the parameter values given in Table 1, is shown in Fig. 6. We note that the experimental data is fitted very well by this simple line shape function on the high-energy side. However, for the low-energy tail, the fitting is unsatisfactory. Eagles [18] observed this discre-

pancy at low temperatures in GaAs and attributed it to the formation of a continuum of energy levels due to impurity interactions [18]. At high temperatures, other broadening mechanisms, including phonon broadening, might set in and cause or contribute to the deviation of the experimental curves from the theory. Such broadening mechanisms can, for instance, be accounted for by convolution with Gaussian functions due to lattice vibrations and impurity distribution (see e.g. Ref. [24]); however, it would dramatically increase

the complexities of the fitting procedure and is not expected to change the impurity ionization energies, which are important for our further analysis. For a FB transition, it then remains to be established whether it is FD or FA. In a prior observation of this transition, in ZnSe, it was suggested that it was FD, with holes recombining with Cl donors located in the tail of a presumed impurity band [25]. However, this explanation seems unlikely for a number of reasons. First, we also observed such PL in our undoped samples (with much lower intensity) and samples with low Cl concentration ($\sim 10^{16}$ cm^{-3}), where no such impurity band is expected. Secondly, we note that the impurity activation energy obtained from our fitting for ZnSe:Cl (see Table 1), is 48 meV, appreciably higher than the Cl activation energy in ZnSe (~ 27 meV [11]). Moreover, one would expect the actual Cl donor activation energy at RT to be even lower than 27 meV due to the screening (for effects of screening on impurity ionization energies, see e.g. Refs. [26,27] and references therein); indeed, formal application of screening theory to Cl gives zero activation energy for our samples with free electron concentrations $\sim 5 \times 10^{17}$ cm^{-3},[3] where this type of PL is still observed, which clearly excludes Cl as the participating donor for this PL. We further note that the fit shown in Fig. 6 was obtained with γ values of about 0.1–0.2. Since such values are appropriate for acceptors ($m_c/m_v \sim 0.19$ for ZnSe assuming that $m_c = 0.15m_0$ and $m_v = 0.78m_0$ [29]), and since we observed that the fit was very sensitive to the γ value, we attribute this transition to a free electron to acceptor recombination. This then leaves the puzzle that the activation energy (48 meV for ZnSe:Cl) is lower than that (> 100 meV) of "standard" acceptors in ZnSe (Li, Na, N); however, lower-than-standard values have already been previously reported (e.g. 56 meV for an unknown acceptor in undoped ZnSe [30], and 85 meV for P acceptors in p-type ZnSe [31]). We note again that the acceptor activation energy obtained by ascribing the 2.742 eV ZnSe:Cl peak

to a DAP peak (at 10 K) is 63 ± 5 meV, which is relatively close to the 48 meV obtained at RT from the FB fitting. The difference between these two energies (~ 15 meV) can be accounted for by screening.[4] Additionally, for ZnBeSe:Cl this energy difference is also in the range of $15 \sim 17$ meV, if one uses band gap values consistently. Therefore, we believe that the FA transition is the most likely mechanism for this PL. The observation of the same PL in undoped samples but with much lower intensities (more than two orders of magnitude) can be explained as follows: first, the free electron concentration in the Cl-doped (n-type) sample is much higher than that in the undoped sample, and as a result, the recombination involving free electrons and acceptor-type centers would be much more significant. Secondly, the concentration of this acceptor-type species might increase as Cl is introduced into Zn(Be)Se, which can also contribute to higher PL intensity in Cl-doped samples.

The origin of this acceptor-type species still remains unclear at this point. However, since the PL is also present in undoped samples, it may well be a native-type defect, although the possibility of a pervasive cantaminant cannot be excluded at this time.

By fitting the FA spectra, we also obtained the acceptor activation energy as a function of Be concentration (see Table 1); the trend is that the activation energy generally increases with Be composition. This can be qualitatively explained as follows. It is well known that the dielectric constant decreases with increasing band gap (see e.g. Ref. [33] for a good qualitative discussion as well as a simple theoretical approach). Furthermore, according to the standard effective-mass theory (see e.g. Ref. [15]), the effective mass generally increases as the band gap increases. Therefore, for an effective-mass-type impurity, its activation energy would increase with the band gap (i.e. with increasing Be), both because of a decrease in the dielectric constant and an increase in effective mass.

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[3] We calculated the Cl activation energy to approach zero for samples with $[n] \sim 5 \times 10^{17}$ cm^{-3}, using the theory developed by J.B. Krieger [28] and G.F. Neumark [26].

[4] It has been observed by Bowers et al. [32] that in p-type ZnSe:N the donor activation energy also decreased; the change is as high as 22% (from 31 to 24 meV) when T increases from 77 K to RT.

4. Conclusions

We have performed a PL study of Cl-doped Zn(Be)Se. The low-temperature PL is, as expected, dominated by the Cl-bound excitonic transitions. As the temperature increases, the PL begins to be dominated by FB transitions. By analyzing the PL spectra at various temperatures, we conclude that the species involved in this transition is of acceptor-type. Interestingly, we also observed the same type of PL in undoped samples. We also found that the activation energy of this species increases with Be concentration, which can be accounted for by the decrease of the dielectric constant and of the increase in effective mass with increasing Be. However, the origin of this acceptor-type species is still unclear at this point and needs further study.

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