

## OPTICAL AND ELECTRICAL PROPERTIES OF $Zn_{1-x}Be_xSe$ GROWN BY MOLECULAR BEAM EPITAXY

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The dopant behaviour in the n-type ZnBeSe:Cl and p-type ZnBeSe:N grown by Molecular Beam Epitaxy (MBE) is investigated. All the samples have been grown on (001) GaAs substrates (conducting or semi-insulating). For the experimental investigation the photoluminescence (PL), Raman Scattering, photoconductivity and I–V measurements are used.

From the temperature (9 K–300 K) and excitation intensity dependent on PL measurements it will be shown that donor and acceptor impurities exhibit a somewhat different behaviour and/or properties from those in ZnSe. We argue that

(i) the activation energy of both the N acceptor and Cl donor increases in ZnBeSe as concentration of Be increases;

(ii) all the undoped and n-type samples exhibit high (>180 K) temperature PL associated with shallow impurity of acceptor type, which also show an increase in the binding energy with Be composition;

Raman scattering experiments have shown that at low Be concentrations ( $x < 0.04$ ) one can use LO photon energy in ZnSe in the analyses of PL spectra from ZnBeSe.

From photoconductivity and I–V measurements we show that

(i) there are a number of carrier traps in ZnBeSe:Cl;

(ii) some of the ZnBeSe samples with Be concentrations over 1% exhibit photoconductivity behaviour associated with the presence of DX centres or other deep trap, i. e., we observe persistent photoconductivity;

(iii) volt-ampere dependencies (with and without irradiation) are different for the samples grown on conducting and semi-insulating substrates.

**Key words:** molecular beam epitaxy, dopant behaviour, photoluminescence, Raman Scattering, photoconductivity, activation energy, donor, acceptor, carrier, trap, photon, volt-ampere dependence.

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### I. INTRODUCTION

II–VI wide bandgap semiconductors are of high interest for fabricating various photonic devices such as laser diodes (LD), light emitting diodes (LED), and solar blind photodetectors (PD). However, for instance, LDs have relatively short "lifetimes" [1]. The use of Be in ZnSe based alloys (i. e.,  $Zn_{1-x}Be_xSe$  ternary alloy) has been suggested [1] to improve the hardness of the material [2–4], and as a result the device lifetime.

In addition,  $Zn_{1-x}Be_xSe$  alloys could be made lattice matched to both GaAs ( $x \sim 0.028$ ) and Si ( $x \sim 0.45$ ); moreover, the addition of Be leads to a larger bandgaps and to a relatively simpler growth procedure than for sulfur containing alloys. Thus, Be chalcogenides are expected to be better for devices than of sulfur based alloys. However, still not much is known about Be chalcogenides, especially about doping and defect structure. The latter is especially important as the presence of deep levels can affect quantum efficiency of the light emitting devices, since Be chalcogenides are to be used in cladding and waveguiding layers.

In this paper we present photoluminescence (PL), electrical and photo-electrical studies of undoped and n-type (Cl-doped) ZnBeSe that shed some light on the defect structure in these materials. All investigated samples were grown by molecular beam epitaxy (MBE) on (001) GaAs substrates. The samples are 800 – 1200 nm thick. The investigated samples have Be concentrations less than 4%. Details of the growth procedure can be found elsewhere [5].

Before we discuss results the from doped alloys, we review some prior results; the PL of undoped samples is dominated by a strong, fairly sharp line (sometimes consisting of two peaks, with a splitting of less than 3 meV) in the near band edge region with several weaker lines on the low-energy side [6]. The dominant line is attributed to bound excitons (see, e. g., Ref. [6]).

### II. PHOTOLUMINESCENCE OF ZNBESE:CL

Figure 1 shows low temperature (10K) PL data from typical ZnBeSe:Cl samples with different Be content. The

PL from a  $\text{ZnSe:Cl}$  sample is also shown. The latter exhibits a peak at 2.797 eV, which has a full-width-at-half-maximum (FWHM) of about 4.9 meV. This peak has usually been attributed to the radiative recombination of neutral donor (Cl) bound excitons. We postulate that it is also the case for the  $\text{ZnBeSe:Cl}$  PL since the peak positions can be easily corrected with the change of the bandgap energy due to the addition of Be. The asymmetric broadening of this excitonic PL has been previously observed [7] and was ascribed to the Stark effect due to the interaction between the charged impurities and bound excitons [8]. Furthermore, such a broadening increases with the increase in Be concentration. Therefore, we suggest that in the  $\text{ZnBeSe}$  case, in addition to the Stark effect broadening, there is also broadening due to an increase in composition fluctuations associated with the presence of Be.

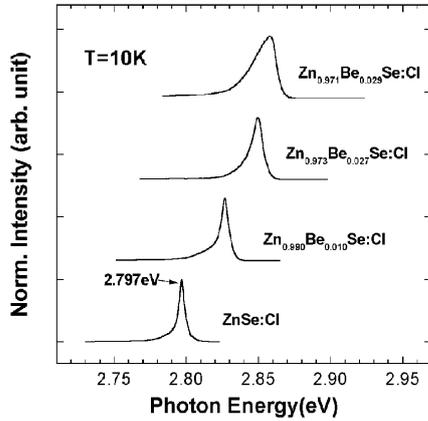


Fig. 1. Low Temperature Photoluminescence of  $\text{Zn}_{1-x}\text{Be}_x\text{Se:Cl}$  ( $x$  values are given in figure). A spectrum from  $\text{ZnSe:Cl}$  is also shown for comparison.

Before discussing our data further, we review reported dependencies of the  $\text{ZnBeSe}$  bandgap as a function of Be, since the knowledge of the bandgap is important for estimating ionization energies of shallow (hydrogenic) impurities. There are several reports on the dependence of the  $\text{ZnBeSe}$  direct or excitonic bandgaps [6,9–10] on Be concentration. In Refs. [10, 11] similar dependencies (23 and 24 meV per percent of Be concentration, respectively) were reported. In Ref. [9] the bandgap values were obtained at room temperature via absorption experiments and have only four data-points. Kuskovsky *et al.* [6] observed negative bandgap bowing at Be compositions below 5%, using PL data. This composition region is the most “difficult” since due to a small lattice mismatch between  $\text{ZnBeSe}$  and GaAs the strain effects are very important. We thus will provide a range of ionization energies, depending on the values of the bandgap used. For the temperature dependence of the  $\text{ZnBeSe}$  bandgap we shall use the formulas obtained for  $\text{ZnSe}$  [12], since the Be concentration in all samples is less than 3%. In fact, Raman scattering has shown that there are no significant

changes in the vibration spectrum of  $\text{ZnBeSe}$  at small Be concentrations (Fig. 2), so the  $\text{ZnSe}$  parameters can be used. Similar results were obtained by Pages *et al.* on Be concentrations up to 3% [13]. We note, however, that the FWHM of the  $\text{ZnBeSe}$  LO peak is somewhat larger (by  $1.2 \text{ cm}^{-1}$ ) than that of the  $\text{ZnSe}$  LO peak; we attribute this to compositional broadening.

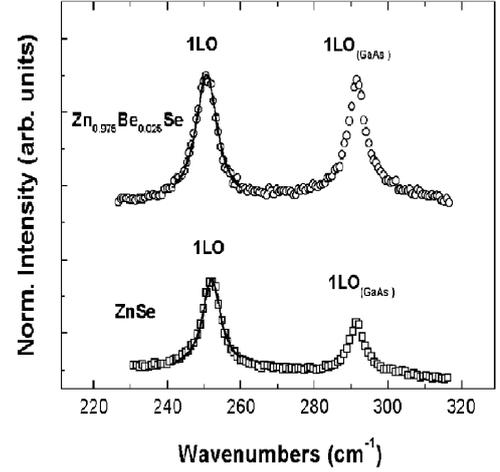


Fig. 2. Results of Raman scattering from  $\text{Zn}_{0.975}\text{Be}_{0.025}\text{Se}$  and  $\text{ZnSe}$ .

Now we discuss the evolution of the PL spectra with temperature using one of the  $\text{ZnBeSe:Cl}$  samples as an example (Fig. 3).

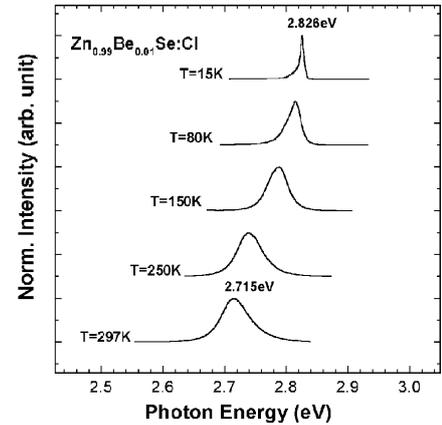


Fig. 3. Temperature Evolution of Photoluminescence from  $\text{Zn}_{0.99}\text{Be}_{0.01}\text{Se}$ .

It is clear that as the temperature increases, the dominant peak becomes broader and more symmetric. At room temperature, we can eventually observe a clear tail extending to the high-energy side other than to the low-energy side. We note that the PL intensity is still relatively high. Since the exciton binding energy in  $\text{ZnSe:Cl}$  is relatively small (5–7 meV), we do not expect the Cl-bound excitonic transition to survive at room temperature ( $T = 296 \text{ K}$ ). Furthermore, based on the lineshape

of the spectra and the proximity of the peaks to the band edge we suggest that this strong PL at the room temperature is due to the free-to-bound transition (FB). In fact, one expects a tail on the high-energy side for FB PL, due to the tail of the carriers density of states in the corresponding band (see also below). We further shall try to determine the nature of the defects involved in this PL.

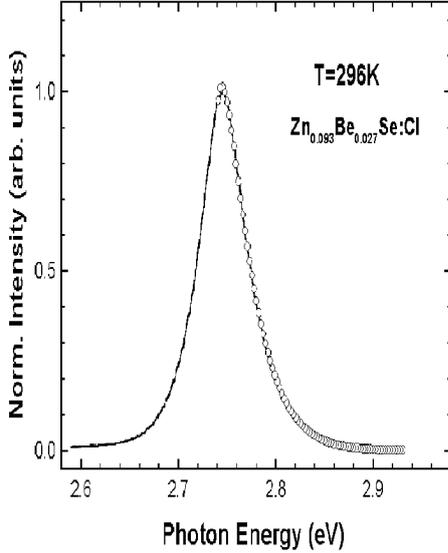


Fig. 4. The fit of the Observed Photoluminescence Lineshape to Eq. (1).

The high concentration of free electrons in our samples (see electrical measurements below) suggests a free-to-acceptor transition; also due to screening effects (e. g., Refs. [14, 15]) the Cl activation energy is expected to decrease with temperature and would not explain the observed peak position. It is well known that the “ideal” lineshape function of such transitions is given by (see, e. g., Ref. [16]):

$$I(h\nu) \propto (h\nu)^2 \frac{\sqrt{\gamma \left( \frac{h\nu - E_G(T) + E_A}{E_A} \right)}}{\left( 1 + \gamma \frac{h\nu - E_G(T) + E_A}{E_A} \right)^4} \times \exp \left[ -\frac{h\nu - E_G + E_A}{k_B T} \right], \quad (1)$$

where  $h\nu$  is the photon energy,  $E_G(T)$  is the bandgap energy at the temperature  $T$ ,  $E_A$  is the ionization energy of the impurity,  $k_B$  is the Boltzmann constant,  $\gamma$ , in the case of a FA transition, is the ratio of the electron effective mass,  $m_e$ , to the hole effective mass,  $m_h$ . In Fig. 4 we plot the result of the fitting of the PL spectrum of a ZnBeSe sample with 2.7% Be using Eq. (1). As can be seen, the experimental data is fitted very well by this simple lineshape using the following parameters:  $E_A = 71$  meV;  $\gamma = 0.13$ ; the temperature and  $E_G$  (296 K) = 2.805 eV (the

value has been obtained from Ref. [6]) have been fixed. Note that the theoretical value of  $\gamma = 0.19$  ( $m_e = 0.15m_0$  and  $m_h = 0.78m_0$  [17]) is very close to that obtained from the fitting procedure. We further note that the low-energy broadening could be due to several broadening mechanisms, including the electron-phonon interaction as well as the interaction with charged impurities [18].

The activation energy of the acceptor impurity, depending on Be concentration, is between 48 and 71 meV, which is one of the lowest ionization energies reported to date. The ionization energy also increases with Be concentration (see Table 1), which suggests effective mass type behaviour — with the change due to a decrease of the dielectric constant and an increase of the carriers effective masses.

Be%	$E_A$ (meV)	$E_A$ (meV)	$\gamma$
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

Table 1. Acceptor activation energy and  $\gamma$  parameter as functions of Be composition.

The increase in the Cl as well as N (p-type) impurity activation energy with Be composition was also previously reported [19]. It seems that this center is either a native defect or a complex of one with the Cl donor. The PL intensity from undoped samples is substantially weaker (see Fig. 5); thus we can assume that n-type doping decreases the formation energy for such an acceptor defect. To elucidate the actual origin of this center, other experiments, such as optically detected paramagnetic resonance or magneto-luminescence, must be performed.

In Figs. 5-(a) and 5-(b) we plot the room temperature photoluminescence of a Cl-doped sample and an undoped sample. Here we would like to note that the intensity of the low energy part of the spectra, which represent recombination on deep optically active centers is much weaker than that of band-edge PL. This is due to a low density of structural defects and the high quality of the samples [6]. The knowledge about deep levels is quite important for materials used for cladding and waveguiding layers in LDs and LEDs; in fact, the absorption of light from the active layer by such defects reduces the quantum efficiency of the devices. Some, optically active, deep centers can be discovered by photoluminescence experiments. However, it is well known that deep centers have relatively strong electron-phonon interaction, so that the observed emission is shifted to lower energies and broadened. At the same time, it is expected that photoconductivity experiments should give “corrected” energy level positions.

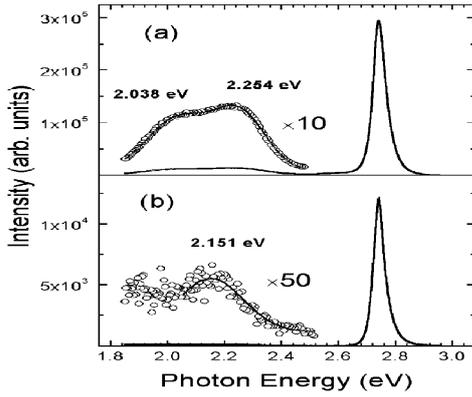


Fig. 5. Room Temperature Photoluminescence from Cl-doped (a) and Undoped (b) ZnBeSe.

### A. Electrical & Photo-electrical Measurements

In this section we plan to study the subsystem of deep levels of Be chalcogenides by investigating the material for its electrical and photo-electrical properties. We, however, first discuss the role of In contacts used in this investigation. Contacts were evaporated on the samples and I-V curves were measured. Initially, the contacts showed Ohmic behaviour as expected for n-type material. However, with time (several weeks) the contacts aged and then showed the existence of Schottky barriers. We plot in Fig. 6 I-V curves at relatively low voltages (curve 1 in the dark and curve 2 with the illumination with monochromatic light with  $\lambda = 810$  nm). The observed behaviour explicitly suggests that even for this n-type material the contacts (indium in this case) form two back-to-back Schottky barriers. We attribute this to relatively low dopant concentrations ( $2 \times 10^{16} \text{ cm}^{-3} \sim 5 \times 10^{17} \text{ cm}^{-3}$ ) in our samples. To estimate the parameters of the system we perform fitting to the “dark” current data according to the model of two ideal Schottky contacts with a series resistance ( $R_{\text{ZnBeSe}}$ ) representing the film. Assuming identical contacts we can use the following equation to describe the curve (see, e. g., Ref. [20] and references therein):

$$V = \eta \frac{k_B T}{q} \ln \left( \frac{I - I_s}{I_s - I} \right) + IR_{\text{ZnBeSe}}, \quad (2)$$

where  $\eta$  is a non-ideality phenomenological factor and  $I_s$  is the saturation current. The fitting is shown in the inset of Fig. 5 is with  $\eta = 44.3$ ,  $I_s = 10 \mu\text{A}$ , and  $R_{\text{ZnBeSe}} = 9.6 \text{ k}\Omega$ , suggesting a fairly conducting film and a low concentration of deep compensating centers, confirming the photoluminescence results (see Fig. 5).

To further investigate our samples, we studied the spectral dependence of the photocurrent in both Cl doped and undoped ZnBeSe. Typical results are shown in Figs. 7-(a) and 7-(b) respectively (compare with the room temperature PL (Fig. 5)). One can discern three different peaks in Fig. 7-(b) and a quite broad distribu-

tion in Fig. 7-(a) between 1.6 and 2.6 eV. Both samples also show strong peak at about 1.45 eV, which we attribute to injection of photo-excited carriers from the GaAs substrate, since the GaAs bandgap is  $\sim 1.43$  eV at 300 K. The other peaks thus represent the deep centers or structural defects [6] within ZnBeSe. It is clear that at least two deep centers are present. It is interesting that while PC and PL spectra are similar, the photoconductivity curves are shifted to somewhat higher energies, as expected due to lack of electron-phonon interaction. We believe that such deep centers are acceptors (in addition to the shallow acceptor shown by the low temperature PL). For Cl doped samples, we suggest that the 2.4 eV band corresponds to A-centers, i. e. complex of Cl donor and doubly charged Zn vacancy (see, e. g., Ref. [21]). The nature of the other centers is not clear right now and they can arise from dislocations.

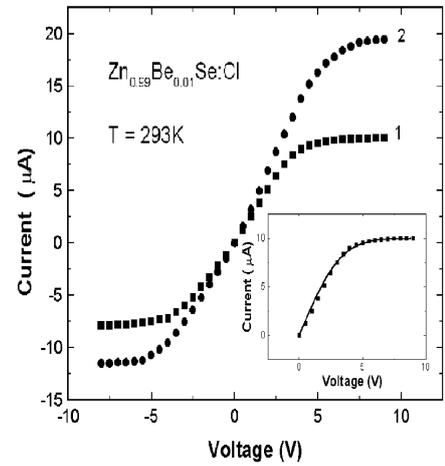


Fig. 6. I-V Characteristics of a ZnBeSe thin film sample with (2) and without (1) illumination. The inset shows the fit using Eq. (2) to the experimental data obtained in the dark (solid squares).

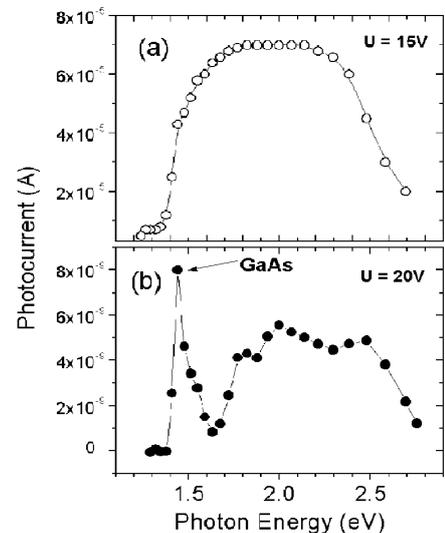


Fig. 7. Spectral Dependence of Photocurrent for Cl-doped (a) and undoped (b) ZnBeSe.

We also would like to add that some of the samples exhibit a relatively strong photo-voltage; however, at this time it is not clear if this effect is due to contact degradation or due to carrier separations inside the material. Preliminary data (to be published elsewhere) suggest that built-in voltages as high as several mV can be obtained under illumination with light corresponding to the energy of the deep defects.

### III. SUMMARY

We have investigated undoped and doped ZnBeSe alloys with Be concentrations less than 3%. We have found

that in ZnBeSe:Cl the dominant radiative transition at low temperatures is due to Cl-donor bound excitons and at high temperatures due to free-to-acceptor transitions. We further concluded that the impurity activation energies increase with Be concentration according to the “effective mass” approximation. The samples show very little in the way of deep centers, although at least two types of such centers are present as shown by high temperature PL and photoconductivity measurements.

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### ОПТИЧНІ ТА ЕЛЕКТРИЧНІ ВЛАСТИВОСТІ СПОЛУК $Zn_{1-x}Be_xSe$ , ЯКІ ОТРИМАНІ МЕТОДОМ МОЛЕКУЛЯРНО-ПРОМЕНЕВОЇ ЕПІТАКСІЇ

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Досліджено нелеговані й леговані сплави ZnBeSe з концентрацією Be менше 3%. Виявлено перехід при низьких температурах, зумовлений зв'язаними екситонами на донорному центрі, створеному Cl, а при високих температурах — переходами вільних носіїв на акцепторний рівень. Зроблено висновок, що зростання енергії активізації домішки залежно від концентрації Be узгоджується з наближенням ефективної маси. Досліджені зразки показали дуже малий вплив глибоких центрів, незважаючи на те, що якнайменше два типи таких центрів наявні в зразках, про що свідчать результати вимірювань фотолюмінесценції й фотопровідності при високих температурах.