Evidence of isoelectronic traps in molecular beam epitaxy grown $Zn_{1-x}Be_xSe$: Temperature- and pressure-dependent photoluminescence studies

Bosang S. Kim, Igor L. Kuskovsky,[a] C. Tian, Irving P. Herman, and G. F. Neumark
Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027

S. P. Guo and M. C. Tamargo
Center for Advanced Technology on Ultrafast Photonic Materials and Applications,
Center for Analysis of Structures and Interfaces (CASI), Department of Chemistry, City College-CUNY,
New York, New York 10031

We have studied undoped $Zn_{1-x}Be_xSe$ alloys grown by molecular beam epitaxy by photoluminescence (PL) as a function of temperature and pressure. We suggest that there are isoelectronic excitonic traps in this material. The binding energy of the isoelectronic bound excitons is deep, between 40 and 50 meV. We have also shown that the temperature and pressure dependences of the $Zn_{1-x}Be_xSe$ PL are close to those of ZnSe. From this we conclude that the dominant excitonic recombination is of an "effective mass" type. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1381039]

II–VI wide band gap semiconductors are of high interest for fabricating devices emitting light in the green and blue spectral regions. However, performance of such devices depends on the adequacy of bipolar doping of the materials and on device "lifetime." Recently, the use of Be in ZnSe based alloys (i.e., $Zn_{1-x}Be_xSe$ ternary alloy) has been suggested.[1] This improves the hardness of the material,[2,3] which is important for longer device lifetime. At the same time, relatively small beryllium concentrations are required to obtain large band gaps and material that is lattice matched to GaAs substrates. While considerable work is currently being done on ZnBeSe, so far relatively little is still known about its optical and other properties.

During formation of semiconductor alloys some of the atoms are replaced by substitutional atoms. Such a system is often described by the virtual crystal model (VCM) (see, e.g. Refs. 4–6 and references therein). The "original" VCM primarily assumed a perfect lattice and an average crystal potential, but subsequent work modified these assumptions in various ways, for instance including fluctuations due to compositional disorder (see, e.g., Refs. 7 and 8 and references therein). In general, these models predict a variation of band gap with alloy composition, with examples for II–VI materials shown, for instance, in Refs. 7 and 9. It has, however, been found that this model works reasonably well if the electronic properties of the two alloy constituents are fairly similar, but if there are large differences in electronegativity and/or size there can be, instead, formation of a localized (isoelectronic) level, which can then result in formation of an "isoelectronic bound exciton" (e.g., Ref. 4 and references therein). This type of level has been observed in a number of systems[4,10–16] with the best-known example being GaP:N. Until very recently[16] all such systems involved disorder on

the anion site. Furthermore, one would expect that formation of localized levels would preclude a change in the band gap, i.e., a given material could not show both a change in the band gap with alloy composition and the formation of localized levels.[17] It is also worth noting that although the Be is on the cation site, which as mentioned, has only one report of isoelectronic excitons, the actual center here appears due to complexes (see below).

In the present letter we report on photoluminescence (PL) of ZnBeSe alloys at low Be concentrations. Interestingly, the PL data give good evidence for both a change in the band gap and an isoelectronic bound exciton. Since, we doubt that a simple substituent can give both effects, we hypothesize that the isoelectronic center results from Be complexes.

Our samples were nominally undoped samples grown by molecular beam epitaxy (MBE). For the details of the growth procedure see Guo *et al.*[18] All the samples showed similar PL. The dominant feature in all cases consists of a strong fairly sharp line (sometimes consisting of two peaks, with a splitting less than 3 meV) in the near band edge region [Fig. 1(a)]. Additional features are several weaker lines on the low-energy side, and in most of the samples two lines on the high-energy side [Fig. 1(b)]. We attribute the peaks on the low-energy side to phonon replicas of the main peak(s). We have previously attributed the latter two peaks to free excitons,[19] with their location giving the excitonic band gap. Such peaks were observed in all but one of the samples we examined; they have the highest energy of all observed peaks and it is well known that nonpseudomorphic epitaxial ZnSe layers show two free exciton peaks.[20] Furthermore, the energy position of these peaks depends on Be composition. If one plots peak energies as a function of the Be concentration one can obtain a smooth extrapolation to the ZnSe values.[19]

Since the dominant emission is sharp, very strong (persisting to high temperatures), relatively close to the excitonic

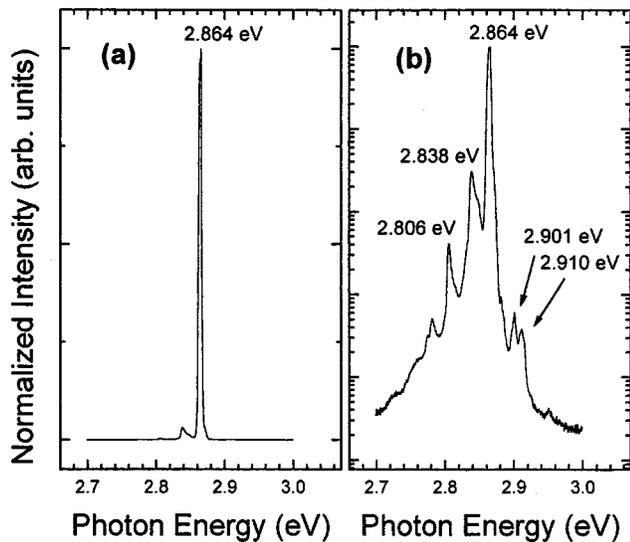[a]Author to whom correspondence should be addressed; electronic mail: ik29@columbia.edu

FIG. 1. Photoluminescence of undoped ZnBeSe: (a) linear scale, (b) semi-log scale.

FIG. 3. (a) Photoluminescence of undoped ZnBeSe under hydrostatic pressure and (b) peak energy of the dominant PL line as a function of applied pressure.

band edge (40–50 meV from the free exciton peaks), and does not shift with excitation intensity it is likely excitonic emission.[21] However, 40–50 meV is actually quite deep for an exciton and there are very few reports of such deep excitons. To obtain a better understanding of this we carried out further studies on the PL as a function of temperature and pressure.

Figure 2 shows the energy of the dominant PL peak as a function of temperature. The PL clearly follows the general temperature dependence of the band gap of semiconductors.[22] From a fitting of the experimental data for several samples (the solid line in Fig. 2) to Varshini's formula[23]

$$E(T) = E(0) - \frac{\alpha_{\mathrm{PL}} T^2}{\beta_{\mathrm{PL}} + T}, \tag{1}$$
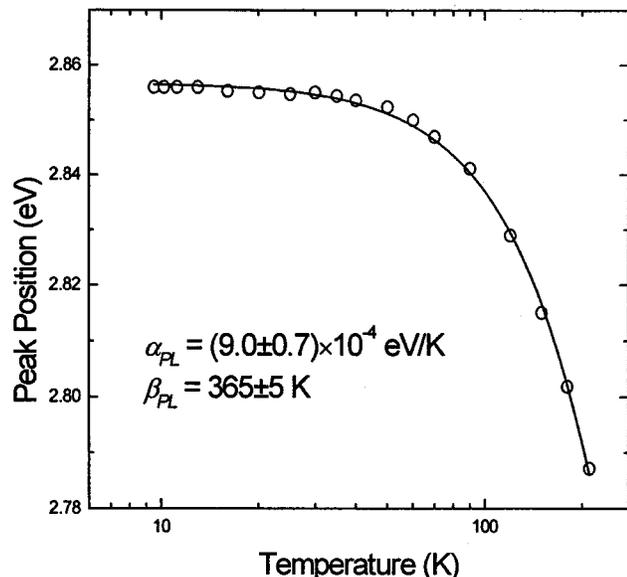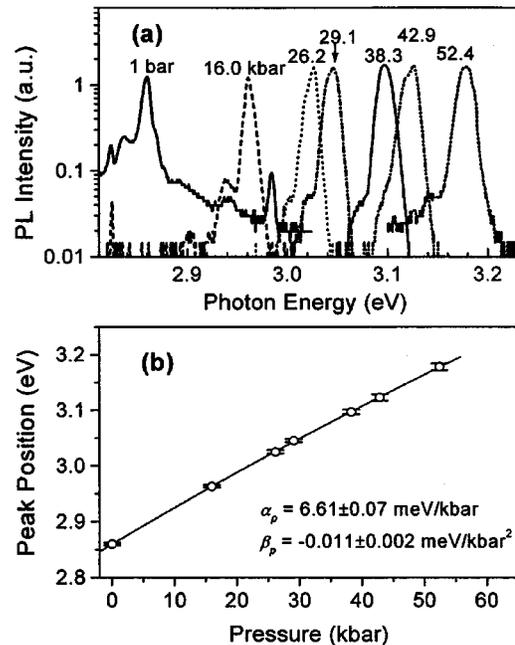

FIG. 2. Peak energy of the dominant PL line as a function of temperature.

we obtain $\alpha_{\mathrm{PL}} = (9.0 \pm 0.7) \times 10^{-4}$ eV/K and $\beta_{\mathrm{PL}} = (365 \pm 5)$ K, which are very close to those obtained earlier for ZnSe.[24,25] This suggests that this line, while relatively deep, is of an "effective mass" type.[26]

The PL was also studied under hydrostatic pressure in a diamond anvil cell within a closed cycle refrigerator system. (For the specifics of the setup see for example Kim *et al.*[14] and references therein.) The spectra obtained at different pressures at 11 K are shown in Fig. 3(a). The energy position of the dominant peak as a function of applied pressure is plotted in Fig. 3(b). It is well known that if the PL is due to an effective mass type defect, the spectrum will shift to higher energy with pressure coefficients close to those of the band gap.[26] Fitting the data [Fig. 3(b)] to a quadratic dependence of the PL energy on the applied pressure (P)

$$E(P) = E(1 \ \mathrm{atm}) + \alpha_p P + \beta_p P^2, \tag{2}$$

where α_p and β_p are the linear and quadratic pressure coefficients respectively, we obtain $\alpha_p = 6.61 \pm 0.07$ meV/kbar and $\beta_p = -(1.1 \pm 0.2) \times 10^{-2}$ meV/(kbar)^2. These values are very close to those obtained for the pressure shift of the ZnSe band gap [$\alpha_p = 6.5 \pm 0.2$ meV/kbar, $\beta_p = -(0.5 \pm 0.3) \times 10^{-2}$ meV/(kbar)^2].[27,28]

Thus, both temperature and pressure studies show effective mass behavior even though the exciton is deep.[29] This suggests that Be (or rather, as discussed earlier, more probably a complex of Be) introduces an isoelectronic trap. Since the Be atom is substantially smaller (about 30%) than Zn it is quite probable that Be will introduce a short-range potential which would lead to the formation of an isoelectronic trap.[12,30] Moreover, since the ionization energy of Be is slightly smaller than that of Zn, according to the theory of Hopfield *et al.*[11] this would lead to having the trap capture a hole first, with an electron then captured via the Coulomb

Appl. Phys. Lett., Vol. 78, No. 26, 25 June 2001

Kim *et al.* 4153

attraction, i.e., there is formation of an isoelectronic donor. Such a donor is expected to be effective mass like[11] and the observed effective mass behavior proves that this is indeed the case.

The above suggestion of an isoelectronic exciton is also consistent with our other observations. Thus, the line is too deep to be due to excitons bound to accidental donors or acceptors in ZnSe. Moreover, in view of the high-purity MBE growth one would not expect much in the way of other impurities, particularly not in concentrations sufficient to give a strong line. Finally, the model also explains the "rich" phonon structure [Fig. 1(b)]. It is significant that the selection rules for electron–phonon interactions are relaxed for isoelectronic donors,[11] and one may observe not only phonon replicas due to longitudinal optical (LO) phonons, but also those due to transverse optical (TO) phonons or to both. We believe that the peak at 2.838 eV is due to a TO phonon while the one at 2.806 eV is due to TO+LO phonons.[31] Furthermore, since the momentum conservation law is relaxed for bound excitons (even more so for isoelectronic bound exciton due to stronger binding),[32] excitons can also couple to acoustic phonons (see, Ref. 15), which can make an isoelectronic spectrum quite rich [Fig. 1(b)].

Both temperature quenching and pressure experiments strongly suggest that the dominant transition from undoped ZnBeSe is due to an effective mass bound exciton. We hope that this, as well as the implication that Be complexes are involved, will stimulate some first principle calculations on this interesting system.

In summary, we have shown that deep bound excitons in undoped ZnBeSe are of the effective mass type, and thus should be of isoelectronic origin. We suggest that these excitons are bound to Be related complexes. We also determined the pressure coefficients for ZnBeSe at low Be concentrations.

[1] A. Waag, Th. Litz, F. Fischer, H.-J. Lugauer, T. Baron, K. Schüll, U. Zehnder, T. Gerhard, U. Lunz, M. Keim, G. Reuscher, and G. Landwehr, J. Cryst. Growth **184/185**, 1 (1998).
[2] C. Verie, J. Cryst. Growth **184/185**, 1061 (1998).
[3] K. Maruyama, K. Suto, and J.-i. Nishizawa, J. Cryst. Growth **214/215**, 104 (2000).
[4] P. J. Dean and D.C. Herbert, in *Bound Excitons in Semiconductors in Excitons*, Topics in Current Physics Vol. 14, edited by K. Cho (Springer, Berlin, p. 55, 1979).
[5] R. J. Nelson, N. Holonyak, Jr., and W. O. Groves, Phys. Rev. B **13**, 5415 (1976).
[6] L. Bellaiche and D. Vanderbilt, Phys. Rev. B **61**, 7877 (1000).
[7] J. E. Bernard and A. Zunger, Phys. Rev. B **36**, 3199 (1987).
[8] L. Bellaiche, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **70**, 3558 (1997).
[9] S. H. Wei, S. B. Zhang, and A. Zunger, J. Appl. Phys. **87**, 1304 (2000).
[10] D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Lett. **15**, 857 (1965).
[11] J. J. Hopfield, D. G. Thomas, and R. T. Lynch, Phys. Rev. Lett. **17**, 312 (1966).
[12] W. Allen, J. Phys. C **4**, 1936 (1971).
[13] S. G. Bishop, B. V. Shanabrook, P. B. Klein, and R. L. Henry, Phys. Rev. B **38**, 8469 (1988).
[14] S. Kim, I. Herman, K. L. Moore, D. G. Hall, and J. Bevk, Phys. Rev. B **53**, 4434 (1996).
[15] M. J. Seong, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **58**, 7734 (1998).
[16] M. J. Seong, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **59**, 12911 (1999).
[17] We believe that it is of importance to distinguish between systems where isoelectronic substituuents form discrete levels and where they form an "alloy" system with a continuous change in band gap. Since ZnBeSe seems to form a continuous alloy system [see, e.g., C. Chauvet, E. Tournié, and J. P. Faurie, J. Cryst. Growth **214/215**, 95 (2000)] we suggest that a single Be atom cannot bind to an exciton.
[18] S. P. Guo, Y. Luo, W. Lin, O. Maksimov, M. C. Tamargo, I. Kuskovsky, C. Tian, and G. F. Neumark, J. Cryst. Growth **208**, 205 (2000).
[19] I. Kuskovsky, C. Tian, G. F. Neumark, S. P. Guo, and M. C. Tamargo, J. Cryst. Growth **214/215**, 1058 (2000).
[20] J. Gutowski, N. Pesser, and G. Kudlek, Phys. Status Solidi A **120**, 11 (1990).
[21] We also performed optically detected magnetic resonant measurements on these samples. However, only a very minimal signal was observed, from which we concluded that the PL decay is too fast for convincing results. This, however, also supports our conclusions about an excitonic nature of the dominant PL.
[22] B. K. Ridley, *Quantum Processes in Semiconductor* (Clarendon, Oxford, 1982).
[23] Y. P. Varshini, Physica **34**, 149 (1967).
[24] Y. Shirakawa and H. Kukimoto, J. Appl. Phys. **51**, 2014 (1980).
[25] K. A. Bowers, Z. Yu, K. J. Gossett, J. W. Cook, Jr., and J. F. Schetzina, J. Electron. Mater. **23**, 251 (1994).
[26] In an effective mass approximation all relevant states are formed from the band wave functions and, correspondingly, all energy levels "follow" the edge with temperature and pressure.
[27] J. A. Tuchman, S. Kim, Z. Sui, and I. P. Herman, Phys. Rev. B **46**, 13371 (1992).
[28] M. Ming Li, D. J. Strachan, Tim. Ritter, M. Tamargo, and B. A. Weinstein, Phys. Rev. B **50**, 4385 (1994).
[29] We use the word "deep" in this letter to underline the relatively large binding energy of this exciton. Although, it is important to understand that often deep impurities do not necessarily mean defects that have energy levels deep into the band gap. For example, P. Y. Yu and M. Cordona, [*Fundamentals of Semiconductors* (Springer-Berlin, 1996), p. 149] defined deep centers as localized defects, whose energies cannot be calculated by means of an effective mass approximation. We wish to point out that in the present instance, we have the opposite situation, i.e., an exciton which is relatively deep in the gap, but does have effective mass character.
[30] S. H. Sohn and Y. Hamakawa, Phys. Rev. B **46**, 9452 (1992).
[31] It is puzzling why no LO phonon is observed. However, it may well be that we are dealing here with localized modes instead; such modes would be expected since Be is lighter than Zn. At this time, we have no alternative explanation for the absence of the "LO" replica.
[32] C. F. Klingshirn, *Semiconductor Optics* (Springer, New York, 1997).