Temperature dependence and bowing of the bandgap in $ZnSe_{1-x}O_x$

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We investigated the temperature dependence of the bandgap of untreated and hydrogen-irradiated $ZnSe_{1-x}O_x$ ($x=0.23\%-0.90\%$) alloys by photoluminescence from $T=10$ K to room temperature. The variation of the bandgap energy with T is similar to that of ZnSe, and does not depend on the oxygen concentration. This indicates that oxygen incorporation in ZnSe does not lead to the carrier localization observed for nitrogen incorporation in GaAs and GaP. Correspondingly, no interaction between hydrogen and oxygen is observed in hydrogenated $ZnSe_{1-x}O_x$. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1719274]

In semiconductor compounds, the substitution of isovalent elements having a large electronegativity and size mismatch with respect to the replaced atoms leads to strong nonlinear effects in the electronic properties of the host crystal. A well-known case is that of nitrogen substituting the group V atom in GaAs and GaP.[1] Indeed, an anomalous giant decrease in the host band gap with increasing N concentration is observed[2–5] along with a slowdown in the response of the band gap to hydrostatic pressure[2,3,6] and temperature[5,7,8] variations. These effects have been rationalized by a band anticrossing (BAC) between a single N level and the extended states of the conduction band (CB) of the host.[3] A more comprehensive theory explains the abovementioned effects by a mixing between localized levels due to N clusters and N perturbed CB states.[9] In both models the isoelectronic impurity induces a real-space localization of the CB states. On the side of the II–VI compounds, an interesting case is represented by O in ZnSe. Besides its technological relevance, this material system may represent an important test bed for the applicability to other compound families of the models developed for explaining the properties of III–N–V alloys. Very recently, $ZnSe_{1-x}O_x$ alloys having $x=(0.35\%-1.3)\%$ have been successfully grown by molecular beam epitaxy (MBE) in spite of the limited solubility of O in II–VI compounds.[10] A large band-gap bowing[10] and a reduced pressure coefficient[11] have been reported and explained successfully in the framework of the BAC model.[11] The photoluminescence (PL) properties of $ZnSe_{1-x}O_x$ in the very dilute limit ($x=0.001\%$) were previously described by Akimoto *et al.*[12] who suggested that the electronic structure of oxygen in ZnSe differs from that of nitrogen in GaAs and GaP. In this letter, we report on a PL study of the temperature dependence of the band gap of $ZnSe_{1-x}O_x$ epilayers both untreated and irradiated with atomic hydrogen. Hydrogen does not affect the band gap of $ZnSe_{1-x}O_x$ contrary to what was previously observed in $In_zGa_{1-z}As_{1-y}N_y$ (Ref. 13) and $GaP_{1-y}N_y$.[14] Moreover, the temperature dependence of the ZnSe band gap does not depend on O incorporation, up to $x=0.90\%$, in contrast with the strong dependence on N concentration observed in $GaAs_{1-y}N_y$ and $GaP_{1-y}N_y$.[5,7,8] A lack of localization in the band-gap edges of $ZnSe_{1-x}O_x$ upon O insertion can account for these differences.

$ZnSe_{1-x}O_x$ layers were grown at 350 °C by MBE on an undoped (001) GaAs substrate (the thickness of the $ZnSe_{1-x}O_x$ films ranges from 600 to 700 nm). A 100-nm-thick ZnSe buffer layer was grown between the GaAs substrate and the $ZnSe_{1-x}O_x$ layers. The oxygen concentration is $x=0.23\%$, 0.57%, and 0.90%, as determined by x-ray diffraction. Further details can be found in Ref. 10. All samples have been hydrogenated at 300 °C by a low-energy ion gun (beam energy ~100 eV).[13,14] The PL signal was excited by the 350–360 nm lines of an Ar^+ laser, spectrally analyzed by a single 1 m monochromator and collected by a GaAs photomultiplier.

Figure 1 shows the PL spectra at $T=10$ K of $ZnSe_{1-x}O_x$ epilayers ($x=0.23\%$ and 0.90%) both untreated (dashed lines) and hydrogenated (continuous lines). In the untreated material several recombination bands can be observed. With increasing x, these bands shift to lower energy in agreement with the O-induced band-gap reduction reported previously.[10,11] The assignment of each band is indicated in the figure and is based on laser power and temperature studies not detailed here. D–A indicates a recombination due to a donor–acceptor pair, BE indicates a bound exciton recombination and the band indicated by LE is due to recombination of excitons localized on potential minima induced by compositional disorder as usually found in semiconductor alloys.[8] Free exciton recombination can be observed for $T>50$ K once localized excitons are thermally ionized (see Fig. 2). Hydrogen irradiation (see continuous lines in Fig. 1) leads to an apparent passivation of the impurity responsible for the BE recombination band. Due to the strong interaction between N and H in ZnSe,[15,16] we argue that the BE band originates from nitrogen acceptors. The D–A pair recombination is affected by H to a smaller extent, thus indicating that the acceptor involved in the D–A pair is not nitrogen. Most importantly, the band gap of $ZnSe_{1-x}O_x$ is not influenced by H since the energy position of each band, as well as

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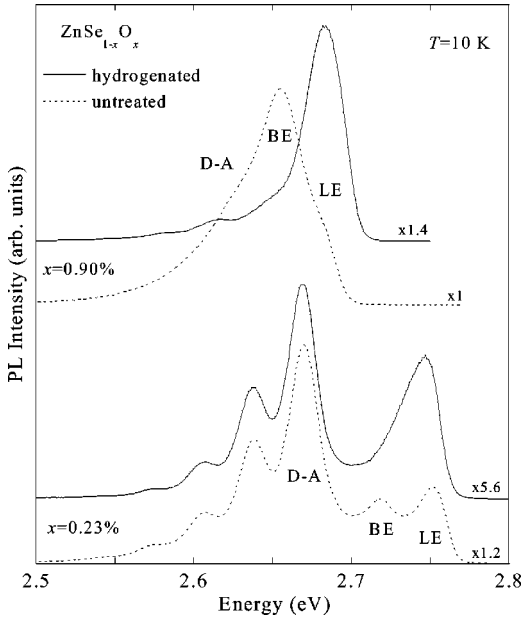

FIG. 1. $T=10$ K photoluminescence (PL) spectra of untreated (dashed lines) and H-irradiated (continuous lines) $ZnSe_{1-x}O_x$ having $x=0.23$ and 0.90%. H dose is equal to 7×10^{18} and 3×10^{18} ions/cm^2 for $x=0.23\%$ and 0.90%, respectively. D–A indicates a donor–acceptor pair recombination, BE is a bound exciton recombination, and LE is due to exciton recombination on localization centers due to alloy disorder. Laser power density $P_{\text{exc}}=1.5$ W/cm^2. PL multiplicative factors are indicated.

of the free exciton observed at higher T, does not change upon H irradiation. This circumstance can be due to the large ionicity difference between III–V and II–VI compounds, which may render unstable in II–O–VI alloys the H complex responsible for N passivation in III–N–V systems. Alternatively, a low or null localized character of the states of the conduction and/or valence band edges of $ZnSe_{1-x}O_x$ can lead to an ineffective interaction between O and H atoms.

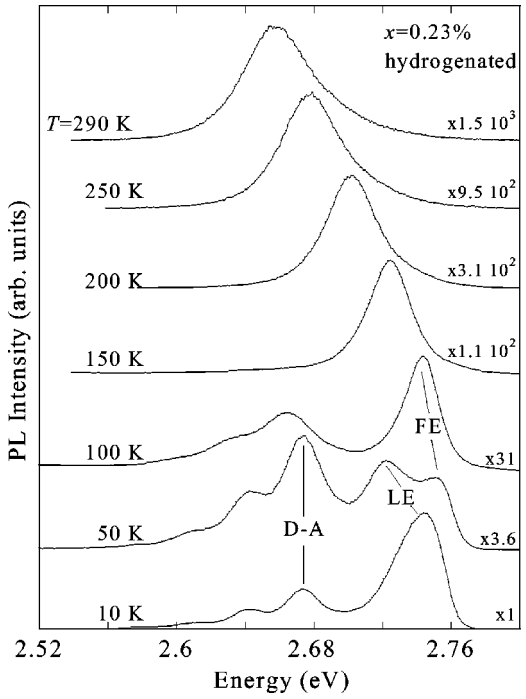

FIG. 2. Photoluminescence (PL) spectra at different temperatures of a $ZnSe_{1-x}O_x$ sample having $x=0.23\%$ hydrogenated with 7×10^{18} ions/cm^2. D–A indicates a donor–acceptor pair recombination, LE and FE are due to localized and free exciton recombination, respectively; laser power density $P_{\text{exc}}=3.0$ W/cm^2; PL multiplicative factors are indicated.

The localized character of an interband transition can be inferred by the temperature dependence of its energy. In particular, the thermal variation of the band gap, E_g, of a crystal is given by

$$\frac{dE_g}{dT}=\left(\frac{\partial E_g}{\partial T}\right)_l+\left(\frac{\partial E_g}{\partial T}\right)_{el-ph}. \tag{1}$$

The first term on the right-hand side of Eq. (1) is due to the lattice thermal expansion and the second term is due to the electron–phonon interaction. Debye–Waller and self-energy terms contribute to $(\partial E_g/\partial T)_{el-ph}$ and give rise to a shift of the gap to lower and higher energies, respectively, with increasing temperature.[17,18] Following Ref. 18, a sizable cancellation of the Debye–Waller and self-energy contributions occurs for energy levels with wave functions strongly localized in real space. In this limit, neighboring orbitals overlap negligibly and $(\partial E_g/\partial T)_{el-ph}$ tends to zero as found in $GaAs_{1-y}N_y$.[8,19]

We consider the T dependence of the $ZnSe_{1-x}O_x$ samples in focus in this study. Figure 2 shows the PL spectra of a hydrogenated $ZnSe_{0.9977}O_{0.0023}$ sample. As T increases the LE band decreases in intensity and shifts rapidly to lower energies due to the preferential ionization of excitons localized on higher energy levels. A new recombination band, FE, appears at about 50 K and remains up to room temperature, while the D–A recombination quenches for $T\sim150$ K. We attribute the FE band to the exciton recombination from the band gap. The FE band maintains a rather symmetric line shape up to 290 K in agreement with its excitonic nature [the exciton binding energy in these materials is about 20 meV (Ref. 20)]. Similar findings have been observed for all $ZnSe_{1-x}O_x$ samples both untreated and hydrogenated.

The BAC model has been successfully employed to account for the variation of the band gap with T (and hydrostatic pressure) in $In_zGa_{1-z}As_{1-y}N_y$.[7,8] In the framework of the BAC model, the temperature dependence of the $ZnSe_{1-x}O_x$ band gap is given by

$$E_g(T)=1/2(E_{\text{O}}+E_{\text{ZnSe}}(T)-\{[E_{\text{O}}-E_{\text{ZnSe}}(T)]^2+4C^2x\}^{1/2}). \tag{2}$$

E_{O} and E_{ZnSe} are the energies of the level of the O isoelectronic impurity and of the ZnSe band gap, respectively, and C is a parameter describing the strength of the interaction between the O level and the ZnSe conduction band states.

Figure 3 shows the temperature shift of the PL peak energy of the free exciton band for all O concentrations considered (symbols). The dashed line is the exciton energy shift of ZnSe with T as reported in Ref. 20. Finally, the continuous lines have been obtained from Eq. (2) using $C=1.8$ eV and $E_{\text{O}}=2.90$ eV as derived in Ref. 11 by fitting within the BAC model the hydrostatic pressure dependence of the band gap in a $ZnSe_{1-x}O_x$ sample similar to those considered here. E_{O} is assumed to be constant with T, as done in the case of the N level in $GaAs_{1-y}N_y$ (Refs. 7 and 8) and accordingly to the strong localized character expected for the O state. Remarkably, the T dependence measured in all $ZnSe_{1-x}O_x$ samples does not depend on the O concentration and follows

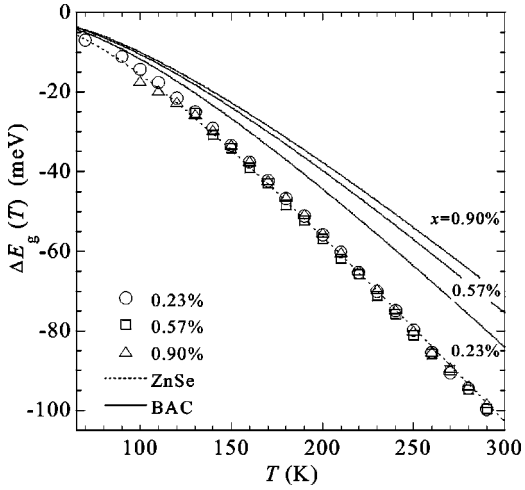

FIG. 3. Shift of the band gap of $ZnSe_{1-x}O_x$ with temperature. All data have been offset for comparison purposes: (○) $x=0.23\%$ hydrogenated with 7×10^{18} ions/cm^2, offset by -2.638 eV; (□) $x=0.57\%$ untreated, offset by -2.595 eV; (△) $x=0.90\%$ hydrogenated with 3×10^{18} ions/cm^2, offset by -2.581 eV. The dashed line is the energy variation of the exciton energy with temperature as reported in Ref. 20 and offset by -2.805 eV. Continuous lines are the expected variation of the band gap of $ZnSe_{1-x}O_x$ according to the band anticrossing model offset by -2.754 eV ($x=0.23\%$), -2.709 eV ($x=0.57\%$), and -2.675 eV ($x=0.90\%$).

very closely the thermal shrinkage expected for the ZnSe host, in contrast with the expectations of the BAC model. This effect has to be attributed to a nearly unchanged value of $(\partial E_g/\partial T)_{el-ph}$ on going from ZnSe to $ZnSe_{1-x}O_x$, namely the band-gap levels do not show the partial cancellation of the Debye–Waller and self-energy terms expected for increasingly localized levels.[21]

We will now discuss some our results. First, we point out that indications of a low localization degree of the $ZnSe_{1-x}O_x$ band extrema are to some extent evident also in the pressure dependence studies performed earlier ($x=0.85\%$).[11] Indeed, the BAC model used to explain those data implies for the O isolated level a pressure coefficient $(\partial E_O/\partial P)=20$ meV/GPa, namely, about a factor three smaller than that of the ZnSe host ($=67$ meV/GPa). On the contrary, for $GaAs_{0.985}N_{0.015}$, it was found $(\partial E_N/\partial P)=15$ meV/GPa, that is a factor eight smaller than the pressure coefficient of GaAs ($=120$ meV/GPa).[3] Another important point is the energy position of the isolated O, which should give rise in the BAC model to a level repulsion with the CB states. In the study performed in Ref. 11, E_O was set equal to 2.90 eV (about 200 meV above the CB bottom) in order to reproduce the energy gap dependence on applied pressure of $ZnSe_{0.9915}O_{0.0085}$. However, from previous PL studies in ZnSe:O ($x=0.001\%$), it was shown that O introduces a *shallow acceptor* level located at about 80 meV above the top of the ZnSe valence band.[12] The position of the O level relative to the band edges is clearly a crucial point to understand the physical properties of O in ZnSe and other II–VI compounds. It might be the case that O occupies different lattice sites (e.g., interstitial versus substitutional) depending on its concentration. Therefore, new samples spanning the O concentration range from the dilute to the alloy limit should be investigated.

In conclusion, O in ZnSe shows several differences as compared to N in GaAs and GaP: (i) H irradiation does not lead to a band-gap reopening or show clear evidences of the formation of O–H complexes; (ii) the response of the $ZnSe_{1-x}O_x$ to temperature variation is the same of ZnSe, independently of the O concentration. These findings point toward an absence of a localized character in the $ZnSe_{1-x}O_x$ band edges.

[1] For a review see, III–N–V Semiconductor Alloys, special issue of Semicond. Sci. Technol. **17**, 741 (2002).
[2] P. J. Klar, H. Grüning, W. Heimbrodt, J. Koch, F. Höhnsdorf, W. Stolz, P. M. A. Vicente, and J. Camassel, Appl. Phys. Lett. **76**, 3439 (2000).
[3] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, J. Appl. Phys. **86**, 2349 (1999).
[4] H. P. Xin, C. W. Tu, Y. Zhang, and A. Mascarenhas, Appl. Phys. Lett. **76**, 1267 (2000).
[5] G. Yu. Rudko, I. A. Buyanova, W. M. Chen, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **81**, 3984 (2002).
[6] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, Y. G. Hong, H. P. Xin, and C. W. Tu, Phys. Rev. B **65**, 241303 (2002).
[7] I. Suemune, K. Uesugi, and W. Walukiewicz, Appl. Phys. Lett. **77**, 3021 (2000).
[8] A. Polimeni, M. Capizzi, M. Geddo, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 195320 (2001).
[9] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).
[10] Y. Nabetani, T. Mukawa, Y. Iti, T. Kato, and T. Matsumoto, Appl. Phys. Lett. **83**, 1148 (2003).
[11] W. Shan, W. Walukiewicz, J. W. Ager III, K. M. Yu, J. Wu, E. E. Haller, Y. Nabetani, T. Mukawa, Y. Ito, and T. Matsumoto, Appl. Phys. Lett. **83**, 299 (2003).
[12] K. Akimoto, T. Miyajima, and Y. Mori, Phys. Rev. B **39**, 3138 (1989); *ibid.*, Jpn. J. Appl. Phys., Part 2 **28**, L531 (1989); K. Akimoto, H. Okuyama, M. Ikeda, and Y. Mori, Appl. Phys. Lett. **60**, 91 (1992).
[13] A. Polimeni, G. Baldassarri H. v. H., M. Bissiri, M. Capizzi, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **63**, 201304(R) (2001).
[14] A. Polimeni, M. Bissiri, M. Felici, M. Capizzi, I. A. Buyanova, W. M. Chen, H. P. Xin, and C. W. Tu, Phys. Rev. B **67**, 201303(R) (2003).
[15] C. Pong, N. M. Johnson, R. A. Street, J. Walker, R. S. Feigelson, and R. C. De Mattei, Appl. Phys. Lett. **61**, 3026 (1992).
[16] E. Ho, P. A. Fisher, J. L. House, G. S. Petrich, L. A. Kolodziejski, J. Walker, and N. M. Johnson, Appl. Phys. Lett. **66**, 1062 (1995).
[17] P. B. Allen and M. Cardona, Phys. Rev. B **27**, 4760 (1983).
[18] P. Allen and V. Heine, J. Phys. C **9**, 2305 (1976).
[19] A. Polimeni, M. Bissiri, A. Augieri, G. Baldassarri Höger von Högersthal, M. Capizzi, D. Gollub, M. Fischer, M. Reinhardt, and A. Forchel, Phys. Rev. B **65**, 235325 (2002).
[20] R. Pässler, E. Griebl, H. Riepl, G. Lautner, S. Bauer, H. Preis, W. Gebhardt, B. Buda, D. J. As, D. Schikora, K. Lischka, K. Papagelis, and S. Ves, J. Appl. Phys. **86**, 4403 (1999).
[21] The contribution of the lattice thermal expansion to the T dependence of the band gap is given by $(\partial E_g/\partial T)_l=-3B\alpha(\partial E_g/\partial P)_T$, where B, α, and P are the crystal bulk modulus, thermal expansion coefficient and applied pressure, respectively. Using $\alpha=7.8\times10^{-6}$ K^{-1} and $B=65$ GPa [U. Rössler, Landolt-Börnstein: *Numerical Data and Functional Relationships in Science and Technology*, New Series, Group III, Vol. 22a (Springer, Berlin, 1987)], and $(\partial E_g/\partial P)_T=56$ meV/GPa as found in Ref. 11 for $T=295$ K and $x=0.85\%$, one obtains $(\partial E_g/\partial T)_l=-0.085$ meV/K, that is 18% of the value of dE_g/dT found experimentally for $T=290$ K and $x=0.90\%$. This corresponds to $(\partial E_g/\partial T)_{el-ph}$ equal to 0.385 and 0.369 meV/K for O-containing and O-free samples, respectively.