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.

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). 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. 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. 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, 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.
and H-irradiated 

ZnSe 1

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FIG. 1. 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 conduc and/or valence band edges of ZnSe1–xOx can lead to an ineffective interaction between O and H atoms.

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

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

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 GaAs1–xN0.8.19

We consider the T dependence of the ZnSe1–xOx samples in focus in this study. Figure 2 shows the PL spectra of a hydrogenated ZnSe0.9977O0.0023 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~150 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 ZnSe1–xOx samples both untreated and hydrogenated.

The BAC model has been successfully employed to account for the variation of the band gap with T (as hydrostatic pressure) in In,Ga1–xAs1–yNz.7,8 In the framework of the BAC model, the temperature dependence of the ZnSe1–xOx band gap is given by

$$E_g(T) = 1/2(E_O + E_{ZnSe}(T) - \left[\left(E_O - E_{ZnSe}(T)\right)^2 + 4C^2\right]^{1/2})^{1/2}.$$

$E_O$ 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 $E_O=2.90$ eV as derived in Ref. 11 by fitting within the BAC model the hydrostatic pressure dependence of the band gap in a ZnSe1–xOx 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 GaAs1–xN0.17,18

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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 $\langle \partial E_g/\partial T \rangle_{\text{int-ph}}$ going from ZnSe to ZnSe$_{1-x}$O$_x$, namely the band-gap levels do not show the partial cancelation expected for the O isolated level a pressure coefficient $\sim 200$ meV/GPa as found in Ref. 290 K, found experimentally for $E_g$ ($x=0.90\%)$. Indeed, the BAC model used to explain those data implies for the O isolated level a pressure coefficient $\langle \partial E_g/\partial P \rangle=20$ 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 $\langle \partial E_g/\partial P \rangle=15$ meV/GPa, that is a factor eight smaller than the pressure coefficient of GaAs ($120$ meV/GPa). 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, $E_0$ 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. 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.

21 The coefficient of the lattice thermal expansion to the T dependence of the band gap is given by $\langle \partial E_g/\partial T \rangle_T=x_13x0.85\%$ of the value of $E_g$ ($x=0.385\%$) and $B=65$ GPa [U. Rüssel, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, Vol. 22a (Springer, Berlin, 1987), Eq. (7)].