Excitonic transitions in ZnSe epilayers grown on GaAs

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ZnSe epilayers grown on GaAs substrates frequently show free- and bound-excitonic transitions in low-temperature photoluminescence. In particular, the excitonic transition at ~ 2.7968 eV (I_2^1) and ~ 2.7948 eV (I_2^2) are commonly observed. The higher-energy transition corresponds closely in energy to a typical donor-bound exciton transition energy in ZnSe. However, there has been much uncertainty as to origin of the lower-energy transition. We show that both of these transitions correspond to a bound-excitonic transition at the same donor which has been split due to the residual *tensile* strain present in the ZnSe heteroepilayers. This strain also causes similar splittings of the free-exciton transitions. We show that our model is consistent with the experimental fact that the precise energy position of the free- and bound-exciton transitions is a function of the epilayer thickness and the growth temperature. The temperature dependence of the photoluminescence in the free- and bound-exciton region is also shown to be consistent with our model of thermal population of the strain-split states.

ZnSe layers frequently show free- and bound-excitonic transitions in low-temperature photoluminescence (PL). The donor-bound excitons are present in two forms: the I_2 lines which involve excitons bound to neutral donors and the I_3 lines, which are bound to ionized donors. The I_1 lines involve excitons bound to neutral acceptors. There has been a number of reports of a strong PL transition at ~ 2.7948 eV (I_2^2) at low temperatures (~ 5 K) in ZnSe heteroepilayers grown on GaAs substrates, the origin of which has been subject to controversy.[1–7] This controversy arises mainly due to the fact that the localization energy of this transition (~ 8 meV) does not correspond to any of the well characterized donor species in ZnSe. Typical neutral-donor-related localization energy in this semiconductor is of the order 5 meV with a spread of only ~ 0.7 meV.[8] Several explanations have been put forward. For example, one suggestion is that the I_2^2 line is actually the I_3 line.[6] In this case, the intensity of I_3 should be much weaker than the I_2 line, especially at very low temperatures. However, the opposite is observed experimentally. Other suggestions include the possibilities that I_2^2 is a lower-energy strain-split component of I_2 (Ref. 2), or that it is due to a native defect.[4] In this paper, we propose a model for the origin of the I_2^2 line which is consistent with several experimental observations described below.

The ZnSe epilayers were grown in a conventional molecular-beam epitaxy system (Varian Gen II). The $\langle 001 \rangle$-oriented GaAs substrates were etched in $8H_2SO_4:1H_2O_2$ prior to *in situ* thermal cleaning at approximately 580 °C. The substrate temperature was kept at 350 °C during the growth. The growth rates were maintained in the range 0.5-1 μm/hr.

In Fig. 1 we show typical PL spectra from a homoepitaxial layer of ZnSe and a heteroepitaxial layer of ZnSe grown on GaAs substrate. The spectrum from the homoepitaxial sample[7] typically consists of a free-exciton
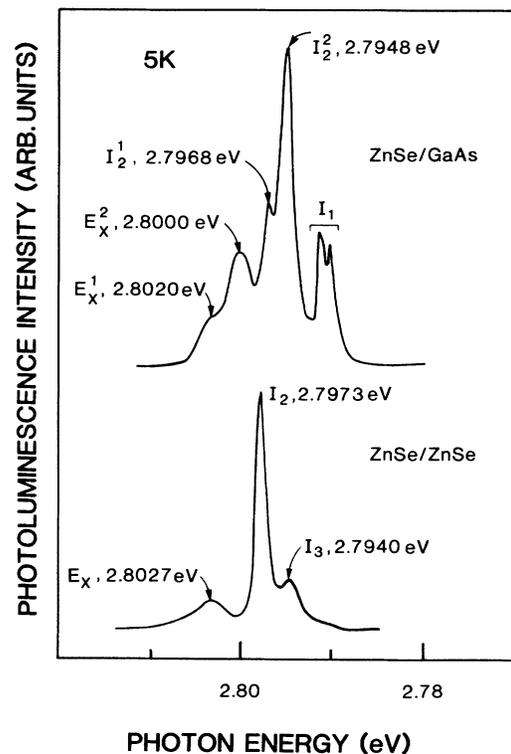
FIG. 1. Low-temperature (5 K) photoluminescence spectrum of a homoepitaxial layer of ZnSe (bottom) showing a free-exciton transition E_X, a neutral-donor-bound exciton transition I_2, and ionized-donor-bound transition I_3 (Ref. 7). At the top is shown a typical spectrum obtained from a thick (~ 4.6 μm) ZnSe epilayer grown on a GaAs substrate. E_X^1 and E_X^2 are related to free excitons and I_2^1 and I_2^2 are related to neutral-donor-bound excitons. In this sample, we also observe acceptor-bound exciton transitions I_1.

transition E_X at 2.8027 eV and a donor-bound exciton peak I_2 at 2.7973 eV with a much weaker peak I_3 at lower energies corresponding to excitons bound to ionized donors. These energies for free- and bound-exciton transitions agree very well with those found in the case of high-quality ZnSe samples grown by liquid-phase epitaxy.[8] In the case of ZnSe heteroepitaxial sample, on the other hand, one typically sees, on the higher-energy side, a weaker transition at ~ 2.8020 eV (E_X^1), a relatively stronger feature at ~ 2.8000 eV (E_X^2), while on the lower-energy side a weaker peak at ~ 2.7968 eV (I_2^1) and a much stronger peak at ~ 2.7948 eV (I_2^2), as indicated in Fig. 1. It has been shown that the position of I_2^2 moves to lower energies when the growth temperature is raised from ~ 350 to ~ 400 °C.[9] However, the *separation* between E_X^1 and I_2^1 or E_X^2 and I_2^2 is found to be *independent* of the growth temperature.[7]

In Fig. 2, we show the temperature dependence for the near-band-edge emission in a 4.6-μm ZnSe layer grown on GaAs. At the lowest temperature (2 K), we see that the lower-energy peak I_2^2 has a much higher integrated intensity compared with I_2^1. As the temperature is increased, we see that the intensities of I_2^1 compared with I_2^2 and E_X^2 compared with E_X^1 increase. At 30 K, for example, I_2^1 appears to be a little stronger than I_2^2. Raising the temperature any further than 30 K broadens the lines so much that the individual features are not discernible.

These observations may be understood if we assume that the ZnSe epilayer grown on GaAs is under slight in-plane biaxial *tension*, despite the fact that the lattice constant of ZnSe is *larger* than that of GaAs. However, this assumption has recently been shown to be correct using x-ray and transmission-electron microscopy (TEM) studies both in our laboratory and elsewhere.[10,11] It is found that epilayer growth is commensurate up until thickness of ~ 150 nm (the critical thickness for ZnSe grown on GaAs with 0.27% lattice mismatch). From ~ 150 to ~ 550 nm of the epilayer growth, the density of misfit dislocations increases rapidly and, consequently, the elastic strain in the epilayer decreases accordingly. As the epilayer thickness increases beyond ~ 550 nm, the relaxation rate slows down until the epilayer is almost, but not fully, relaxed after about 880 nm of growth.[11] Increasing the epilayer thickness any further results in it being under biaxial *tensile* strain once the sample is cooled down to room temperature, due to the larger thermal expansion coefficient of ZnSe compared with that of GaAs. However, the precise amount of the tensile strain is found to be a function of not only the growth temperature but also the layer thickness. For example, it is found using TEM measurements that at the growth temperature of 350 °C, the epilayer is not fully relaxed despite the fact that it is ~ 4.6-μm thick but, instead, it has a residual compressive strain ϵ_{res} of about -0.005%. Now, the strain due to the *thermal* mismatch ϵ_{therm} at 350 °C is about $+0.040\%$. Therefore, when this epilayer is cooled down to the room temperature, the net strain ϵ_{net} is given by $(\epsilon_{therm} - \epsilon_{res}) = +0.035\%$. As the epilayer thickness increases, ϵ_{res} decreases as seen in the case of the ~ 6-μm-thick sample so that ϵ_{net} increases. Hence, the position of free- and
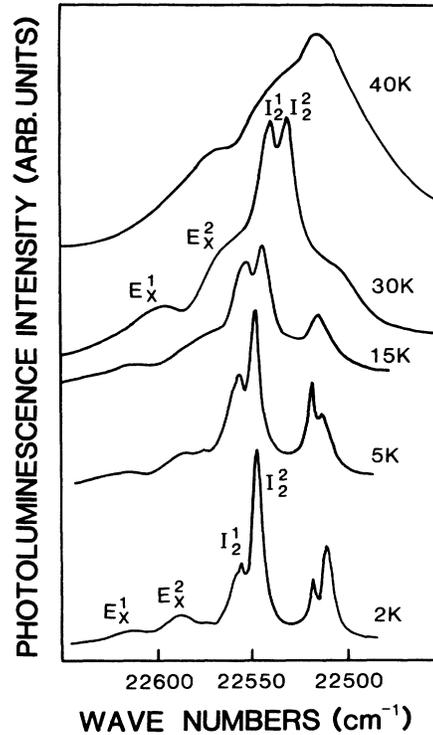
FIG. 2. Temperature dependence of the near-band-edge emission for the ZnSe epilayer grown on GaAs. At 2 K, the lower-energy peak I_2^2 has much higher integrated intensity compared with I_2^1. At 30 K, the relative intensities of the two peaks are comparable.

bound-exciton lines is found to be at a slightly lower energy for the 6-μm sample compared with that of 4.6-μm sample, as shown in Fig. 3. On the contrary, as the thickness of the epilayer decreases, ϵ_{res} increases and so ϵ_{net} decreases, shifting the excitonic transitions to higher energies. This case is indicated for the 1.4-μm layer in Fig. 3. It is also clear from Fig. 3 that as the epilayer thickness decreases from 6.0 to 1.4 μm, the splitting between I_2^1 and I_2^2 or E_X^1 and E_X^2 also becomes smaller due to reduced amount of net strain ϵ_{net}. It was shown by Dean et al. by selective excitation, that this strain splitting is also observed in the two-electron region of the spectrum.[2] It is found empirically that if the heteroepilayer thickness is below ~ 0.88 μm, then ϵ_{net} becomes negative, i.e., the layers are left under net biaxial *compressive* strains. This region has been studied earlier using various experimental techniques.[4,5] Detailed discussion of the strain relaxation for heteroepilayers thicker than one micrometer, as mentioned above, will be the subject of a future study. In the context of the present study, it suffices to say that if the ZnSe epilayer thickness is of the order of one micrometer or larger, then it will be left under net tension and, as discussed in the following paragraphs, it will give rise to various transitions.

For a zinc-blende-type semiconductor, like ZnSe, the valence band at the zone center and at zero strain consists of a fourfold $J_{3/2}$ multiplet and a spin-orbit split-off

FIG. 4. Splitting of the valence band at $k = 0$ as a function of the in-plane biaxially tensile strain (top). At the bottom is shown the effect of 0.04% tensile strain on the free-exciton E_X and donor-bound-exciton I_2 transitions.

FIG. 3. Photoluminescence in the excitonic region for ZnSe epilayers of various thicknesses grown on GaAs substrates. E_X^1 and E_X^2 represent the strain-split components of the free-exciton transitions while I_2^1 and I_2^2 represent that of bound-exciton transitions. As the layer thickness decreases, these transitions move to higher energies due to reducing amount of tensile strain left in the epilayers. The two vertical arrows at the bottom indicate the unperturbed nonsplit energy positions of the free and, as an example, gallium-donor-bound exciton transitions. Note also that the energy separation between E_X^1 and E_X^2 or I_2^1 and I_2^2 decreases as the epilayer thickness decreases.

$J_{1/2}$ multiplet. The bottom of the conduction band, at the zone center, is given by $J_{1/2}$. For the epilayers grown on $\langle 001 \rangle$-oriented substrates, the strain tensors are given by $\epsilon_{xx} = \epsilon_{yy} = \epsilon = (a_{\parallel} - a_{\mathrm{ZnSe}})/a_{\mathrm{ZnSe}}$ and $\epsilon_{zz} = -2(C_{12}/C_{11})\epsilon$, where the bulk unstrained lattice constant of ZnSe is given by a_{ZnSe} and $a_{\parallel}$ gives the in-plane value of the lattice constant along the (x,y) directions in the epitaxial layers and C_{ij} are the elastic constants. For the tensile strain, the fourfold degenerate $J_{3/2}$ splits into two doubly degenerate bands. The energy separation between the bottom of the conduction band and the top of the two strain-split valence bands is given by[12]

$$\Delta E_1 = E_H + E_U ,\tag{1a}$$

$$\Delta E_2 = E_H - E_U ,\tag{1b}$$

where

$$E_H = 2a \left[\frac{C_{11} - C_{12}}{C_{11}} \right] \epsilon_{xx} ,$$

$$E_U = -b \left[\frac{C_{11} + 2C_{12}}{C_{11}} \right] \epsilon_{xx} ,$$

and a is hydrostatic deformation potential and b is the shear deformation appropriate to tetragonal distortion. For ZnSe, $a = -5.4$ eV and $b = -1.2$ eV,[5] and this gives

$$\Delta E_1 = -1.64\epsilon_{xx} \text{ eV} ,\tag{2a}$$

$$\Delta E_2 = -6.94\epsilon_{xx} \text{ eV} .\tag{2b}$$

For the tensile strain, $\epsilon_{xx} > 0$, so the energy gaps for both of the bands decreases. However, ΔE_2 formed with $|\frac{3}{2}; \pm \frac{1}{2} \rangle$-like valence band decreases more than four times faster than ΔE_1 formed with $|\frac{3}{2}; \pm \frac{3}{2} \rangle$-like valence band. Hence, under in-plane tensile strain the minimum band gap in the ZnSe layer will be given by the separation between the bottom of the lowest conduction band and the top of the $|\frac{3}{2}; \pm \frac{1}{2} \rangle$-like valence band.

For the case of an unstrained ZnSe layer, E_X represents the unperturbed free exciton transition energy at 2.8027 eV, while I_2 gives the unperturbed position of a donor-bound exciton at 2.7973 eV. For the case when the ZnSe epilayer is left under tensile strain, the valence band splits into two components as shown in Fig. 4. Therefore, each excitonic transition at zero strain now gives rise to two transitions: one associated with the $|\frac{3}{2}; \pm \frac{1}{2} \rangle$-like valence band (the lower energy peak), and the other associated with the $|\frac{3}{2}; \pm \frac{3}{2} \rangle$-like valence band giving rise to the higher-energy component. For the particular case of the 4.6 μm heteroepitaxial sample discussed above, the tensile strain as measured by x-ray

diffraction and TEM was $\epsilon \sim +0.04\%$,[11] giving rise to a splitting between the two bands of about 2 meV; the separation of the top of the $\mid \frac{3}{2};\pm\frac{3}{2}\rangle$ valence band from its unperturbed position is only about 0.7 meV and that for the $\mid \frac{3}{2};\pm\frac{1}{2}\rangle$ valence band, it is about 2.7 meV (Fig. 4). Hence, the unperturbed I_2 line at 2.7975 eV in the case of an homoepitaxial layer would split into 2.7968- and 2.7948-eV components (Fig. 4). Similarly, the free-exciton line splits into 2.8020- and 2.8000-eV components as observed in the case of heteroepitaxial sample (Fig. 1).

The behavior of these excitonic transitions as a function of the growth temperature can now be easily understood. The growth temperature and, hence, the net strain would affect the separation between the I_2^1 and I_2^2 lines or between E_X^1 and E_X^2 lines. However, since E_X^1 and I_2^1 are related to the same valence band, namely $\mid \frac{3}{2};\pm\frac{3}{2}\rangle$, their separation would not be affected with the growth temperature, and, indeed, as mentioned above, this is found experimentally.[7] Similar arguments apply for the case of E_X^2 and I_2^2 transitions. The behavior of various peaks in photoluminescence as a function of increasing temperature can now be regarded as simply the thermal population of the higher-energy components. As the temperature is raised from 2 K, the higher-energy $\mid \frac{3}{2};\pm\frac{3}{2}\rangle$ component becomes increasingly populated at the expense of the lower energy $\mid \frac{3}{2};\pm\frac{1}{2}\rangle$ band and so the intensities of E_X^1 and I_2^1 are seen to increase relative to their lower-energy counterparts. At around 30 K ($kT \sim 2.5$ meV), the relative intensities of the lower-energy components have increased considerably (Fig. 2), consistent with a strain splitting of the order of 2 meV for $\epsilon = +0.04\%$.

In summary, we have shown that for the case of ZnSe epilayers thicker than 1 μm grown on GaAs, the residual tensile strain due to the thermal mismatch between ZnSe and GaAs, leads to a small, but clearly observable, splitting of the free- and bound-exciton transitions. The lower-energy component is believed to be associated with $\mid \frac{3}{2};\pm\frac{1}{2}\rangle$-like valence band which has a much stronger dependence on the strain than the higher-energy component associated with $\mid \frac{3}{2};\pm\frac{3}{2}\rangle$-like valence band. This leads to the energy-level scheme depicted in Fig. 4. The energy difference between the split valence bands is a function of the strain and, hence, the growth temperature of the sample. This leads to the experimentally observed facts that the separation between I_2^1 and I_2^2 or E_X^1 and E_X^2 are a function of the growth temperature; however, the differences between I_2^1 and E_X^1 or I_2^2 and E_X^2 are not dependent upon the growth temperature. We also showed photoluminescence spectra as a function of temperature for the heteroepitaxial layer, which clearly supported our model by showing that, as the temperature increases, the higher-energy components of the strain-split excitonic transitions increase in intensity relative to their lower-energy counterparts, due to thermal population. Similarly, it was shown in Fig. 3 that, as the epilayer thickness decreases from 6.0 to 1.4 μm, the peak energy position of, for example, I_2^2 line moves to higher energies, and that the splitting between I_2^1 and I_2^2 reduces due to decreasing amount of tensile strain.

Note added in proof. The author has recently learned that another group arrived at basically similar conclusions about E_x^2 and I_2^2 peaks.[13]

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