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Optical transitions in ultra-high-purity zinc selenide

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We present photoluminescence (PL) and PL excitation data for unintentionally doped zinc selenide epilayers grown by molecular-beam epitaxy using ultra-high-purity sources. In particular, we discuss a transition I_V^0 at 22380 cm^{-1} (2.7738 eV) which had been identified as an LO replica of the free excitons in the past. We present data to show that I_V^0 is *not* related to the formation of free excitons even though it is always observed in samples which show strong free-exciton transitions. Evidence is also presented to show that I_V^0 may be a result of recombinations involving selenium-site-related effects.

In this Rapid Communication, we are mainly concerned with the nature of certain low-temperature photoluminescence (PL) features, located below donor- and acceptor-bound exciton transition energies, and which are observed especially in those unintentionally doped (n-type) epitaxial ZnSe layers which are grown from ultra-high-purity sources of zinc and selenium. In particular, we are concerned with a transition I_V^0 occurring at 22380 cm^{-1} (2.7738 eV) which was previously identified with an LO phonon replica of the free excitons in ZnSe.[1] We show that this transition is not related to the recombination processes of either free or bound excitons but, instead, is associated with an independent luminescent transition, possibly involving a defect associated with the selenium sites. It is well recognized that the near-band-edge transitions at low temperatures in a typical ZnSe layer, regardless of the growth technique, result from free- and impurity-bound exciton recombinations.[2] Figure 1(a) shows such a typical PL spectrum taken with the sample at ~6 K, using above-band-gap excitation radiation, E_{exc}~23000 cm^{-1} ~2.9 eV (band gap at 6 K=2.821 eV). This sample, like all the other samples discussed in this paper, was grown by molecular-beam epitaxy (MBE) on either n-type or semi-insulating GaAs substrates in a Varian Gen II machine using one part per million pure grade elemental zinc and selenium from Osaka Asahi Metal Manufacturing Co., Ltd. Typical carrier concentration in these samples was found to be of the order of 10^{15} cm^{-3} which is roughly an order of magnitude less than most of the samples studied previously in the literature.[3] The substrate temperatures and growth rates used were 300–350 °C and 0.5 μm/h, respectively. The thickness of the epilayer discussed in Fig. 1 was ~3 μm. Although there is a 0.27% lattice mismatch between ZnSe and GaAs, it has been shown that most of the biaxial compressive strain in the epilayer due to this mismatch is relaxed for such thick layers at the growth temperatures. However, once the layers are cooled down to room temperature or below, the ZnSe epilayers undergo in-plane biaxial tension due to the *thermal* mismatch with the GaAs substrates.[4] This gives rise to the splitting of the free-exciton transitions associated with light- and heavy-hole bands as indicated in Fig. 1(a), denoted by FX^{lh} and FX^{hh}, respectively.[5] Unintentionally doped samples grown from high-purity sources frequently exhibit transitions due to neutral donor-bound excitons (D^0,X) associated with light- and heavy-hole bands, represented as I_{20}^{lh} and I_{20}^{hh}, respectively.[5,6] The very weak shoulder on the lower energy side of I_{20}^{lh} indicates those transitions which are due to excitons bound to ionized donors, I_3.[2] It is important to note that the samples grown from high-purity sources typically show a spectrum, such as in Fig. 1(a), in which the ratio R of the overall integrated intensity of the donor-bound exciton (D^0,X) region to that of the free-exciton region is very small relative to most of the samples studied previously (see also, Ref. 7). With such weak (D^0,X) transitions, the two-electron satellites ($2EL$) are generally extremely weak, as indicated in the vicinity of 22400 cm^{-1} in Fig. 1(a). There are additional features, discussed below, that are typically observed in such high-purity samples in the

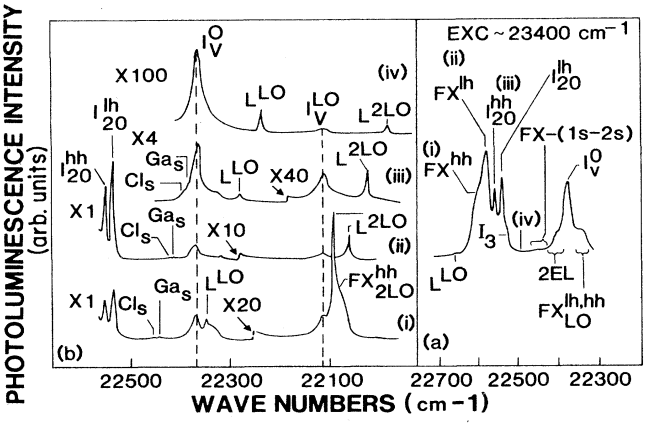

FIG. 1. (a) Typical ~6 K photoluminescence spectrum, using above-band-gap excitation radiation, from a ~3-μm ZnSe/GaAs epilayer, grown by molecular-beam epitaxy using ultra-high-purity sources of zinc and selenium. The peak labeled I_V^0 at 22380 cm^{-1} is routinely observed in such samples of very low background impurities. (b) Selective PL at 6 K with excitation positions indicated in (a). The peak I_V^0 is still very clearly visible (iv) even when excitation radiation well below the exciton transition energies is used.

vicinity of the transition region resulting from the inelastic scattering of FX^{hh} and FX^{lh} excitons by longitudinal-optical (LO) phonons, $FX_{LO}^{lh,hh}$.

We are particularly interested in an intriguing feature which is found to lie very close in energy to $FX_{LO}^{lh,hh}$, labeled I_V^0 in Fig. 1(a) with the transition energy of 22 380 cm^{-1} (2.7738 eV). On a cursory sight, one can easily confuse this peak with $FX_{LO}^{lh,hh}$, especially in the samples where it is very weak.[1] However, selective PL (SPL) and PL excitation (PLE) experiments conclusively show that I_V^0 is indeed due to an independent transition. SPL spectra for the sample, whose above-band-gap spectrum is given in Fig. 1(a), are shown in Fig. 1(b), for various excitation energy positions labeled (i)–(iv). These selective excitations were carried out using radiation from the Stilbene-III dye, pumped by ~2 W of ultraviolet (363.8–351.1 nm) light from an Ar-ion laser. Exciting into the excitonic regions (i)–(iii), no observable change in the shape and intensity of I_V^0 is detected [spectrum (iii) is amplified by a factor of 4 compared with (i) and (ii)]. However, we do observe various weak scattering processes. For example, we observe the Raman processes whereby the exciting photons are not only scattered by the LO phonons (L^{LO}), but also by the two residual donor impurities believed to be present in this sample, chlorine and gallium, denoted by Cl_s and Ga_s, respectively.[8] This assignment is based on the fact that the localization energies of Cl_s and Ga_s, with respect to the exciting photon energies, remain constant at ~19.1 and ~20.1 meV, respectively, close to the established ($1s$-$2s$) energies for chlorine and gallium donors. For the present study, the important point is that if we excite below the excitonic region, for example, at 22 500 cm^{-1} [position (iv) in Fig. 1(b)], we *still* observe I_V^0 and its LO-phonon replicas. Other evidence which points to the fact that I_V^0 is not related to free excitons is as follows.

The energy separation between I_V^0 and FX^{hh} is ~28.4 meV, which is much smaller than the low-temperature LO(Γ) phonon energy (~31.8 meV) and larger than the TO(Γ) energy (~26.4 meV) in ZnSe. Also, the intensity of I_V^0 is too high to be an LO replica of free excitons. Comparing the values of Huang-Rhys coupling factor of free excitons to LO phonons for several samples, we generally find a value close to 0.1, a value much too small to produce I_V^0 in Fig. 1. Another feature is the half width of I_V^0. Generally, free-exciton transitions are found to be much broader (~4 meV) compared with (D^0,X) transitions (<0.7 meV), and therefore their corresponding LO phonon replicas are also very broad (~4 meV). This is inconsistent with the sharpness of I_V^0 (~2 meV). It is interesting to note here that in the spectra of the samples, such as the one shown in Fig. 1, the LO replicas related to both the light- and heavy-hole components of the free exciton are generally observed, appearing as one broad overlapping band corresponding to both components. However, we find that in other samples, where the ratio R is larger, we observe predominantly the heavy-hole-related free-exciton FX_{LO}^{hh} replicas (see also Fig. 4).

The lack of relationship of I_V^0 to the creation of various excitonic processes is further exemplified in the PLE spectra of the sample corresponding to Fig. 1. Tuning the detector to the high-energy side of I_V^0, the region characterized by weak $2EL$ satellites, Fig. 2, spectrum (a) shows the usual absorption peaks at the $I_{2^0}^{lh}$ and $I_{2^0}^{hh}$ positions, and dips in the vicinity of $n=1$ and $n=2$ free-exciton transitions, caused by surface recombination enhanced by intense absorption of the light at these resonant energy positions. With the detector tuned to the I_V^0 transition energy [spectrum (b)], we no longer observe such sharp absorption features related to (D^0,X) transitions, as expected. However, the shape of the rest of the spectrum is virtually the same as the previous case. With the detector tuned below the I_V^0 energy position [spectrum (c)], we can also observe absorption corresponding to I_V^0 itself. From these data, we can conclude that there is no resonant enhancement of any exciton-related transitions correlated with I_V^0. We also note the presence of a relatively strong peak at ~22 462 cm^{-1} in the PLE spectra of this sample. The analogous transition is not observed in PL, however.

In Fig. 3, we show 6-K PL spectra of three ZnSe epilayers of comparable thicknesses. The spectrum in Fig. 3(a) is from the same sample that was discussed in Figs. 1 and 2, which has a relatively small ratio R, while trace (b) shows a spectrum with an intermediate value of R and, finally, spectrum (c) shows the largest value of R, by comparison, where the free-exciton peaks are barely discernible. First of all, we note that in these cases, the *overall* intensity of the band-edge luminescence (free- and bound-exciton related) increases as the ratio R increases, pointing to the fact that (D^0,X) transitions have a much larger oscillator strength compared with that of free excitons, so that, as the number of available donors increases, the intensity of donor-bound exciton peaks increases much more rapidly compared with that of free excitons. Concomitant with this increase in the (D^0,X) intensity, we see a clear reduction in the intensities of I_V^0 and a frequently observed line Y_0 at ~21 000 cm^{-1} (~2.6 eV). This general trend between (D^0,X) and Y_0 has already been observed previ-

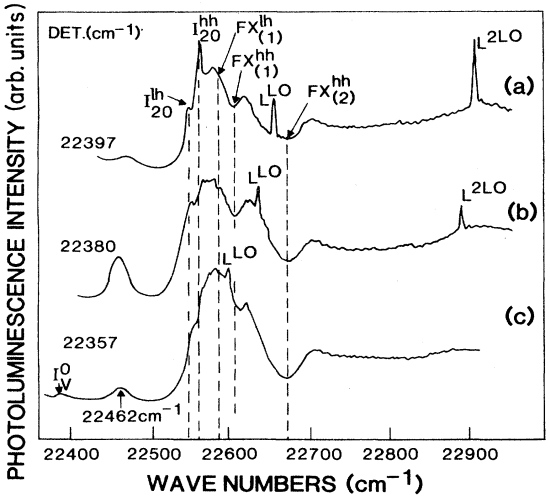

FIG. 2. (a) 6-K PL excitation spectrum with the detector at 22 397 cm^{-1}; (b) with the detector at the I_V^0 peak energy; (c) with the detector placed below the I_V^0 peak energy.

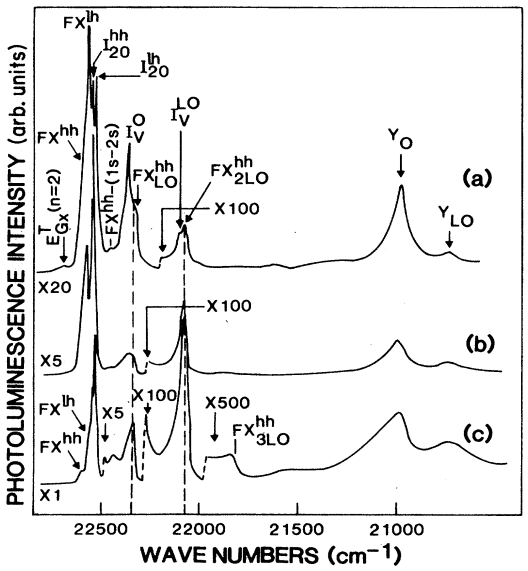

FIG. 3. 6-K PL spectra from three different ZnSe/GaAs epilayers. Spectrum (a) shows the smallest ratio of donor-bound to free-exciton integrated intensities; (b) shows an intermediate ratio, while (c) shows the highest ratio. As this ratio increases, the intensities of both I_V^0 and Y_0 are observed to decrease.

ously.[1] Although we also find that there may be a weak interplay between (D^0,X) and Y_0, our data, accumulated for more than 20 samples, do not show a very clear relationship between the two. Nevertheless, we find that I_V^0 becomes unobservable as soon as (D^0,X) intensity increases. Therefore, only the very pure samples, as defined by weak or no (D^0,X) transitions, show I_V^0.

We also find that as we increase the Zn/Se beam pressure ratio (BPR) during the growth, we observe an increase in the I_V^0 intensity. An example of such an increase is illustrated in Fig. 4. The upper trace shows a spectrum from a sample which was grown with a Zn/Se BPR of 0.22, where (D^0,X) intensities are relatively much stronger than those due to free excitons. We note that the I_V^0 line is barely present in this case. By contrast, we notice in the lower trace, for a sample of comparable thickness which was grown with a BPR of 0.58, where the (D^0,X) intensity is much weaker by comparison, that the peak I_V^0 appears much stronger. Therefore, increased Zn/Se BPR (zinc-richer environment) appears to have reduced the gallium substitution at the zinc site, as evidenced by the reduced intensity of mainly the FX_{2s}^{Ga}(hh) peak and the absence of gallium-related $2EL$ satellites. In addition, the peak FX_{2s}^{Ga}(hh), due to inelastic scattering of FX^{hh} excitons by gallium donors, is much stronger than that for chlorine FX_{2s}^{Cl}(hh) (barely discernible) for the upper trace. We also observe, only in the upper trace, the $2EL$ transitions involving inelastic scattering of I_{20}^{lh} and I_{20}^{hh} excitons from the gallium donors.

Figure 5 shows the temperature dependence of PL of a sample with a particularly strong I_V^0 line. As the temperature is increased from 6 K, we observe the Boltzmann thermal population of heavy-hole-related strain-split components which results in an enhancement of FX^{hh} and I_{20}^{hh} lines relative to their lower energy counterparts, as well as the red shift of the band gap. Concomitant with this, a decrease in the intensity of I_V^0 is observed and, by the time the temperature of the sample is raised to ~45 K, the peak I_V^0 is barely discernible. This behavior suggests that the level responsible for I_V^0 lies close to the conduction-band edge so that as we raise the temperature of the sample, thermal depopulation of the state responsible for I_V^0 takes place relative to the donor and conduction-band states lying above it. On the contrary, if the level were close to the valence-band edge, then we would expect that

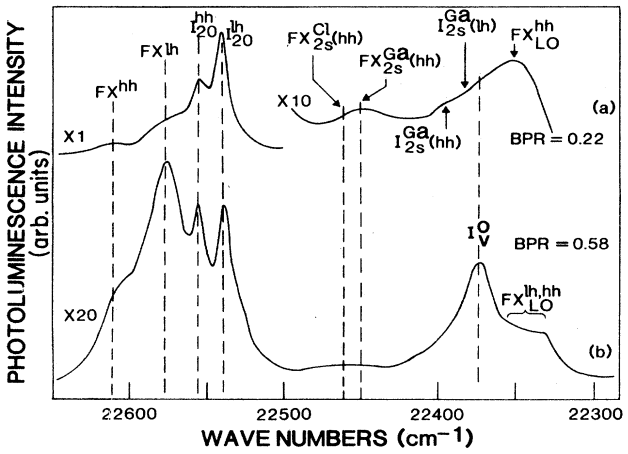

FIG. 4. (a) 6-K PL from a ZnSe epilayer which was grown with a Zn/Se beam pressure ratio (BPR) of 0.22. (b) Same as (a), but for a sample grown with a Zn/Se BPR of 0.58.

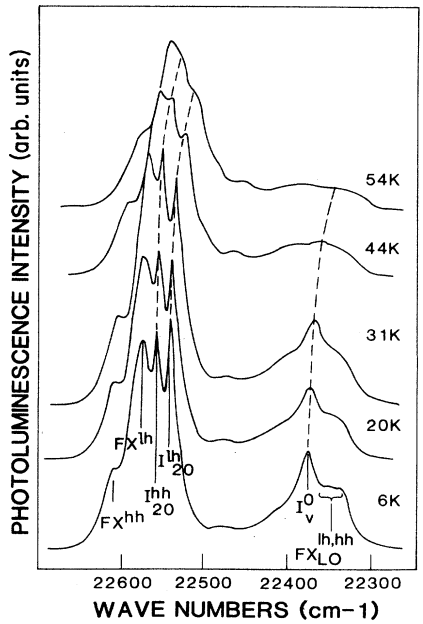

FIG. 5. PL as a function of the lattice temperature of a ZnSe epilayer to study the behavior of the peak I_V^0.

its population with temperature would not be significantly affected since the Fermi level still lies well above it (for n-type material) at 50 K. Furthermore, the temperature-dependence data also show that the emission due to donor-bound excitons is clearly observed even above 50 K. It follows that if I_V^0 was due to an excitonic defect, where the binding energy of the electron hole to the defect is expected to be at least as much as for the case of donor- or acceptor-bound excitons, it should also persist above 50 K. Therefore, we believe that I_V^0 is probably not due to excitonic recombination.

The data of Figs. 1 and 2 clearly demonstrate that I_V^0 is not a by-product of free or bound exciton creation but is, instead, an independent entity. The LO phonon coupling S for I_V^0 is very weak ($\sim$0.04) considering the fact that its localization energy is $\sim$29 meV. This is to be contrasted with the case of, for example, I_i^{Li} in ZnSe with $S\sim0.05$ and a localization energy of 10.5 meV. Generally, the LO coupling is expected to increase monotonically with the localization energy of the center.[9] This suggests that I_V^0 may be a result of recombinations involving states, due to some localized defect complexes containing several recombination sites, which have only a small variation in energy to produce line broadening. We rule out structural defects or dislocation loops since most of our samples showing strong I_V^0 are fairly thick (>3 μm), and we believe, based on transmission electron microscope investigations,[4] that there is no obvious evidence of such defects, so long as we probe far away (>1 μm) from the ZnSe/GaAs interface. Most of the PL signal, even for resonant excitation conditions, is originating from the top 1 μm or less of the epilayer, which is expected to be free of these macroscopic defects. Since only those samples show strong I_V^0 which show very weak or no impurity-bound exciton transitions, i.e., very pure samples, we suggest that this peak may be related to an intrinsic type of defect. Among the intrinsic defects or defect complexes one can expect selenium or zinc vacancies, antisite defects, or other vacancy-donor complexes. We believe that there must be a negligibly small concentration of zinc vacancy-related defects in our undoped epilayers, which manifest themselves typically in the form of self-activated luminescence associated with (V_{Zn}-donor) complexes. Furthermore, PL data as a function of different BPR (Fig. 4) show that, as we increase BPR (by reducing the selenium flux), we observe a strong increase in the intensity of I_V^0, suggesting that it may be a function of a selenium-site-related defect. The temperature-dependence behavior also suggests that I_V^0 may be due to a state which may be close to the conduction-band edge. Therefore, with the aforementioned data and analysis, a compelling assignment is to relate I_V^0 to a selenium-site-related defect. As an example, a selenium vacancy or a defect complex involving selenium vacancies is expected to behave as a donor.[10]

In summary, we have presented optical data for a transition I_V^0, which is observed in only those epilayers which have a very low residual background impurity concentration. We showed that this transition is not related to the formation of free and bound excitons, as was previously suggested, even though it is strongly present in those epilayers which show dominant free-excitonic transitions. The temperature-dependent data show that I_V^0 may be due to a state which lies close to the conduction-band edge. Contrasted with other typical impurity-bound exciton transitions in ZnSe, I_V^0 is found to be very broad, but, at the same time, its coupling to LO phonons is very weak for such high localization energy. Also, upon examination of various samples grown under different Zn/Se beam pressure ratios, we suggest that I_V^0 may be a result of recombination at some localized, intrinsic defect complex, possibly involving selenium-site-related defects.

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