

# Optical properties of $\delta$ -doped ZnSe:Te grown by molecular beam epitaxy: The role of tellurium

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We have studied the optical properties of the  $\delta$ -doped ZnSe:Te system using photoluminescence (PL) and x-ray and Raman scattering. Two different types of sample were investigated, (1) with a single  $\delta$  layer and (2) with three adjacent  $\delta$  layers separated by undoped layers. All of these samples are of reasonable crystalline quality and have the symmetry of the host ZnSe lattice as determined by x-ray and Raman scattering. The PL from each sample is very similar to the PL from bulk Zn-Se-Te solutions at low Te concentrations. The PL from the single- $\delta$ -doped material shows emission relatively close to the band edge which we attribute partly to  $\text{Te}_2$  clusters (nearest-neighbor pairs) and partly to non-nearest pairs. This PL changes with storage time, from which we conclude that the nearest-neighbor pairs are more stable than non-nearest-neighbor pairs. The triple- $\delta$ -doped material also shows a deeper PL feature, with a peak at about 2.48 eV, which we attribute to  $\text{Te}_{n \geq 3}$  clusters as well as to corresponding non-nearest-neighbors pairs.

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## I. INTRODUCTION

II-VI wide band gap semiconductors are of great interest as blue and green light emitters.<sup>1,2</sup> For these, as well as for many other devices, good bipolar conductivity is required. For the semiconductors of specific interest in this paper (ZnSe and related alloys) it has been difficult to obtain good  $p$ -type material. For this reason, the  $\text{ZnSe}_{1-x}\text{Te}_x$  system has long been of interest, since it is relatively easy to obtain  $n$ -type ZnSe and  $p$ -type ZnTe. Therefore many studies on both bulk<sup>3-9</sup> and epitaxial<sup>10-13</sup> [molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition]  $\text{ZnSe}_{1-x}\text{Te}_x$  have been performed to understand this system. Another area where the role of the ZnTe/ZnSe system is important is in the use of ZnSe/ZnTe:N superlattices as contact layers for ZnSe based devices.<sup>14</sup> For example, Jung *et al.*<sup>15</sup> have reported hole concentrations up to  $7 \times 10^{18} \text{ cm}^{-3}$  by using  $\delta$ -doped superlattices of ZnSe/ZnTe:N. Furthermore, it has recently been proposed<sup>16</sup> that the Zn-Se-Te system be used for light emitting devices in the green spectral region.

The undoped  $\text{ZnSe}_{1-x}\text{Te}_x$  system has been studied fairly extensively, and there is considerable work on its photoluminescence (PL) properties. It is generally agreed that the dominant PL from  $\text{ZnSe}_{1-x}\text{Te}_x$  is due to excitons bound to various Te-related defects. However, the microscopic origin of these excitons is still uncertain. Some of the published identifications of the PL are summarized in Table I. A band at around 2.65 eV usually dominates in  $\text{ZnSe}_{1-x}\text{Te}_x$  with small Te concentrations (up to  $x < 1.5\%$ ), while a band with a maximum at about 2.45–2.48 eV dominates in samples with larger Te concentrations. These bands are generally attributed to excitons bound to isoelectronic  $\text{Te}_{\text{Se}}$  atoms and/or clusters in ZnSe. Specifically, Refs. 3, 4, 8, 11 and 12 attributed the higher-energy band to excitons localized at  $\text{Te}_2$  complexes and the lower-energy line to those at  $\text{Te}_{n > 2}$  com-

plexes. It is important to note that Akimova *et al.*<sup>3</sup> used cathodoluminescence to obtain the most direct evidence that the 2.65 eV band is due to  $\text{Te}_2$  complexes and that the 2.45–2.48 eV band is predominantly due to  $\text{Te}_n$  clusters with  $n = 3$ . In Refs. 5–7, on the other hand, these two lines were attributed to self-trapped excitons at a single Te atom and at  $\text{Te}_2$  complexes, respectively. Furthermore, in some samples with very low Te concentrations ( $< 1\%$ ), lines in the 2.75–2.784 eV region,<sup>7,8,12</sup> and sharp lines attributed to LO phonons<sup>17</sup> or impurity-related<sup>3</sup> PL have also been reported.

The present paper also investigates this Zn-Se-Te system, but using  $\delta$ -doped ZnSe:Te grown by MBE on (001) GaAs substrates. We shall show that this ‘‘unusual’’ Te configuration gives an unambiguous identification of the Te related PL from ZnSeTe. We would like to note that some results on  $\delta$  superlattices were reported by Fu *et al.*<sup>18</sup>

We have investigated two types of sample: sample A, consisting of one Te-containing layer per 10 undoped layers of ZnSe ( $\delta$ -ZnSe:Te) and sample B, consisting of three adjacent Te-containing layers per 10 undoped layers of ZnSe ( $\delta^3$ -ZnSe:Te). We used primarily low-temperature photoluminescence to analyze these samples, complemented by x-ray diffraction (XRD) and room temperature polarized Raman spectroscopy.

## II. GROWTH

The samples were grown on (001) GaAs substrates by MBE in a Riber 2300 system which includes III-V and II-VI growth chambers connected by ultrahigh vacuum (UHV). Oxide desorption of the GaAs substrates was performed in the III-V chamber by heating the substrates to 590 °C with an As flux impinging on the surface. Then, a 200 nm GaAs buffer layer was grown at 580 °C with a streaky ( $2 \times 4$ ) reflection high-energy electron diffraction (RHEED) surface pattern. The substrate with the GaAs buffer layer was trans-

TABLE I. Comparison of assignments in Te-related PL in  $\text{ZnSe}_{1-x}\text{Te}_x$ .

| Reference | Blue band              |                                    | Green band             |                                 | Te conc. (%)      |
|-----------|------------------------|------------------------------------|------------------------|---------------------------------|-------------------|
|           | Position (eV)          | Assignment                         | Position (eV)          | Assignment                      |                   |
| 3         | 2.61–2.63              | $\text{Te}_2$ clusters             | 2.48–2.50              | $\text{Te}_3$ clusters          | <2                |
| 4         | 2.65                   | $\text{Te}_2$ clusters             | 2.50                   | $\text{Te}_3$ clusters          | 1–2               |
| 5         | 2.65                   | $\text{Te}_1$                      | 2.50                   | $\text{T}_2$ clusters           | 1                 |
| 17        | 2.67                   | small Te clusters                  | 2.50                   | small Te clusters               | 1                 |
| 6         | 2.67                   | $\text{Te}_1$                      | 2.48                   | $\text{Te}_{n \geq 2}$ clusters | 10–40             |
| 7         | 2.65                   | $\text{Te}_1$                      |                        |                                 | 1                 |
| 12        | 2.65                   | $\text{Te}_{n \geq 2}$ (distant)   | 2.45                   | $\text{Te}_2$ clusters          | 1–4               |
| This work | 2.64–2.66 <sup>a</sup> | $\text{Te}_2$ defects <sup>b</sup> | 2.48–2.50 <sup>c</sup> | $\text{Te}_{n \geq 3}$ clusters | <1.8 <sup>d</sup> |

<sup>a</sup>Dominant in  $\delta$ -doped ZnSe:Te.

<sup>b</sup>This band is a combination of the PL due to nearest- and non-nearest-neighbor Te pairs (for more details see Sec. IV).

<sup>c</sup>Dominant in  $\delta^3$ -doped ZnSe:Te.

<sup>d</sup>Averaged over the sample.

ferred to the II-VI chamber under UHV. Prior to the growth of the II-VI epilayers, we performed a Zn irradiation of the GaAs surface. This step is intended to suppress the formation of  $\text{Ga}_2\text{Se}_3$  at the III-V/II-VI interface, which is believed to be related to the formation of stacking faults.<sup>19</sup> Then a 400 nm thick undoped ZnSe buffer layer was grown at 250 °C under Se rich conditions with a growth rate of  $\sim 0.8 \mu\text{m/h}$ . The RHEED pattern is a streaky ( $2 \times 1$ ) after the buffer layer growth. The  $\delta$ -doped region was grown on the ZnSe buffer layer.

Two samples (A and B) were grown. Sample A consists of 140 periods of single Te-containing layers separated by 10 monolayers (ML) of ZnSe spacers and sample B consists of 120 periods of three consecutive Te-containing layers separated by 10 ML of ZnSe spacers. Sample A is about 4000 Å thick and sample B is about 5000 Å thick. Figure 1 shows the shutter control sequence used for the  $\delta$  doping. The Zn and Se shutters were first opened for 13 s to grow 10 ML of a ZnSe spacer, after which the Se shutter was closed for 5 s to produce a Zn-terminated surface. Then all shutters were closed for 5 s to desorb excess Zn from the surface. After this the Te shutter was opened for 5 s to deposit Te onto the Zn-terminated surface, and then all shutters were closed for 5 s followed by opening the Zn shutter for 5 s to produce another Zn-terminated surface. The Se shutter was then opened to start the next growth sequence. This sequence was repeated for 140 periods (sample A) in order to obtain layers thick enough for measurement. For sample B, the shutter control sequence is similar to that of sample A except that the Te doping steps were repeated three consecutive times, as shown in Fig. 1 by the dashed arrow, and the total sequence was repeated for 120 periods. The RHEED pattern is ( $2 \times 1$ ) during the ZnSe spacer growth. It changes to  $c(2 \times 2)$  after the ZnSe surface is exposed to Zn and remains  $c(2 \times 2)$  after the surface is exposed to Te. Since a very small Te flux is used during  $\delta$  doping, only a fraction of a Te layer is deposited.

### III. EXPERIMENTAL PROCEDURE AND RESULTS

The quality of the samples and the average Te content were assessed by single-crystal x-ray diffraction, using Cu

$K\alpha$  and the (004) reflection. Polarized Raman scattering was measured at room temperature using the 488 nm line of an  $\text{Ar}^+$  laser in the  $z(x,x)\bar{z}$ ,  $z(x,y)\bar{z}$ ,  $z(x',x')\bar{z}$ , and  $z(x',y')\bar{z}$  polarization configurations, where  $x$ ,  $y$ , and  $z$  refer to the principal cubic axes with  $z$  being parallel to the growth direction;  $x'$  and  $y'$  are obtained by rotating the  $x$  and  $y$  axes, respectively, by  $45^\circ$  in the  $xy$  plane. Incident laser light was focused to a spot size of  $\sim 2 \mu\text{m}$  in diameter. The backscattered light was dispersed by a 0.6 m single-dispersive/double-subtractive monochromator, and collected by a cooled charge-coupled device array, leading to a resolution of the Raman spectra better than  $1 \text{ cm}^{-1}$ .

For PL measurements, the samples were kept either in He gas ( $T=5 \text{ K}$ ) or at the cold stage of a closed cycle refrigerating system ( $T=11 \text{ K}$ ). The temperature in both cases was monitored by a silicon diode mounted in the vicinity of the sample. The 325 nm line of a He-Cd laser was used as the excitation source. The PL was dispersed through a 3/4 m monochromator and was detected with a low-noise photomultiplier tube, whose output was connected to either a SR400 photon counter or a lock-in amplifier.

From the (004) reflection XRD curves we estimate that the average Te concentration is 1.4% for sample A and 1.8% for sample B, assuming that Vegard's law is valid and that the epilayers are fully relaxed. (Note that since the epilayers may not be fully relaxed the estimated values represent the upper limits for the Te concentration.)

The polarized Raman spectra were obtained from the Te-

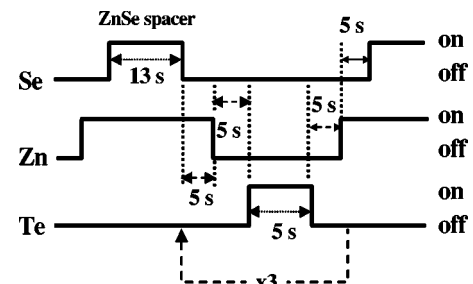


FIG. 1. Shutter sequence for growth of  $\delta$ -doped layers.

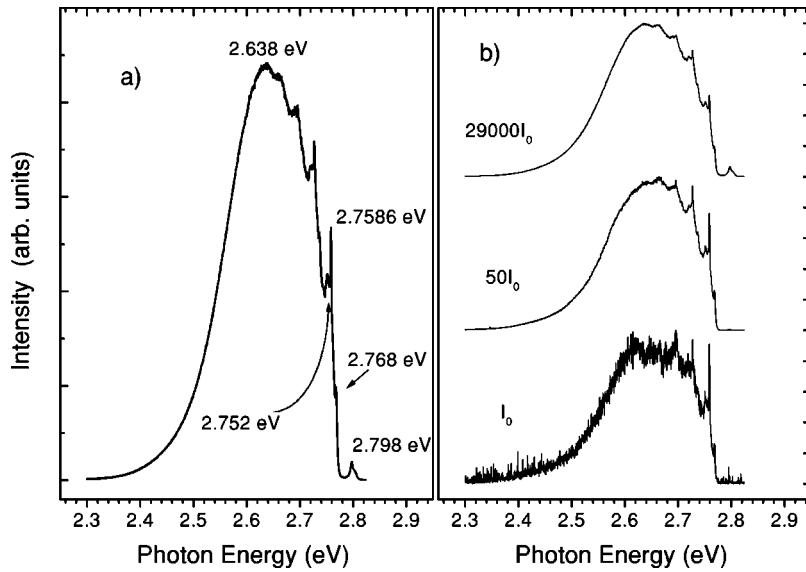


FIG. 2. (a) Low-temperature (10 K) photoluminescence from the  $\delta$ -ZnSe:Te sample; (b) the same spectrum recorded at different excitation intensities (spectra arbitrarily shifted in vertical direction for convenience).

doped samples and for comparison, from a pure ZnSe sample. The scattering from all samples exhibits two peaks at about  $252 \text{ cm}^{-1}$  and  $291 \text{ cm}^{-1}$  for the  $z(x',y')\bar{z}$  configuration and no peaks for the  $z(x',y')\bar{z}$  configuration. The peaks are due to ZnSe and GaAs LO phonons, respectively. No TO phonons were observed. Further, in each case LO phonons were observed for  $z(x,y)\bar{z}$ , but not for  $z(x,x)\bar{z}$ , and no TO phonons were observed either.

We plot in Fig. 2(a) the PL spectrum from the  $\delta$ -ZnSe:Te sample. There is a broad band with a maximum at around 2.64 eV, which is overlaid by sharp peaks on the high-energy wing. These sharp peaks can be grouped into three series, with the lines in each series separated by the ZnSe LO phonon (0.031 eV) energy: (a) 2.768 eV, 2.736 eV, 2.705 eV; (b) 2.758 eV, 2.727 eV, 2.696 eV, 2.665 eV, 2.634 eV; and (c) 2.751 eV, 2.720 eV, 2.689 eV. The low-energy side does not have any sharp structure. Figure 2(b) shows the PL spectra for this sample taken at different excitation intensities. (For convenience, these curves and all subsequent ones are normalized to the corresponding maxima and arbitrarily shifted on the intensity scale.) There is no substantial peak shift with excitation intensity, either for the band as a whole or for the sharp peaks. At high excitation intensities one can also observe a small peak at about 2.798 eV.

It is noteworthy that this spectrum initially changed during storage. Figure 3 shows spectra taken shortly after growth and three months later, under similar conditions. It can be noted that the maximum of the main band moves to lower energies, and the sharp lines become more pronounced. Moreover, the sharp lines also become sharper at lower temperatures and excitation intensities (Figs. 2–4). In Fig. 4 we plot spectra from the sample A taken at different temperatures, with Fig. 4(a) showing the PL obtained at the maximum excitation density and Fig. 4(b) at an intensity about two orders of magnitude lower. A further noteworthy feature of the spectra in Fig. 4 is that they indicate the presence of a peak at about 2.61 eV, which can best be seen in the 50 K curves (also see Sec. IV).

The PL spectra from sample B are shown in Fig. 5. This

sample exhibits two broad Gaussian-shaped bands with the maxima at about 2.664 eV (blue band) and at 2.493 eV (green band). Both peaks show little or no shift with excitation intensity. In contrast to sample A, we did not see any significant changes with time in the PL from this sample. We have also performed temperature studies on sample B using low and high excitation intensities. As expected, the green band dominates at lower excitation intensities and higher temperatures. We used the temperature dependence of the PL at low excitation intensities to obtain the activation energy of thermal quenching for the green PL. (Contributions to the PL from the blue band are almost completely suppressed at low excitation intensity.) Figure 6 shows the peak intensity vs inverse temperature (circles) for this band and the fitting (solid curve), using the following expression (e.g., Ref. 20):

$$I_{\max}(T) = \frac{I_{\max}^0}{1 + CT^2 \exp[-E_A/k_B T]} \quad (1)$$

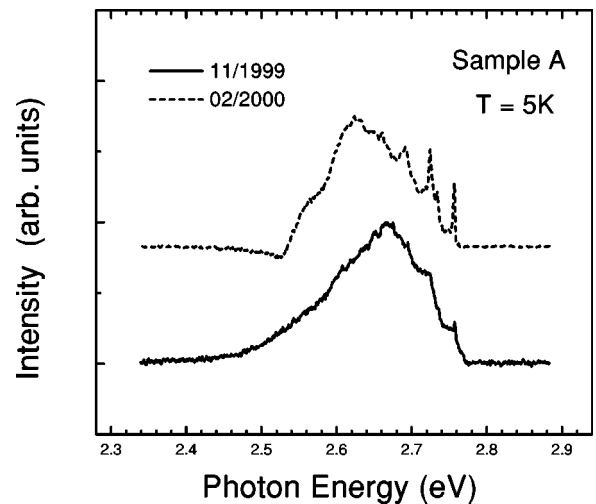


FIG. 3. Low-temperature (5 K) photoluminescence from the  $\delta$ -ZnSe:Te sample recorded on different dates.

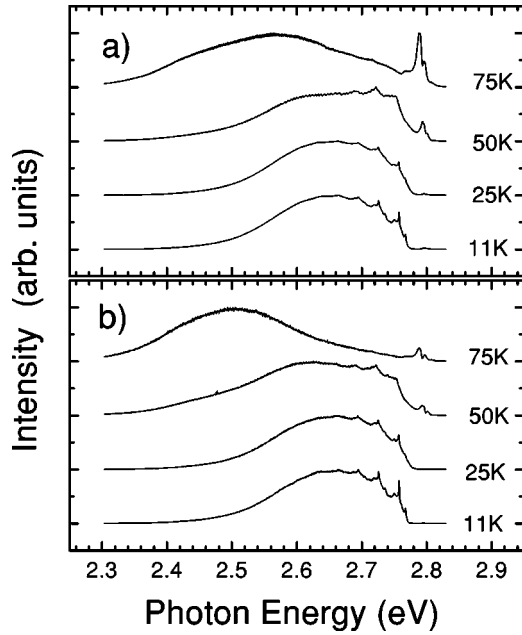


FIG. 4. Temperature evolution of PL from the  $\delta$ -ZnSe:Te sample (a) at highest excitation intensity and (b) at an excitation intensity about two orders of magnitude lower.

Here  $I_{\max}^0$  and  $C$  are constants,  $T$  is the temperature,  $k_B$  is the Boltzmann constant, and  $E_A$  is the activation energy.<sup>21</sup> Such a fitting resulted in  $E_A = 178$  meV. A rather detailed discussion of the temperature dependence of PL from ZnSeTe alloys and a specific model of the exciton capture process can be found, for example, in Ref. 11. We note here that our value of the activation energy is quite close to that (160 meV) obtained by Dhese *et al.*<sup>11</sup>

Furthermore, we plot in Fig. 7 the full width at half maximum (FWHM) for the green band as a function of temperature. It is interesting to note that, contrary to expectations, FWHM decreases initially when the temperature is raised. The possible cause of such behavior is discussed in the next section.

#### IV. DISCUSSION

The observations of polarized Raman scattering are in excellent agreement with theoretically predicted selection rules for the Raman spectra from (001)-oriented zinc blende crystals.<sup>22</sup> Yang *et al.*,<sup>13</sup> however, did see the TO phonons in their MBE-grown ZnSe<sub>1-x</sub>Te<sub>x</sub> alloys with  $x \geq 4\%$ , which could be attributed to the presence of compositional disorder that relaxes the selection rules. Given the layered structure of our system, one might have expected quite large fluctuations; however, the Raman scattering results show that this is not the case. Of course, nonresonant Raman data do not prove the absence of fluctuations, but they do show that such fluctuations are not strong, i.e., that the samples are of reasonably good quality. Furthermore, these results support our conclusions about low Te content, obtained from XRD, since we also did not see any changes in the LO shift from the values observed in pure ZnSe. It has been shown previously<sup>9</sup> that the LO shift decreases linearly with Te content, but changes in the Raman shift that are associated with less than 2% Te are expected to be smaller than instrumental limits. In addition, the FWHM's of all Raman peaks from our samples are smaller than or comparable to those previously reported for ZnSe<sub>1-x</sub>Te<sub>x</sub> with low Te concentrations.<sup>9,13</sup>

To explain the PL data, we first note a strong similarity in many respects to the PL of bulk ZnSe<sub>1-x</sub>Te<sub>x</sub> solid solutions with relatively low Te content. We note in particular the following features. A band at around 2.65 eV usually dominates in ZnSe<sub>1-x</sub>Te<sub>x</sub> with  $x < 1.5\%$ , while a band with a maximum at about 2.45–2.48 eV dominates in samples with larger Te content. These bands have generally been attributed to excitons bound to isoelectronic Te<sub>Se</sub> (atoms and/or clusters) in ZnSe; however, the microscopic nature of the binding sites is still controversial. References 3, 4, 8, 11, and 12 attributed the higher-energy band to excitons localized at Te<sub>2</sub> complexes, and the lower-energy line to those at Te<sub>n>2</sub> complexes, quite likely  $n = 3$ .<sup>3</sup> In Refs. 5–7 these two lines were attributed instead to self-trapped excitons at a single Te atom and at Te<sub>2</sub> complexes, respectively. In samples with

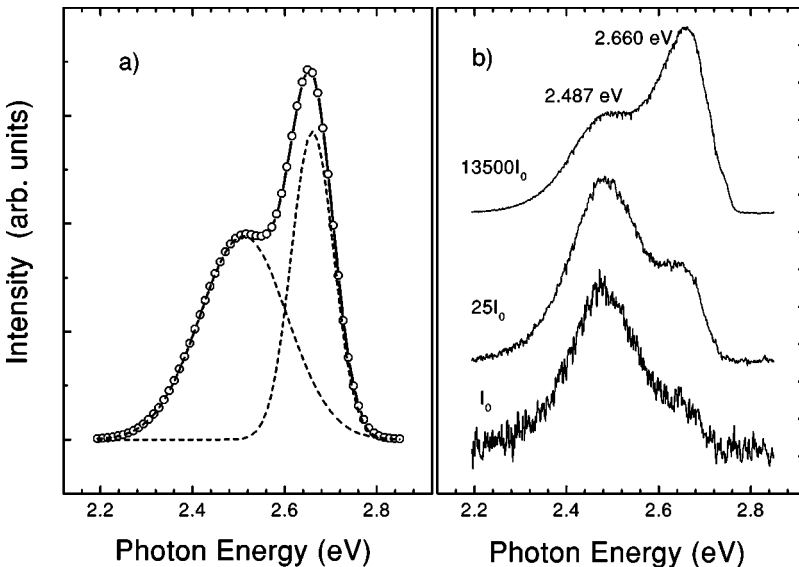


FIG. 5. (a) Low-temperature (10 K) photoluminescence from the  $\delta^3$ -ZnSe:Te sample; the dashed lines are a Gaussian fit. (b) The same spectrum recorded at different excitation intensities (spectra arbitrarily shifted in the vertical direction for convenience).

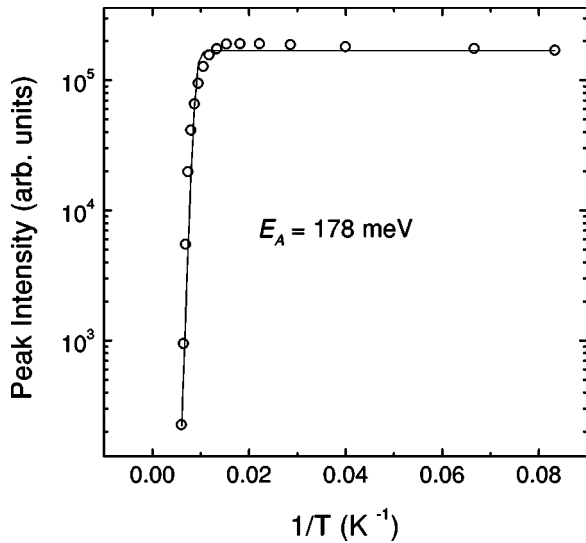


FIG. 6. Peak intensity of the green band of the  $\delta^3$ -ZnSe:Te sample as a function of inverse temperature.

very low ( $<1\%$ ) Te concentrations lines at 2.75–2.784 eV were reported<sup>7,8,12</sup> and attributed either to free excitons<sup>7</sup> or to an exciton localized either at a Te atom<sup>12</sup> or in compositional fluctuations.<sup>8</sup> Sharp “LO” lines<sup>3,17</sup> were attributed to resonant<sup>8,17</sup> excitons or to an “impurity-Te” complex.<sup>3</sup>

In most of the previous literature, there is little distinction between Te clusters (nearest neighbors) and other configurations. Such a distinction, to some degree, was pointed out by Yang *et al.*<sup>12</sup> These authors attributed the peak with the maximum at 2.65 eV to excitons bound to two or more isolated Te atoms (i.e., pairs or triplets on non-nearest-neighbor sites in our terminology); however, this seems unlikely in view of current results, since this peak is observed in both our samples. They<sup>12</sup> attributed their 2.78 eV transition to excitons localized at  $Te_1$ . (A similar peak at 2.75 eV reported by Permogorov and Reznitsky<sup>8</sup> was attributed by them to free excitons localized by compositional disorder.) However, it is unclear how such  $Te_1$ -bound excitons, which are expected to have a lower binding energy than those localized at  $Te_2$  pairs, become dominant at higher temperatures.<sup>12</sup> As we will discuss further below, the assignment of this 2.78 eV peak to a free-to-donor (FD) transition would be more appropriate, since a FD peak usually dominates in ZnSe at higher temperatures<sup>23,24</sup> (see also the discussion in Ref. 3).

Since our samples are  $\delta$  doped, it is very unlikely that single Te atoms are present in sufficient concentrations to give a strong PL band; consequently, excitons localized at clusters [two or more nearest-neighbor (NN) Te atoms] or Te pairs, triplets, etc. (configurations other than NN) seem more likely. Further, PL from the ZnSe layers, if any, is quite weak, so the  $\delta$ -doped regions are primarily responsible for the PL. Presumably, this PL is due to the recombination of excitons at the above mentioned centers; the possibility of capture at quantum-well-like defects in the  $\delta$  region cannot be totally excluded at this point, but seems quite unlikely in view of the similarities to the data from bulk samples.

It is very clear from the variation with storage time [a

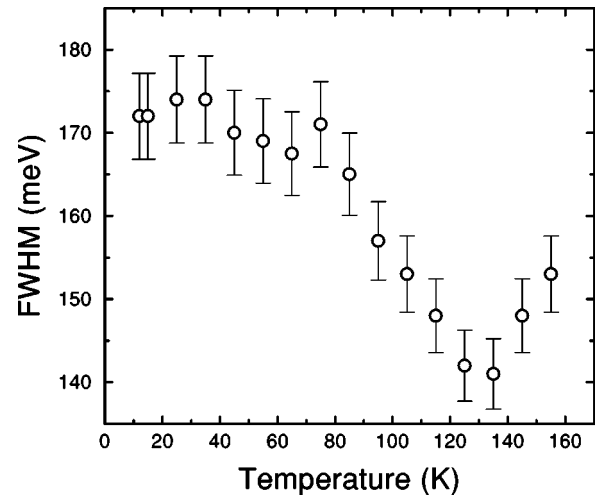


FIG. 7. Full width at half maximum (FWHM) of the green band of the  $\delta^3$ -ZnSe:Te sample as a function of temperature.

maximum at 2.67 eV initially and a maximum at 2.62 eV after 3 months, (Fig. 3)] that two or more different centers must be playing roles in the PL from this broad band. In examining the lowest-intensity curve in Fig. 2(b) and the data at 50 K (Fig. 4), we estimate that the band with maximum at about 2.64–2.65 eV consists of a band with a maximum at around 2.61 eV and contributions from the higher phonon replicas of the 2.758–2.768 eV transitions (see further discussion below). Note that some contribution from the band with the maximum at  $\sim 2.50$  eV is also possible, as seen at high temperatures (Fig. 4). It would be logical to assume that larger Te clusters would be responsible for deeper PL,<sup>25</sup> so we ascribe the 2.50 eV band to excitons localized at  $Te_n \geq 3$  clusters (following Ref. 3) and the 2.61 eV band to excitons localized at  $Te_2$  clusters. Interestingly, the observation of the 2.50 eV band shows that even in single  $\delta$ -doped layers there are enough large ( $Te_{n \geq 3}$ ) clusters to give substantial PL.

In view of the above, it is emphasized that the commonly reported peak at 2.64–2.65 eV (see Table I) is not due to a single center, but is, instead, a composite of several peaks due to several centers.

The several fairly similar sharp line series at 2.751, 2.758, and 2.768 eV with LO phonon replicas would be expected to be due to similar types of center. We suggest that these sharp lines are due to excitons bound to non-nearest-neighbor pairs; it seems reasonable that there would be a number of such pairs at different separations. [The phonon replicas are strong due to a relatively large Huang-Rhys factor<sup>26,27</sup> ( $S$ ) (also see Ref. 28)]. This is consistent with the assignment of the 2.61 eV peak to clusters, since one expects deeper levels for binding to nearest neighbors; our assignments are also consistent with observations and interpretations of the extensively studied case of N in GaP.<sup>29,30</sup> It is important to note, however, that recent calculations<sup>31</sup> on GaP:N showed that there is no unique relationship between neighbor separations and the energies of associated transitions; moreover, it has been suggested that at least one PL line in the GaP:N system

belongs to triplets. Therefore, we believe that ascribing each peak to a specific pair is not reasonable at this time.

Since the series of sharp lines is due to non-nearest neighbors and there are no higher-energy peaks associated with the Te-doped layers (see below), we excluded single Te atoms as candidates for the binding of excitons. This is already expected since there should be only a minimal number of single Te atoms in the  $\delta$  layers. Furthermore, systems that form alloys, i.e. give a change in band gap, such as Te in ZnSe, would not form “ideal” isoelectronic levels. Moreover, isoelectronic substituents should have a large difference in either electronegativity<sup>29,30</sup> or size<sup>32</sup> with the host atoms,<sup>26,30,33</sup> which is not the case here. Also, some theoretical first principles calculations suggest that a single Te atom should not bind an exciton.<sup>34</sup>

The changes observed with storage time in the PL of sample A (Fig. 3) are consistent with the diffusion of Te atoms. One can note that the maximum of the original PL is at about 2.67 eV and based on our assignments it is mainly due to non-nearest-neighbor pairs (and the corresponding phonon replicas); the maximum of the later PL is at about 2.62 eV, and more of it is due to Te<sub>2</sub> clusters. Since the total amount of Te is constant if one neglects the formation of single Te atoms (where only minimal such species are expected with  $\delta$  doping), this means that more Te<sub>2</sub> clusters form with time. It can be further noted that the sharp line structure also increases with storage time. We suggest the following explanation: the non-nearest-neighbor pairs are relatively shallow and thus have large Bohr radii; such large radii in turn lead to strong interaction between nearby centers, and resultant smearing of the sharp phonon structure. That is, we suggest that it is only when there are relatively few non-nearest pairs that one can observe the sharp phonon replicas. Details of these effects remain to be investigated.

Finally, we would like to comment on the peak at 2.798 eV. We note that this dominates at high temperatures and high excitation intensities (Fig. 4). We believe it is due to a free hole to shallow donor transition. Note (1) if this line were due to a donor bound exciton, it would not dominate at high temperatures, while it is well known that FD transitions dominate in ZnSe at high temperatures;<sup>23,24</sup> (2) this transition seems broader than expected for a “standard” bound excitonic recombination.

We believe that a shoulder on the high-energy side of this 2.798 eV line is due to free excitons which possibly originate from either the undoped ZnSe layers or the buffer layer (undoped ZnSe).

Now we discuss the PL from sample B (Fig. 5). This sample has a relatively low Te content ( $x < 1.8\%$ ), but exhibits PL that is characteristic of bulk ZnSe<sub>1-x</sub>Te<sub>x</sub> with  $x \geq 4\%$ . Since there are three adjacent Te layers in this sample, the probability of forming large complexes (Te <sub>$n \geq 3$</sub> ) should be high, while the presence of single Te atoms should be relatively quite low. The blue band observed from this sample peaks at an energy of 2.664 eV, close to that of the

dominant broad PL in sample A, and so we assign it to excitons localized at Te<sub>2</sub> centers. The lower-energy band, at 2.493 eV, is attributed to excitons localized at Te centers with  $n \geq 3$  (mostly Te<sub>3</sub> aggregates<sup>3</sup>). Both peaks can be fitted well by a Gaussian line shape, which results from large Huang-Rhys factors.<sup>26,28,35</sup> A relative decrease of the blue PL with decreasing excitation intensity is due to the movement of the hole quasi-Fermi level deeper into the band gap with decreasing excitation, and, once it “crosses” the hole energy level of the Te<sub>2</sub> clusters, the PL related to these clusters is effectively quenched. From the temperature quenching (Fig. 6) we have determined that the thermal activation energy of excitons localized at large clusters is close to 178 meV. Using a band gap of 2.82 eV for ZnSe (which is approximately that of our  $\delta$ -doped ZnSe:Te), the thermal activation energy gives the approximate energy of the no-phonon line for the green band of about 2.640 eV. This confirms that this band contributes to the apparent width of the PL due to Te<sub>2</sub>-localized excitons, as previously suggested. From the dependence of the FWHM of the green band on the temperature (Fig. 7), we can draw the important conclusion that this band is also due to several transitions, as has been suggested above for the blue band. Thus, it is expected that the FWHM will increase with increasing temperature due to an increase in the phonon density.<sup>36</sup> However, if we assume that this band has contributions from several centers, we can expect that the thermal ionization of the “shallower” transitions will lead to narrower spectra. Thus we conclude that the green band has a multicenter origin as well.

## V. SUMMARY

We have investigated the optical properties of single- and triple- $\delta$ -doped ZnSe:Te samples grown by MBE. These have the advantage of close clustering of Te atoms, which has allowed us to identify the origin of the Te-related PL in a manner that is consistent for both samples. We have concluded the following: (1) single Te atoms do not bind an exciton; (2) the bands with broad peaks near 2.50 eV are due to excitons trapped at large Te <sub>$n$</sub>  ( $n \geq 3$ ) clusters (NN) and related complexes; (3) the band with a maximum close to 2.61 eV is due to Te<sub>2</sub> clusters (NN), while non-nearest-neighbor Te pairs and more distant complexes are responsible for the PL at 2.751 eV, 2.758 eV, and 2.768 eV, and phonon replicas of these. These pairs strongly contribute to the 2.64–2.65 eV band due to strong hole-phonon interactions and the resultant phonon replicas. Previously, this commonly reported peak at 2.64–2.65 eV was attributed to a single center.

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