Temperature Dependence of Near Band-edge Luminescence in ZnSe

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Photo-luminescence near the band-edge region for undoped ZnSe single crystals are studied for a wide temperature range between 4 K and 200 K. Luminescence lines due to the recombination of bound excitons disappear between 50 K and 80 K because of the thermal dissociation and the polariton plays an important role in the near band-edge luminescence process even at higher temperature.

1. Introduction

Among II-VI semiconducting materials, ZnSe is known as one of the most promising materials for the blue light emitting devices. Luminescence properties concerning to excitonic and donor-acceptor pair (DAP) recombination over the wide temperature range have been studied by many investigators [1-8]. From the applicational standpoint, the most attention has been paid to the light emitting mechanisms in blue region at room temperature, and the following mechanisms may be responsible for the emission of blue light; (1) the free exciton (polariton) recombination [9,10], (2) the recombination of the excitons bound to neutral donros (acceptros) [11], (3) band-to-band recombination [6], and (4) the recombination between free electrons (holes) and acceptor holes (donor electrons) [8].

This paper is concerned with the observation of excitonic luminescence

200 K. The results show that luminescence from polaritons has a dominant contribution in the near band-edge region at an intermediate temperature range.

2. Experimental

ZnSe single crystals used in this work are prepared by the melt. The crystals are annealed in Zn vapor at 900℃ and then are etched in the hot NaOH solution to remove remained Zn on the surface and also deformed layer prior to the optical measurements. These procedures are effective in obtaining the sharp excitonic luminescence lines. The glass cryostat is used for the measurement at the liquid helium temperature (LHeT), and the helium gas flow type cryostat (OXFORD Model CF-4) is used for the measurements at elevated temperatures. During the measurements the sample temperature is controlled within the accuracy of 1 K. Ultra-violet light from the filtered Xe lamp is used for the excitation light source for the photoluminescence measurements and the non-filtered Xe lamp is used for the measurements of the reflection spectra. Luminescence is detected by an S-20 photomultiplier after dispersed by an 1-m monochromator (JOBIN YVON HR-1000).

3. Results and discussion

Photo-luminescence (solid curves) and reflection (dotted curve) spectra near the band edge region for an excellent ZnSe single crystal measured at 4.2 K are shown in Fig.1. The luminescence lines due to the annihilation of bound excitons, i.e. $I_2(1)$, $I_2(2)$, I_1^d, I_1^s, I_3 and also the luminescence lines due to the 2-electron transition are also observed. Their energetic positions are consistent with the previously reported results[2-4]. At highest energy region one small peak named LP and a shoulder named UP are also observed. It is noted that the reflection dip which is considered usually to be the position of free exciton, is situated just between the UP and LP lines. This kind of relation is widely observed for direct band gap semiconductors such as ZnTe[12] and GaAs[13], and the two luminescence lines have been ascribed to the annihilation luminescence of the polaritons in the upper polartion branch and in the lower one. Thus the UP and the LP lines in the present case also may be ascribed to the polariton luminescence in its upper

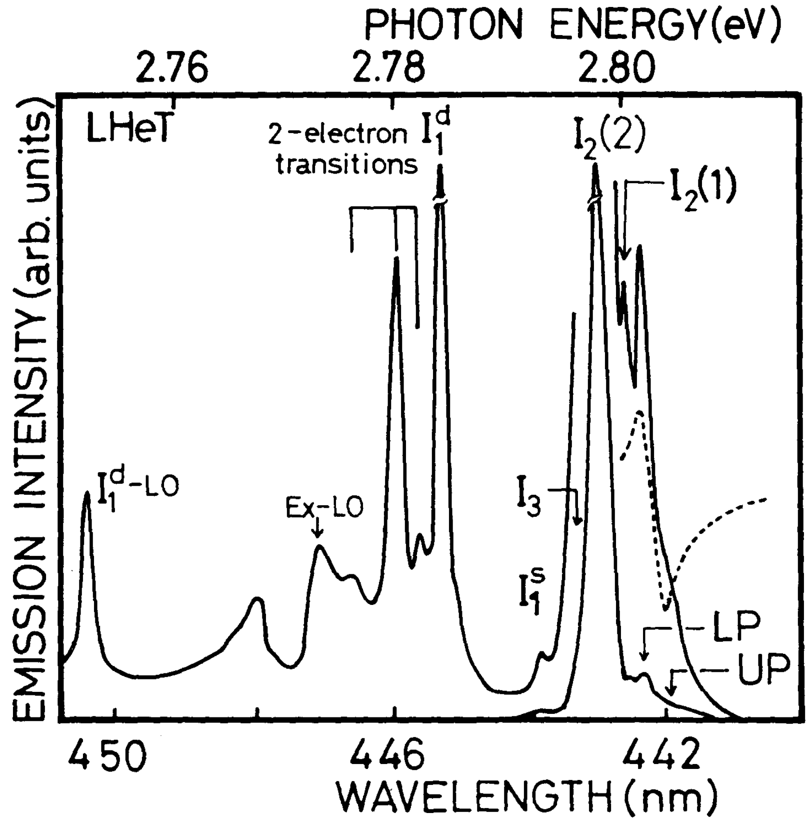

Fig. 1. Luminescence and reflection spectra near the band edge region for ZnSe single crystal measured at 4 K. Solid line shows the luminescence spectrum and broken line shows the reflection spectrum. $I_2(1)$ and $I_2(2)$ denote the luminescence from the exciton bound to neutral donors, I_1^s and I_1^d correspond to the exciton bound to shallow and deep acceptors, respectively. 2-electron transitions are associated with neutral donors. UP and LP show the polariton luminescemce in their upper and lower branches, respectively. Ex-LO is the LO-phonon assisted recombination of the free exciton.

We have performed detailed measurements of luminescence spectra at band-edge region for temperature range from 4.2 K to 80 K to make this assumption assure. Typical results are shown in Fig. 2. Arrows in Fig. 2 indicate the position of the reflection dip. Temperature dependence of the position of the reflection dip is given by Varshini's formula, i.e.,

$$E = E_0 - A \cdot T^2/(T+B),$$

where E_0 is the energy corresponding to the reflection dip energy at 0 K, and T is temperature[14]. By fitting to the observed results we obtained $A=8.89\times10^{-4}\ K^{-1}$ and $B=386$ K and $E_0=2.8045$ eV. These values are found to agree well with those obtained by Shirakawa and Kukimoto[8], i.e. $A=8.92\times10^{-4}\ K^{-1}$ and $B=405$ K.

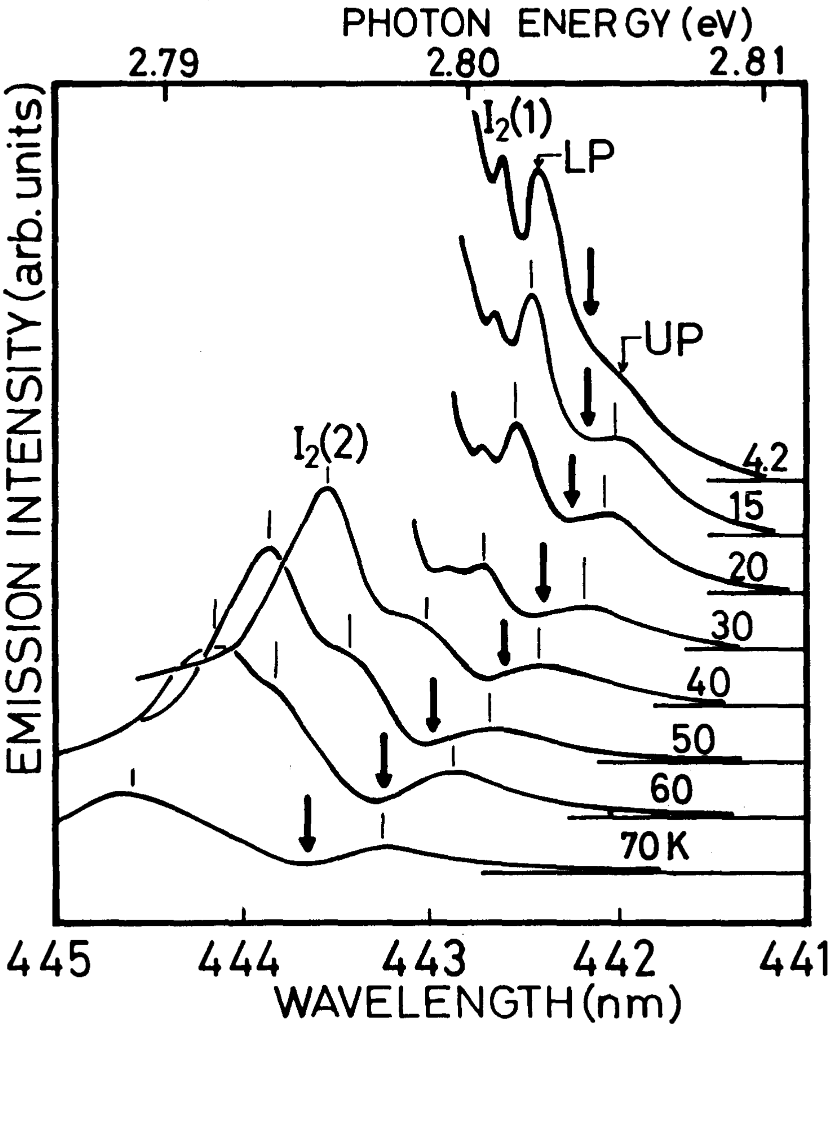

Fig. 2. Typical luminescence spectra near band edge region measured at the temperature range between 4 K and 80 K. The arrows indicate the energy position for the reflection dip.

In order to see more clearly the relative position or shift of each lumiescence lines in Fig. 2, we plotted the position measured with respect to the position of the reflection dip for the UP, LP, $I_2(1)$, $I_2(2)$, and I_3 lines in Fig. 3 as a function of temperature. One can clearly recognize that the position of UP and LP lines depend on temperature quite differently from those of bound excitons. The energy separation of the UP and the LP line with respect to the reflection dip remains unchanged up to about 20 K, but above 20 K the UP and the LP line shift to opposite direction, and therefore the energy separation between them increases with temperature. (Note that both the UP and LP lines shift to low energy side with temperature; see Fig. 2.) These features resemble to the polartion luminescence from

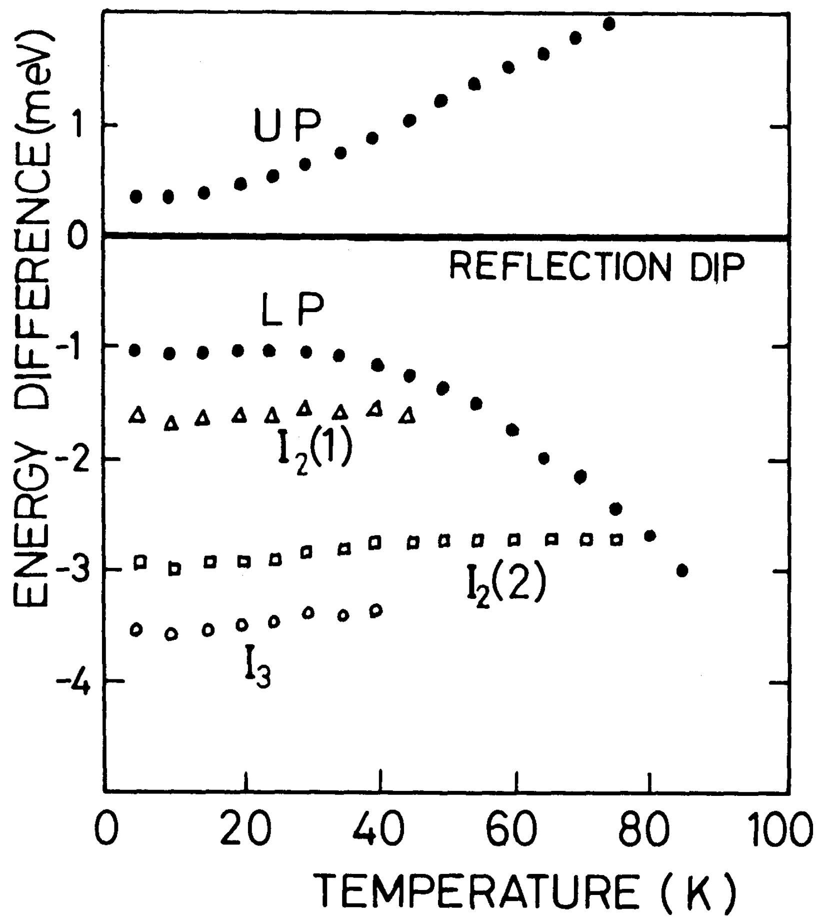

Fig. 3. The energy separation of the UP, LP and three kinds of bound excitons with respect to the reflection dip energy as a function of temperature.

CuCl [15]. The energy separation between the UP and LP lines at 4 K, 1.4 meV, corresponds to the energy splitting between the longitudinal and the transverse excitons. This L-T splitting value is nearly the same as that given by Sermage and Voos[10], 1.1 meV, which is obtained by analyzing the spectral shape of the LO-phonon assisted luminescence line for free exciton in ZnSe.

Contrary to the UP and LP lines, the energy separation of the bound excitons, $I_2(1)$, $I_2(2)$ and I_3, with respect to the reflection dip remains almost unchanged for the entire temperature range measured. That is, the bound excitons shift to low energy side with temperature in the same manner as the band-gap energy. The energy separation between the bound exciton and the reflection dip thus yields the binding energy of the exciton to the respective donor, and is found to be 3.2 meV for $I_2(1)$ and 5.6 meV for $I_2(2)$. With increasing temperature the I_2 bound exciton lines merge into the broader LP line, and seem to disappear due to the thermal dissociation at temperatures corresponding to their binding energies. It makes much sense to plot the intensity of each luminescence line against temperature.

Figure 4 shows the intensity for I_2 and E_x lines against temperature by open circles for a wider temperature range between 4 K and 200 K. The highest quality sample shows weaker luminescence intensity at high temperature, and therefore the sample used in Fig. 4 has less quality than that used in Figs. 1-3. We can observe only a broad luminescence line near I_2 position in Fig. 1, which, named I_2, is composed of the $I_2(1)$ and $I_2(2)$, and also a broader and structreless line near the reflection dip, which, named E_x, seems to correspond to the UP line. The LP line may be masked by the broader tail of the I_2 line.

The E_x line decay with temperature rather smoothly and disappears suddenly at around 200 K. In contrast to this, the decay characteristics of the I_2 line is somewhat complicated; below 50 K the I_2 decays with the thermal dissociation energy of about 5 meV, which is nearly the same value as the binding energy of the $I_2(2)$ bound exciton, 5.6 meV, mentioned above. At higher temperature above 80 K, on the contrary, the decay manner for the I_2 line is just the same as that of the E_X line. This fact strongly suggests

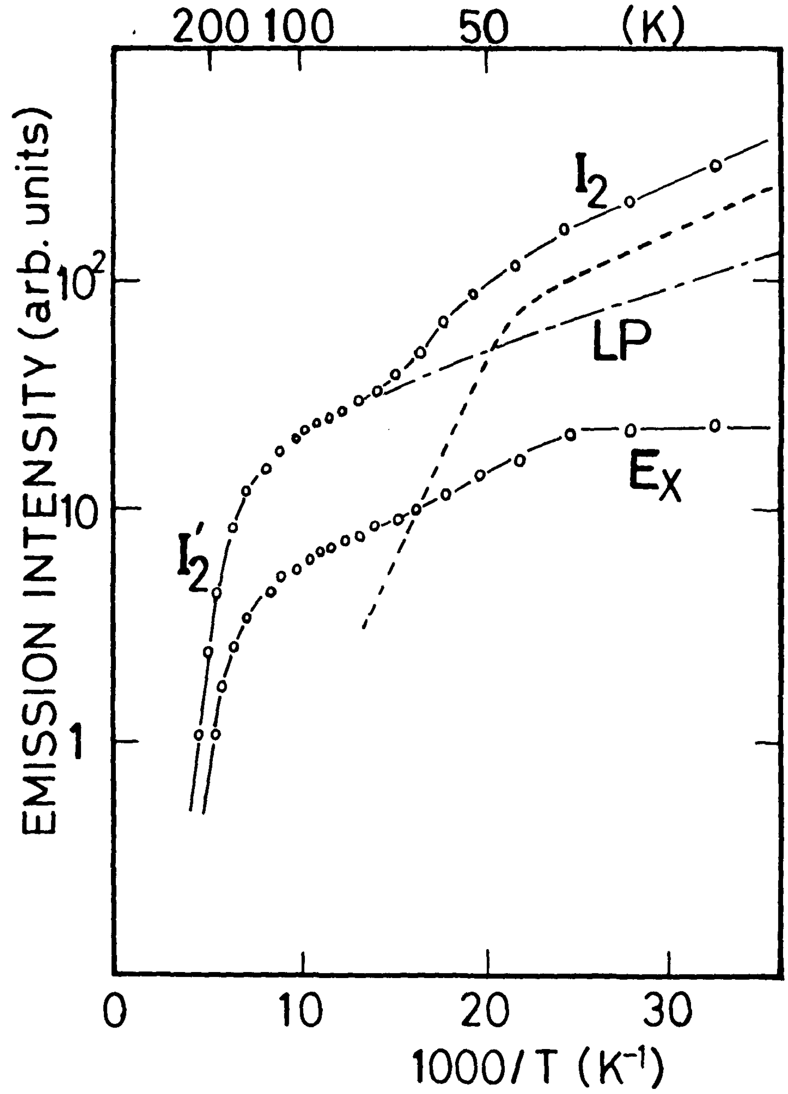

Fig. 4. Temperature dependence of luminescence intensities for the I_2 and E_X. The broken and dotted-dashed curves indicate the estimated temperature dependence of the I_2 and the LP intensity, resectively, as described in the text.

that the I_2 line above 80 K, denoted by I_2', is replaced by the exciton luminescence line, probably the LP line.

Then the decay characteristics for the I_2 (I_2') line can be divided into two different decay processes as shown by the dashed curve and the dotted-dashed curve in Fig. 4, where the decay manner for the dashed curve below 50 K should coincide with that of the I_2 line. Thus the following two results are deduced; the steeper decay for the dashed curve in the intermediate temperature range yields the activation energy of about 30 meV. This value corresponds to the binding energy of electron to a donor which is responsible for the I_2 line, and is found to be in good agreement with that reported by Merz et. al.[2] Secondly the dotted-dashed curve denoted by LP decays nearly in the same manner as that of the E_x line in the intermediate temperature range. Thus we can conclude that the luminescence line due to the bound exciton (I_2) disappears in the temperature range between 50 K and 80 K, and that the luminescence line observed at the position of the I_2 at high temperature is replaced by the luminescence of polariton in its upper branch.

Summarizing the results, photo-luminescence near band-edge region for undoped ZnSe single crystals are studied for a wide temperature range between 4 K and 200 K. From the temperature dependence of several luminescence lines due to the annihilation of bound excitons and of polariton, the following results are obtained; the luminescence lines due to the recombination of the bound excitons disappear in the temperature range between 50 K and 80 K because of the thermal dissociation of the exciton from the donors. The decay of the polariton takes place rather slowly with temperature and the polariton plays an important role in the near band-edge luminescence process even at higher temperature.

References

1) P. J. Dean and J. L. Merz, Phys. Rev. **178**, 1310 (1969)
2) J. L. Merz, H. Kukimoto, K. Nassau and J. W. Shiever, Phys. Rev. **B 6**, 545 (1972)
3) J. L. Merz, K. Nassau and J. W. Shiever, Phys. Rev. **B 8**, 1444 (1973)
4) H. Röppischer, J. J. Jacobs and B. V. Novikov, Phys. Stat. Sol. (a) **27**, 123 (1975)
5) V. Swaminathan and L. C. Greene, Phys. Rev. **B14**, 5351 (1976)
6) S. Fujita, H. Mimoto and T. Noguchi, J. Appl. Phys. **50**, 1079 (1979)
7) R. N. Bhargava, R. J. Seymour, B. J. Fitzpatrick and S. P. Herko, Phys. Rev. **B20**, 2407 (1979)
8) Y. Shirakawa and H. Kukimoto, J. Appl. Phys. **51**, 2014 (1980)
9) M. D. Ryall and J. W. Allen, J. Phys. Chem. Solids **34**, 2137 (1973)
10) B. Sermage and M. Voos, Phys. Rev. **B15** 3935 (1977)

11) M. Yamaguchi, A. Yamamoto and M. Kondo, J. Appl. Phys. **48**, 196 (1977)

12) M. S. Brodin and M. G. Matsko, Solid State Commun. **35**, 375 (1980)

13) D. P. Sell, S. E. Stockowski, R. Dingle and J. V. DiLorenzo, Phys. Rev. **B 7**, 4568 (1973)

14) Y. P. Varshni, Physica **34**, 149 (1967)

15) S. Suga and T. Koda, Phys. Stat. Sol. (a) **66**. 255 (1974)