PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 193–196

EXCITATION AND RELAXATION PROCESSES OF DONOR-ACCEPTOR PAIRS IN ZnTe UNDER SELECTIVE EXCITATION

Shin-ichi Nakashima and Arao Nakamura†

Department of Applied Physics, Osaka University,
Suita, Osaka 565 Japan

†Institute for Solid State Physics
University of Tokyo, Minato-ku,
Tokyo 106 Japan

Excitation intensity dependence of the selective photoluminescence and its excitation spectra has been measured for donor-acceptor pairs in ZnTe. Saturation of the first excited state of the pairs is observed at highly exciting levels. The intensity of the acoustic phonon wing relative to the zero-phonon lines grows strikingly along with the saturation. The results indicate that under the saturation the acoustic-phonon assisted electronic transition is an important absorption process for the donor-acceptor pairs.

1. Introduction

The photoluminescence from selectively excited donor-acceptor(d-a) pairs is a powerful tool to investigate the mechanism of the excitation and recombination[1], and also of the electron-phonon interaction[2] in semiconductors.

In this work we will represent the results of selective photoluminescence of shallow d-a pairs under the high excitation intensities in ZnTe. Our measurements by use of a pulsed dye laser have shown that the first excited state of the d-a pairs saturates at highly exciting levels and that acoustic phonon wings of the selective lines in both emission and excitation spectra grow along with the saturation. It is found that these acoustic phonon wings are due to the d-a transition accompanied with the acoustic phonon emission in the absorption process. The lineshape of the acoustic phonon wing is calculated based on the theory of the electron-acoustic phonon interaction and is compared with the experiment.

Luminescence was excited with a dye laser pumped by a nitrogen laser whose peak power was about 1 MW and repetition rate was 20cps. The d-a pair luminescence was analyzed by a 0.75m monochromator and the signals were measured by a box-car integrator.

2. Experimental Results and Analysis

When the laser light causes the transition to the higher excited states of a d-a pair with a given distance R, e.g. $\{D(1s)A(2s)\}_R$, sharp selective-emission lines resulting from the recombination of the d-a pair appear superimposed on a broad non-selective-band[2]. The intensities of the selective lines relative to the broad d-a band decrease with increasing intensity of the exciting light and eventually diminish. The similar feature is found also in the excitation spectra.

Temperature variation of the selective luminescence has been measured by use of a cw dye laser. The acoustic phonon wing on the high energy side appears with increasing temperature and the emission line becomes symmetric at elevated temperatures. These results indicate that the disappearance of the selective lines at highly exciting levels is not due to the heating effect of the sample.

Next we have observed luminescence of the 1-LO phonon sideband and its excitation spectra for the excitation energy range corresponding to the zero-phonon transition, $(D^+A^-) \rightarrow \{D(1s)A(1s)\}$. Figure 1 shows the excitation-power dependence of the luminescence in the energy region of the 1-LO phonon sideband and the excitation spectra around the zero-phonon band region in ZnTe:Li. The broad band in the emission spectra is a non-selective d-a band which is excited by the acceptor-to-conduction band transition.

The peak intensity of the selective and non-selective d-a emission bands is plotted as a function of the excitation intensity in Fig.2. The peak intensity of the selective emission line varies sublinearly and saturates at the high excitation level, whereas that of the non-selective band shows nearly linear dependence. The saturation effect was prominent for more close pairs. The sub-linear dependence of the selective d-a band is due to the saturation in the direct transition of the d-a pair with a certain distance.

Recent measurement[3] of the lifetime for the first excited state of the d-a pair in ZnTe:Li showed that the relaxation time of electrons (holes) from the higher excited states to the first excited state in d-a pairs is much shorter than the lifetime of the first excited state and the lifetime of the donor-Li acceptor pair with R > 50Å is long enough compared with exciting laser pulse. The lifetime was independent of the excitation intensity. These results are consistent with the saturation phenomenon.

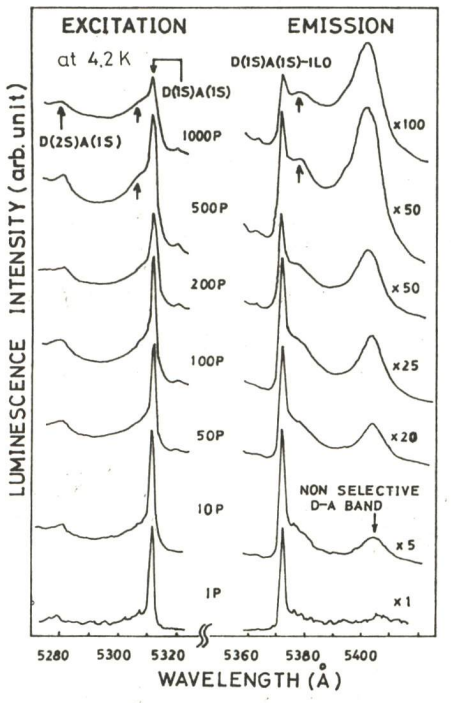

Fig.1 The luminescence spectra selectively excited at 5310 Å and its excitation spectra of ZnTe observed at 5371 Å for various exciting intensities

The acoustic phonon wing on the lower energy side of the selective emission line, which is observed weakly at low excitation level, grows as the exciting light intensity is increased and can be observed as a peak. Growing of the acoustic phonon wing is also found on the higher energy side of the selective band in the excitation spectra. The observed acoustic phonon wings in the emission and the excitation spectra do not show a complete reflection symmetry.

The growing acoustic-phonon wings are explained as follows. There are three competing excitation processes of d-a pairs for the below-bandgap-excitation; (i) the direct excitation, (ii) indirect excitation for which the acoustic phonons are emitted

simultaneously and (iii) the non-resonant transition via the continuum state. When the saturation takes place for the first excited state of the d-a pair whose energy is equal to that of the exciting photons, the photon energy is not spent any more for the direct excitation of the d-a pairs and will be dissipated to excite more distant pairs accompanying the acoustic-phonon emission. Therefore, in the emission spectra under the highly exciting condition the acoustic phonon wing consists of the radiation from the "indirectly excited" various d-a pairs with longer distances.

The structure of the acoustic phonon wing in the emission spectra with the saturation relates with the distribution N(R) and the transition probability W(R) of the d-a pairs with longer distance as well as the electron-phonon coupling. The luminescence intensity which is proportional to W(R)N(R) has been measured as a function of R by the selective excitation technique using a cw dye laser.

Figure 3 shows the emission spectra under the highly exciting condition for the different excitation energies. The broken lines display the shape of the acoustic phonon wing which is derived from the data of the luminescence-intensity distribution N(R)W(R) and from the observed shape of the wing under the weak excitation condition with the assumption that the acoustic phonon wing is due to the radiation from the "indirectly excited" various d-a pairs. The predicted acoustic phonon wing explains qualitatively the observed shape and its excitation energy dependence, although there is some deviation in the tail. The resolved peak of the acoustic phonon wing observed for the higher energy excitation reflects larger population of the d-a pairs whose distance is longer than that of the monitored pair.

On the other hand, the acoustic phonon wing in the excitation spectra under the highly exciting condition corresponds to that of the d-a pair with the same distance R_0, which is monitored. When

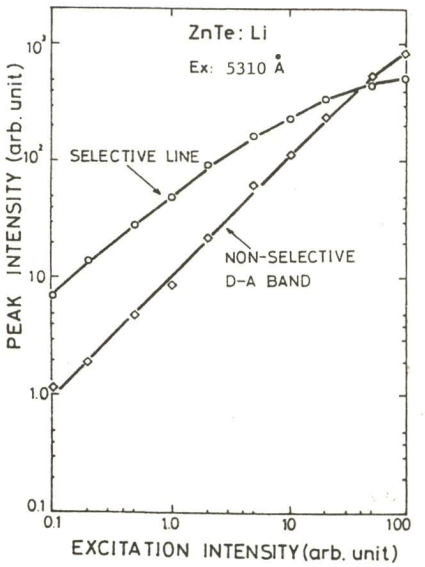

Fig.2 Peak intensities of the selective and non-selective 1 LO-phonon sidebands vs the exciting power

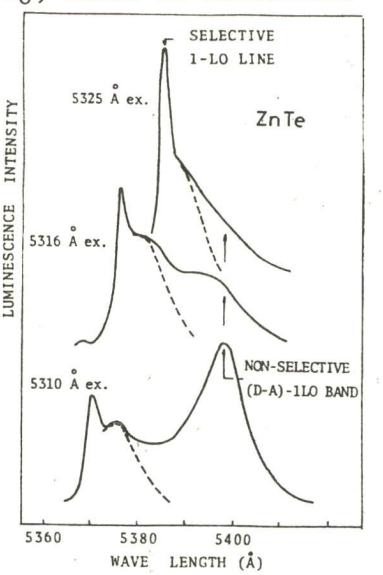

Fig.3 Emission spectra of 1 LO phonon sideband with the acoustic phonon wing for different excitation energies

the excitation energy is varied in the direction higher than the energy of the monitored d-a pairs with the distance R_0, the saturation takes place only for more close pairs ($R < R_0$) and the photons will be absorbed more effectively to excite indirectly the monitored d-a pair. Therefore, the resolved peak as in the emission spectra is not expected to be observed in the excitation spectra.

The shape of the acoustic phonon wing is determined by the coupling of acoustic phonons and bound electrons(holes). The coupling function, $D(\omega)$, for the d-a pairs is calculated following Toyozawa[4]. Hydrogenic donor and acceptor wavefunctions are assumed for simplicity, though the contribution of d-like wavefunction of the acceptor is important to the electron-phonon interaction.

Evaluating the coupling functions for the piezoelectric(D_p) and deformation potential interactions(D_d) gives the following results,

$$D_p(\omega) = A_0 I(\omega) = A_0\{[1 + (\omega/C_s\alpha)^2]^{-4} + [1 + (\omega/C_s\beta)^2]^{-4} - 2(C_s/\omega R)\sin(\omega R/C_s)[1 + (\omega/C_s\alpha)^2]^{-2}[1 + (\omega/C_s\beta)^2]^{-2}\},$$

and $D_d(\omega) = D_0 \omega I(\omega)$,

where $C_s = \omega/k$ is the average sound velocity, α and β are twice of the inverse of the donor and acceptor Bohr radii, respectively, and A_0 and D_0 are constants. A fit to the experimental phonon wing, for large value of ω is better for the piezoelectric coupling than the deformation potential one. However, the calculated shapes do not agree well with the experimental one near $\omega=0$ for both couplings. Another coupling mechanism will be necessary to explain the experimental result near $\omega=0$.

The saturation of the first excited state of d-a pair at highly exciting levels results from the rapid relaxation from the higher excited state to the first excited state and the slow radiative recombination. The saturation allows us to discriminate the acoustic-phonon assisted transitions of d-a pairs in the excitation and the recombination processes.

The authors are grateful to Professor S. Shionoya for his support and encouragement during the course of this research.

References

1) S. Nakashima and S. Yasuda: phys.stat.sol.(b) 96 (1979) 211.

2) S. Nakashima and S. Yasuda: Proc.Int.Conf.Phys.Semiconductors, Edinburgh 1978, p.509 .

3) S. Nakashima and A. Nakamura: to be published.

4) Y. Toyozawa: Dynamical processes in solid state optics, ed. by R. Kubo and H. Kamimura (Syokabō, Tokyo and W. A. Benjamin, New York) 1970, p.90 .