DYNAMICS OF BOUND-EXCITON ENERGY TRANSFORMATION TO EDGE-LUMINESCENCE CENTERS IN CdS

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Dynamics of energy transfer among bound-excitons and donor–acceptor pairs (DAPs) in CdS have been investigated by using time-resolved edge luminescence excitation spectroscopy. Intensity peaks associated with the creation of I_1 excitons (exciton bound to neutral acceptor) at short delay times indicate that the efficiency of bound exciton decay into impurity centers is high. However, evolution of the I_1 intensity peak into a dip with increasing delay-time has been observed. This has been interpreted in terms of the decay rate of DAP luminescence increase caused by the electric field in the surface region.

Excitons are elementary excitations of solids. They are important in understanding many basic properties of semiconductor materials at low temperatures. CdS is a widely used model substance for studies of the principal channels of exciton recombination. There are basically two series of edge emission bands present in CdS crystals. One is the low-energy series (LES) emission due to the radiative recombination between a hole bound to an ionized acceptor and an electron bound to an ionized donor, which is referred to as the "Donor–Acceptor-Pair" (DAP) transition; the other, denoted as the high energy series (HES) emission, is due to the recombination of free electron in the conduction band with neutral acceptors, and is also referred to as "free-to-bound" transition [2,1]. In CdS, excitation spectra of LES luminescence induced by free excitons or bound excitons show dips in the energy regions corresponding to the emission luminescence peaks. This lower emission intensity at the excitation absorption resonances was interpreted in terms of surface defects and surface fields [3]. In this paper, additional dynamics of energy transfer among bound-excitons and donor–acceptor pairs have been investigated for pure, undoped n-type CdS crystal at liquid helium temperatures.

The sample used in this work is an uncompensated ultrahigh purity (UHP) CdS crystal of approximate thickness $d = 2.6$ mm. The excitation source consists of a high resolution (0.01-nm) dye laser pumped by a 3-ns pulsed N_2 laser (Laser Science, Inc). The excitation radiation, transmitted by a fiber optic of 3 mm^2 cross section, is perpendicularly incident on the front surface of the sample, and the transmitted luminescence is collected on the rear surface by a similar fiber optic bundle. The optical c-axis of the sample is parallel to the light wave-vector direction. The effective time resolution of the detection system is about 10 ns.

Previously reported time-resolved excitation spectra of DAP luminescence show characteristic features [3], which include sharp emission intensity dips at 485.5 nm, 483 nm, and 489 nm due to the creation of A-exciton (polariton), B-exciton and I_1 exciton (exciton bound to neutral acceptor), respectively. These results imply that the efficiency of resonantly excited excitons decaying into edge-luminescence centers is lower than for the nonresonant excitations. In order to further elucidate the dynamics of the energy transfer processes among excitons and edge-luminescence centers, we measured time-resolved excitation spectroscopy of DAP luminescence using high spectral resolution in the short delay time region. A time-integrated excitation spectrum of DAP luminescence (518 nm) is shown in fig. 1. This spectrum is obtained using an excitation intensity (≈ 0.5 MW/cm^2) about 4 times higher than that used in ref. [3]. The absorption coefficients of bound excitons are about 3 orders of magnitude lower than those of free excitons, and the relative absorbed excitation power density is thus lower for resonant excitation at bound excitons. Increased excitation intensity is essential to fully explore the bound exciton effects on DAP luminescence. In contrast to previous reported DAP excitation spectra, intensity dips corresponding to free excitons are completely suppressed in fig. 1. However, the I_1 region dip is very pronounced.

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It is well known that resonant excitation causes stronger absorption of light in the crystal [4], thus creating neutral pairs in a thinner surface layer compared to the nearby excitation. The emission dips at exciton energies, therefore, can be attributed to the fact that the density of non-radiative defects is higher near the surface. Additionally, the presence of a space charge layer induced surface electric field will reduce the population of neutral DAPs by field ionization.

The absence of the free exciton intensity dips in fig. 1 can be attributed to the nonlinear optical absorption effect due to increased excitation intensity. In that context, absorption coefficients decrease with increase of the excitation intensity. The optical power density corresponding to the onset value for saturation phenomena in the absorption line is especially easy to achieve for free exciton resonant excitation [5]. Therefore, once this condition is achieved, resonant excitation at free exciton lines no longer induces stronger absorption compared to nonresonant excitation. This can account for the disappearance of intensity dips in the free exciton energy region. At I_1 bound exciton energy region, the excitation volume is larger, and thus the corresponding effect does not occur. Instead, we excite a higher density of bound excitons in the absorption layer, so the excitation processes of DAPs by dissociated bound excitons can be seen more clearly.

Time-resolved excitation spectra of DAP transition are presented in fig. 2. For shape comparison, each spectrum is normalized to the same intensity at the peak. The delay time dependence of DAP transition at I_1 is evident. These spectra clearly demonstrate that the
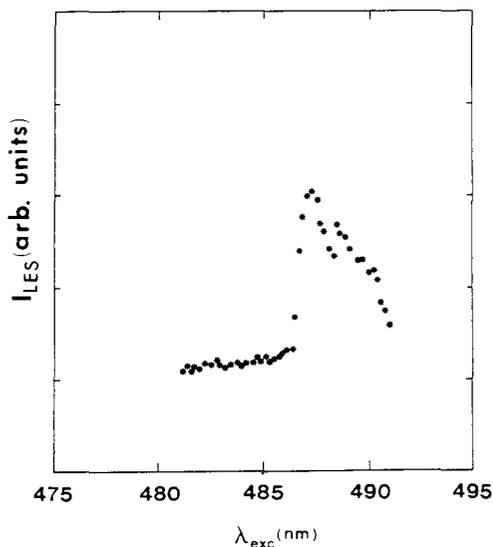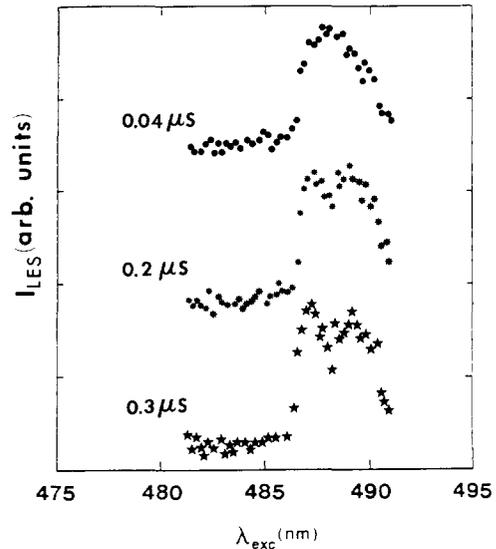

Fig. 2. Time-resolved DAP excitation spectra. Each spectrum is normalized to the same intensity at the peak. All conditions are the same as in fig. 1.

DAP luminescence generated by I_1 resonant excitation evolves from an emission peak into dip with increasing delay time. The intensity peak at short delay time indicates that the DAP luminescence can be excited very effectively by resonant absorption creating an I_1 bound exciton, which implies that the capture probability of charge carriers dissociated from bound excitons by D^+-A^- pairs is high. However, the evolution of the I_1 intensity peak into a dip with increasing delay-time is still the consequence of the reduced excitation layer in the crystal due to a relatively stronger I_1 resonant absorption compared to nonresonant absorption. Therefore, the observed results can be interpreted in terms of the DAP transition rate increase caused by the surface electric field, since DA centers nearer the surface region are the ones excited by dissociated bound excitons. This interpretation is further supported by time-resolved excitation spectra of the "free-to-bound" transition, in which the emission intensity at I_1 shows very sharp maxima for all delay times. This is because the effect of the surface electric field on the decay rate of the "free-to-bound" transition is negligible. These results indicate that processes of exciton excitation, dissociation, and capture by impurities occur primarily in the near surface region. Thus surfaces are the most important regions for generating excitons as well edge luminescence. This is also supported by the observation of a second peak appearing at 380 ns in the DAP luminescence temporal response, which corresponds to bottleneck exciton–polariton propagation and excitation of DAP luminescence at the rear surface [6].
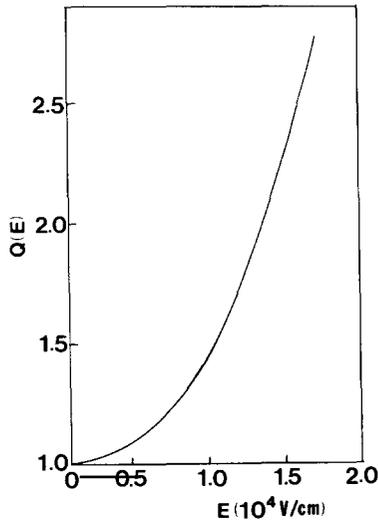

Fig. 1. Time-integrated DAP excitation spectrum of UHP CdS sample with 2.6 mm thickness at $T = 4.2$ K. Excitation intensity is about 0.5 MW/cm^2.

Fig. 3. Increase in the decay rate of neutral DAP recombination, $Q(E)$, as a function of electric field E.

The kinetics of the DAP recombination in semiconductor materials within a uniform electric field has been investigated theoretically [7]. The transition rate in a weak field has been calculated by a variational method and can be written as

$$\langle W_E \rangle = W_0 Q(E),$$

where W_0 is the transition rate of DAP recombination in the absence of the electric field. The principal contribution from the final state $D^+ - A^-$ electric dipole interaction with E increases the DAP transition rate by a factor of $Q(E)$. In fig. 3, we plot $Q(E)$ as a function of

the electric field strength E. We see that $\langle W_E \rangle$ increases as E increases. For UHP CdS crystals, the average electric field in the depletion layer is of the order of 10^4 V/cm [7], thus the decay rate is 40% higher for DA centers created near the surface region than for those in the bulk. Therefore, with an increased decay rate of DA pairs with the same emission (518 nm) created by I_1 resonant excitation in the surface space charge region compared with those in the interior, the luminescence intensity should change from a peak to a dip with increasing delay time.

In conclusion, dynamic processes of bound exciton energy transfer to edge luminescence centers have been investigated. We found that edge luminescence can be excited by dissociated bound excitons very effectively. Our results indicate that surfaces are the most important regions for generating excitons as well as edge luminescence.

References

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