Direct observation of edge luminescence excited by long-lived-exciton-polariton propagation in CdS

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Low-temperature time-resolved edge-luminescence excitation spectroscopy has been used to probe the exciton-polariton transport properties in CdS crystals of up to 3 mm thickness. We report the first direct experimental observation of edge luminescence excited by long-lived polaritons with lifetimes exceeding 400 ns which propagate from their origin at the front sample surface to the rear surface, appearing as delayed peaks in the temporal response of edge luminescence. The A exciton-polariton group-velocity distribution is obtained. A group-velocity minimum of 6.8×10^5 cm/s corresponding to the "bottleneck" energy has been observed.

Due to the photon-exciton interaction in semiconductors, there arise new elementary excitations, which are essentially mixed states of the photon and exciton: excitonic polaritons. Exciton polaritons are very important in understanding the optical properties of many semiconductors at low temperatures and their properties are still being investigated extensively.[1]

In this paper, dynamics of long-lived exciton polaritons in model substances, CdS crystals, have been investigated by using time-resolved edge-luminescence excitation spectroscopy. 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 also referred to as the "bound-to-bound" or "donor-acceptor pair" transition; the other, denoted as the high-energy series (HES) emission, due to the recombination of a free electron in the conduction band and a neutral acceptor, is the "free-to-bound" transition.[2,3] From edge-luminescence emission-intensity measurements on CdS, it was deduced[4] that the edge emission from the rear surface is generated by polaritons propagating from their front surface origin. It was also shown by Kuwata *et al.*[5] that in thin (2-20 μm) CuCl single crystals, polariton propagation effects play an essential role in determining the temporal behavior of the free-exciton luminescence. In order to fully explore the polariton effect, we present experimental results of very monochromatic excitation measurements on bound-to-bound and free-to-bound transitions for excitation energies in the vicinity of the highly absorptive region of the A exciton resonance, which corresponds to the lower-polariton branch in the dispersion curve. We directly observed the delayed rear surface polariton-generated edge luminescence in CdS crystals of thicknesses up to 3 mm.

The uncompensated ultrahigh purity (UHP) CdS samples of cross-sectional area of approximately 30 mm^2 and thicknesses $d = 2.6$ and 0.83 mm, grown by vapor phase transport starting from high-purity powder, were obtained from Eagle-Picher Industries, Inc. Two laser excitation source configurations were employed in this work. They consist of (i) a high spectral resolution (0.01-nm) dye laser driven by a 3-ns pulsed N$_2$ laser (Laser Science,

Inc.) and (ii) a medium spectral resolution (0.3-nm) dye laser driven by a 0.3-ns pulsed N_2 laser. The excitation radiation is transmitted by a fiber optic bundle of cross-sectional area 3 mm^2 and is perpendicularly incident on the front surface of the sample, and the transmitted luminescence signal is collected on the rear surface by a similar fiber optic bundle. The optic c-axis of the sample is parallel to the excitation light wave-vector direction. Luminescence was dispersed by means of a grating monochromator and detected by a photomultiplier. The output signals were then sent to a transient digitizer. The effective time resolution of the detection system is about 10 ns.

Figures 1 and 2 show logarithmic plots of the temporal responses of bound-to-bound and free-to-bound emissions,
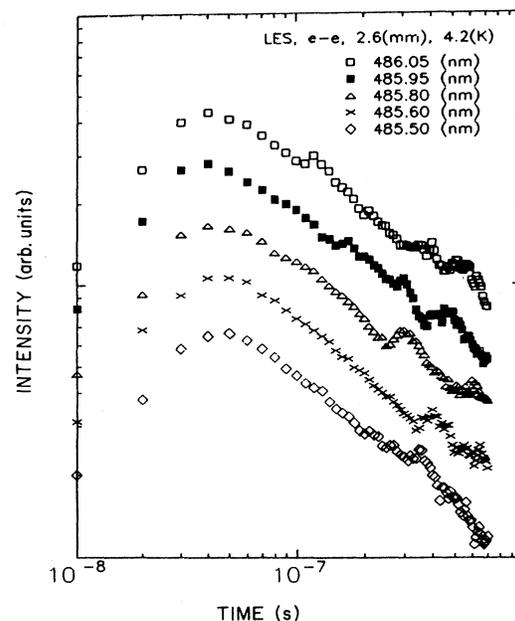

FIG. 1. Logarithmic plots of temporal responses of the bound-to-bound transition for various excitation photon wavelengths in the vicinity of the A-exciton region at 4.2 K for a 2.6-mm CdS sample.
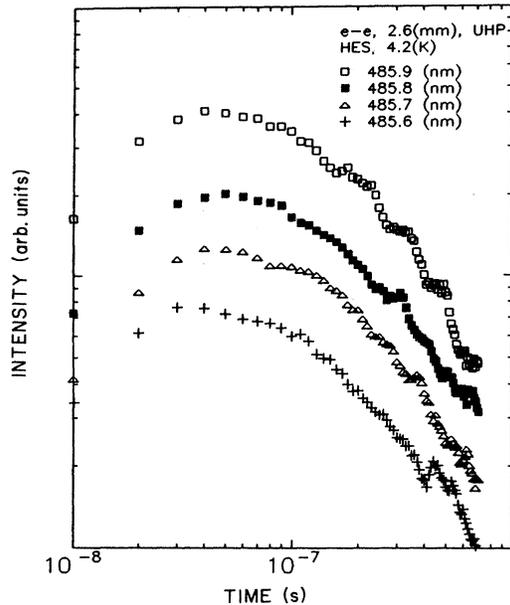
FIG. 2. Logarithmic plots of temporal responses of the free-to-bound transition for various excitation photon wavelengths in the vicinity of the A-exciton region at 4.2 K for a 2.6-mm CdS sample.

respectively, for various excitation photon wavelengths near the A-exciton resonance, for a 2.6-mm UHP sample at 4.2 K. The measurements were made with laser source (i). The usual edge-luminescence power-law decay[6] is seen, corresponding to front surface excitation, with steps occurring within the investigated time interval. The striking feature is delayed luminescence peaks in both edge-luminescence bands, with the delay time of the second peak showing a systematic dependence on the excitation energy. The longest delay time, T_0, which we ascribe here to the bottleneck-point propagation time, is measured to be about 380 ns at $\lambda_{exc} = 485.6$ nm. The same value was found with source (ii). In the polariton description, the edge-luminescence process, particularly at the rear surface, is regarded as a combined process of polariton propagation and subsequent neutralization of D^+ and A^- resulting in edge luminescence. In the present case, the excitation is in the A-exciton resonance region, where the linear absorption coefficient is larger than 10^4 cm^{-1} (Ref. 7), and thus the penetration depth of the excitation photon is less than 1 μm. Therefore, the A excitons are created just adjacent to the front surface and generate edge luminescence in the region near the front surface; the remaining portion of the polaritons travel through the sample at their respective group velocities $V_g(\lambda)$ in the direction of their momenta to the rear surface and subsequently create edge luminescence there. This is the origin of the delayed second peak in the temporal response of edge luminescence. We assume that the generation times of the edge luminescence are the same at both surfaces, the travel distance of the polaritons is equal to the thickness of the sample d and thus, the corresponding delay time of the second peak is d/V_g. With the sample thick-

ness of 2.6 mm and the longest bottleneck propagation time (T_0) of 380 ns, we obtain a group velocity of 6.8×10^5 cm/s. This value is about 4.5 times slower than the bottleneck velocity obtained by measuring the propagation times of picosecond light pulses in thin CdS crystals.[8]

Since the propagation times show a systematic dependence on the excitation photon energies below the bottleneck region, we conclude that thermal equilibrium is not established near or below the bottleneck region at 4.2 K. It is well known that polaritons above the bottleneck are strongly scattered by acoustic phonons.[9,10] With decreasing polariton energy, the acoustic-phonon scattering rate decreases rapidly around the bottleneck, whereas the radiative decay rate increases. Therefore, polaritons above the bottleneck can cascade down towards the bottleneck region via emission of acoustic phonons within a few nanoseconds, then travel within the sample at the bottleneck velocity. Our results show that propagation times for states created above the bottleneck are about the same as for those states excited at the bottleneck point. This indicates that the distance traveled by polaritons during the relaxation process is almost negligible compared to the sample thickness. Thus, for our case, a group-velocity distribution cannot be obtained for states populated above the bottleneck region. However, polaritons excited below the bottleneck have a negligible phonon scattering probability, and in addition, phonon absorption is unlikely to occur at low temperatures. Since the group velocity is at its minimum at the bottleneck point, directly excited polaritons below the knee region travel in the sample at larger V_g's and arrive at the rear surface within shorter time periods. Therefore, the group-velocity distribution below the bottleneck can be obtained. For our case, the combination of using a thick sample and a high spectral-resolution laser has many advantages for obtaining accurate group-velocity measurements. A plot of experimentally observed polariton group velocities versus excitation energies is shown in Fig. 3, where an enormous variation in group velocity around the A-exciton resonance is observed. We see that V_g increases by a factor of 5 within 2.5 meV. By using the polariton dispersion equation and appropriate CdS parameters provided in Ref. 9, the velocity distribution was also calculated. We found that the results agree well with our observation in the energy region below the bottleneck.

In addition to the above results, we noticed multiple delayed luminescence peaks in the temporal responses of edge emission, corresponding to polariton traversals back and forth in the sample via reflections from the front and rear surfaces, generating luminescence at each arrival at a surface. This indicates that the interactions between polaritons and other entities (electrons, phonons, defects, etc.) are very small at the interior of the CdS crystal and thus implies that surfaces are the most important regions for generating (annihilating) polaritons as well as edge luminescence.

In order to further confirm the polariton propagation and excitation effects, we have performed experiments on similar sample of thickness 0.83 mm, using source (ii). In Fig. 4, we present temporal responses of bound-to-bound
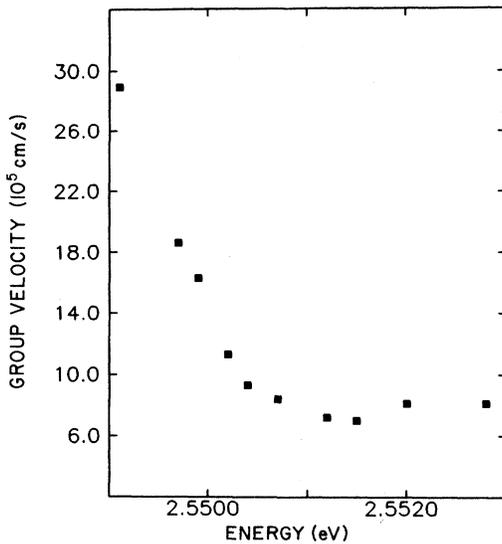
FIG. 3. Experimentally observed polariton group velocities vs excitation photon energies at 4.2 K for the 2.6-mm CdS sample.
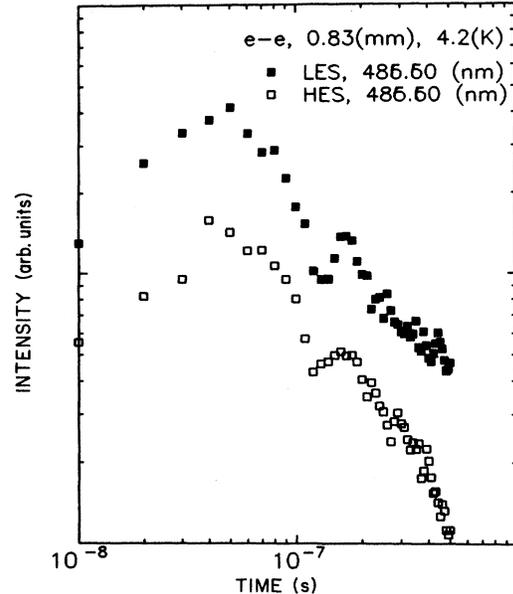

FIG. 4. Logarithmic plots of temporal responses of the bound-to-bound and free-to-bound transitions at the A-exciton resonance $\lambda_{exc} = 485.6$ nm for the 0.8-mm CdS sample at $T = 4.2$ K.

and free-to-bound transitions at the A-exciton resonance, $\lambda_{exc} = 485.6$ nm. Compared to the bottleneck-point propagation time of the 2.6-mm sample shown in Fig. 1, a reduction in delay times of the second luminescence peaks is observed. The bottleneck propagation time (T_0) is measured to be 120 ns. From this we obtain a bottleneck group velocity of 6.9×10^5 cm/s, which agrees well within the estimated 10% error, due to the 10-ns temporal resolution, with the results from the 2.6-mm sample, and supports our interpretation that the delayed appearance of these luminescence peaks represents the polariton generated edge luminescence at the rear surface.

In conclusion, our results show that in the highly absorptive photon energy region, an edge-luminescence contribution from the rear surface is generated by polaritons propagating from their front surface origin. One of the most important results we have obtained here is that the lifetimes of the "slow" polaritons observed here exceed

several hundred nanoseconds, in contrast to values of only a few nanoseconds reported in previous investigations.[11] We attribute this to the fact that in the past, by detecting exciton luminescence directly for above band-gap excitation, emission spectroscopy experiments were performed only on very thin samples (a few microns), and thus the lifetimes were limited by rapid polariton conversion into photons at the surfaces. Therefore, we think that their measured values represented the polariton propagation times in thin crystals rather than the true, bulk polariton lifetimes. Detailed experimental investigations and analyses, including temperature, sample type, and crystal surface treatment effects will be published in a forthcoming paper.

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