Energy relaxation during hot–exciton transport in quantum wells: Direct observation by spatially resolved phonon–sideband spectroscopy

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We investigate the energy relaxation of excitons during the real–space transport in ZnSe quantum wells by using microphotoluminescence with spatial resolution enhanced by a solid immersion lens. The spatial evolution of the LO–phonon sideband, originating from the LO–phonon assisted recombination of hot excitons, is measured directly. By calculating the LO–phonon assisted recombination probability, we obtain the nonthermal energy distribution of excitons and observe directly the energy relaxation of hot excitons during their transport. We find the excitons remain hot during their transport on a length scale of several micrometers. Thus, the excitonic transport on this scale cannot be described by classical diffusion.

Excitons and their dynamics determine most of the linear optical properties of a semiconductor quantum well (QW). For nonresonant excitation, excitons are generated in a QW with a nonzero center–of–mass kinetic energy. Such a hot–exciton injection is followed by the evolution of the hot–exciton distribution in energy space and real space towards equilibrium, i.e., by relaxation and transport. The excitonic transport can be divided into three essentially different regimes according to the relevant status of the relaxation, namely the transport before, during, and after the relaxation. The first regime extends up to the first step of the relaxation, i.e., the first phonon–emission event. Till then the exciton energy is conserved and one talks about ballistic transport (when no scattering occurs at all) or quasiballistic transport (only elastic scattering occurs). The duration of this process is as short as several picoseconds, determined by the phonon scattering time. The last transport regime starts when the excitons have reached quasi–equilibrium with the lattice. Since the typical relaxation time of hot excitons is several 100 ps, this transport regime can be observed only if the lifetime of the excitons is long enough. Because the energy distribution remains constant, one can apply a classical description using the diffusion equation. Up to now, this classical diffusion has been assumed to be the dominant process in excitonic transport in QWs. In this letter, we will show that generally the second regime, i.e., the transport during relaxation, dominates the excitonic transport. Such a process is composed of the simultaneous evolution of the exciton distributions in energy space and real space.

Hot excitons are difficult to be studied by conventional optical techniques. Since the photon momentum is very small, the direct coupling of the hot excitons is measured only if the lifetime of the excitons is long enough. Because the energy distribution remains constant, one can apply a classical description using the diffusion equation. Up to now, this classical diffusion has been assumed to be the dominant process in excitonic transport in QWs. In this letter, we will show that generally the second regime, i.e., the transport during relaxation, dominates the excitonic transport. Such a process is composed of the simultaneous evolution of the exciton distributions in energy space and real space.

In this letter, we show that an LO–phonon sideband (PSB) can be used as an ideal tool for direct investigation of the hot excitons. By performing spatially resolved PSB spectroscopy, we observe directly the energy relaxation of hot excitons during their real–space transport in ZnSe QWs. We find that the excitons remain hot on a length scale of several micrometers and that their energy distribution remains nonthermal during their lifetime–limited transport. Our result shows clearly that for nonresonant excitation, the excitonic transport cannot be described by classical diffusion.

The sample is a ZnSe (7.3 nm)/ZnSSe (10.7 nm) multiple QW grown by Metal organic vapor phase epitaxy. Figure 1 shows schematically the exciton formation and relaxation processes of the QW. After an optical excitation in the continuum, the generated electron–hole pairs rapidly form excitons assisted by LO–phonon emission within few picoseconds. The hot excitons then relax to the band minimum by acoustic–phonon emission. After relaxation, the cold excitons recombine radiatively, resulting in the ZPL. From ZPL spectroscopy, we observe directly the energy relaxation of the hot excitons. By performing spatially resolved PSB spectroscopy, we have obtained indirect hints for the hot–exciton behavior. As we discussed earlier, the hot excitons cannot directly couple to the photon due to the momentum difference. However, the LO phonon can assist the hot exciton in coupling to the photon by taking away its momentum. The simultaneous well–defined energy loss to the LO phonon leads to the appearance of the PSB, as shown in Fig. 1. Since the spectral shape of the PSB reflects the kinetic–energy distribution of excitons, this LO–phonon assisted recombination process provides an ideal tool for direct investigation of hot excitons. Figure 2 shows several spectra of the PSB excited by a cw laser at various photon energies $E_{\text{exc}}$. The PSB always appears in the photon–energy range below the LO–phonon energy $E_{\text{LO}}$ and below the $E_{\text{exc}}$. The shape of the PSB is related to the energy distribution of excitons, $f(\varepsilon)$, by the LO–phonon assisted recombination probability, $W(\varepsilon)$, i.e., $f(\varepsilon) = \text{PSB}(\varepsilon)/W(\varepsilon)$. $E_{\text{LO}}$.
In order to get the energy distribution from the PSB, we calculate \( W(\varepsilon) \). In the case of first order LO–phonon assisted luminescence, the recombination probability is

\[
W(\varepsilon) \propto | \sum_i |\psi_i(0)H_{\varepsilon-E_{LO}}|^2 |
\]

(1)

where \( |\psi_i(0)|^2 \) is the oscillator strength of the optical transition from the state \( i \) in dipole approximation. The summation is over all possible intermediate states. For 1s excitons, the main intermediate state is 1s(\( K \approx 0)\). \( H \) is the Fröhlich scattering matrix element. Since we are only interested in the energy dependence of the recombination probability, we omit the energy–independent parameters, and get

\[
W(\varepsilon) \propto \frac{[1 + (a_0q_{e}/2)^2]^2 - [1 + (a_0q_{v}/2)^2]^2 - q(\varepsilon-E_{LO})^2}{q(\varepsilon-E_{LO})^2}.
\]

(2)

Here \( a_0 \) is the exciton Bohr radius, \( q \) is the wave vector of the LO phonon, \( q_{e,v} = q(\mu/m_e,m_v) \), where \( \mu = m_e m_v/(m_e + m_v) \). The inset of Fig. 2 shows the calculated result by using the parameters of ZnSe QW. We find an increase of the recombination probability with the exciton kinetic energy.

The spatially resolved PSB spectroscopy is performed with a solid immersion lens (SIL)–enhanced confocal \( \mu-\)PL system. The details of the system has been reported previously.[15] The sample is excited locally by a tunable cw laser through the objective, with an excitation spot of about 200 nm half width at half maximum. The size of the pinhole–defined detection spot is 460 nm in diameter. Although the resolution of this system is lower than that of a scanning near field optical microscope (SNOM) using coated fiber tips, the collection efficiency is much higher than for the latter. Since the PSB is much weaker than the ZPL (see Fig. 1), a high collection efficiency is paramount for the PSB spectroscopy. One can improve the collection efficiency of a SNOM by using an uncoated fiber tip,[17] but simultaneously the spatial resolution drops. Furthermore, a SNOM experiment has another disadvantage: one cannot detect spectra from positions outside of the excitation spot since local excitation and detection are achieved by the same fiber tip. In contrast, by moving the pinhole in the image plane of the microscope we can detect spectra from positions outside of the excitation spot in a well–defined way. This enables us to investigate the transport rather directly.

By scanning the pinhole thus varying the distance between the excitation and detection spots, \( d \), we detect the spatially resolved PSB spectra, as shown in the left part of Fig. 3. With increasing the \( d \), we observe the change of the PSB spectral shape. From these PSB spectra, we deduce the kinetic–energy distributions of the excitons as shown in the right part of Fig. 3. The energy relaxation of the nonthermal excitons during the transport is clearly...
FIG. 3: Left part: The spectra of PSB measured at different positions \(d\) with respect to the excitation laser spot. The excitation intensity is 1 kW/cm\(^2\). The sample temperature is 7 K; Right part: The corresponding kinetic–energy distributions of excitons deduced from the spectra of PSB.

FIG. 4: The average kinetic energy of excitons as function of \(d\), the distance between the excitation and the detection spots. The initial kinetic energies of the excitons are (from top to bottom) 20.7, 17.6, 14.3, 11.0, 7.9 and 4.8 meV, respectively. The bar above the horizontal axis indicates the FWHM of the excitation laser spot.

observed. We note that after a transport of 1380 nm, the exciton distribution is still nonthermal.

From the kinetic–energy distribution, we calculate the average kinetic energy of the excitons. The spatial profiles of the average kinetic energy are shown in Fig. 4 for several values of \(E_{\text{ini}}\), the initial kinetic energy of the excitons for the relaxation and transport processes. Such a quantity is well–defined by \(E_{\text{exc}}\) (see Fig. 1). We find the reduction of the average energy is only \(\sim 20\%\) after a transport of about 1500 nm. By comparing the slopes of the curves in Fig. 4, we also find that the spatial energy relaxation is slower for excitons with less kinetic energy. This feature is consistent with the fact that the rate of the acoustic–phonon emission, being the dominant relaxation mechanism, increases with the exciton energy.[18]

In our experiment, we cannot measure the average energy of excitons at a position further than 1500 nm from the excitation spot since the signal is too weak. However, we can conclude from the earlier two facts that the excitonic transport on a length scale of at least several micrometers is coupled to the energy relaxation. Although the experiment is done on ZnSe QWs, the conclusion is qualitatively general among other structures. In GaAs QW, the hot–exciton transport feature is anticipated to be even more pronounced due to the weaker Fröhlich coupling (thus longer energy–relaxation time) and the generally higher sample quality (e.g., better interface quality thus higher mobility). Up to now, excitonic transport in QWs after hot–exciton injection was generally discussed in terms of classical diffusion. For example, excitonic transport experiments of GaAs QWs performed on micrometer length scale were modeled by diffusion equation, although the carriers are excited with an excess energy of several 100 meV.[5, 6, 7, 8] In investigations of ZnSe based QWs, diffusion length and diffusivity of excitons were also deduced based on diffusion equations.[9, 10, 12] In the InGaN/GaN system, the transport within 1 \(\mu\)m was analyzed by neglecting relaxation/thermalization processes.[11] Our experiment shows clearly that in the case of nonresonant excitation, the excitons remain hot and nonthermal on a length scale of several micrometers, thus the transport is not a classical diffusion.

In summary, we show that the LO–phonon assisted recombination process can be used for direct investigation of hot excitons. By performing spatially resolved PSB spectroscopy, we observe directly the spatial evolution of the nonthermal kinetic–energy distribution of excitons. We find that at low temperatures the excitonic transport on a length scale of several micrometers is coupled to the energy relaxation, thus cannot be described as a classical diffusion process.

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