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Long delays of light in ZnO caused by exciton-polariton propagation

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We study propagation of exciton-polaritons through bulk ZnO using time-resolved photoluminescence (PL) complemented by time-of-flight measurements of laser pulses. When photon energy approaches donor bound exciton resonances, substantial time delays in PL light propagation are observed which reach up to 210 ps for a 0.55 mm-thick crystal. By comparing results from time-of-flight measurements performed using PL light and laser pulses, the observed delay is shown to be due to for-

mation of exciton-polaritons and their spectral dispersion. It is also shown that the main contribution to the slow-down effect arises from free excitons-polaritons, whereas bound-exciton polaritons become important only in the close vicinity to the corresponding resonances

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1 Introduction ZnO has in recent years been a subject of extensive research efforts driven by the prospect of potential applications of this material in a wide variety of areas ranging from optoelectronics to spintronics [1 - 3]. As a wide bandgap semiconductor with a direct bandgap, ZnO is considered as a key candidate for applications in solid-state optoelectronics including blue-to-UV light emitting and laser diodes, as well as in solid-state lighting. It has advantages over its main competitor GaN because of (1) the availability in bulk single-crystals which eliminates usage of foreign substrates and simplifies material fabrication, and (2) a larger exciton binding energy (~ 60 meV vs 25 meV for GaN) which make excitonic emissions important even at room temperature. Moreover, a combination of the large exciton binding energy with the polar bonding character and large polarizability of the ZnO matrix leads to strong light-matter interaction effects, such as polariton formation [4 - 6]. These polaritonic effects are foreseen to contribute to novel fascinating applications of this material, such as in polariton lasers utilizing quasi Bose-Einstein condensation which allows extremely low threshold power operation [7].

By utilizing the fact that group velocity of light in a dispersive media reduces in the vicinity of resonances [8-12], the polariton formation could also allow control of

light propagation and realization of slow light, which is attractive for quantum information storage and processing. The first experimental verification that light can indeed be slowed down in ZnO has recently been obtained from time-of-flight studies of a donor bound exciton (DX) emission [13] and laser pulse propagation [14]. The group velocity of light propagating through bulk ZnO was found to significantly decrease when photon energy approached the absorption edge of the material, and was explained within the exciton-polariton framework. However, the exact origin of the observed effect remains somewhat controversial. Whereas the results of time-of-flight photoluminescence (PL) studies [13] were interpreted in terms of dispersive propagation of the bound exciton polaritons, formation of free exciton (FX) polaritons was concluded as the main source of light delay in our time-of-flight experiments [14] performed utilizing laser pulses.

The purpose of the present study is to resolve this issue by directly comparing propagation of both photoluminescence (PL) and laser pulses through the same bulk ZnO crystals. We show that the observed slow-down of the light velocity in the vicinity of the absorption edge is caused by the formation of free exciton-polaritons and is determined by their dispersion, whereas contributions of the DX polar-

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itions become important only in close proximity of the corresponding resonances.

2 Experimental In this study we used commercially available c-plane ZnO substrates from Cermet Inc. and Denpa Co. with thicknesses of 0.25 and 0.55 mm, respectively. Time-resolved PL measurements were carried out within the temperature range of 4 - 300 K. PL was excited by the third-harmonic pulses of a mode-locked Ti:sapphire laser with an excitation wavelength of 266 nm and duration of about 150 fs, at a repetition rate of 76 MHz. PL measurements were performed both in the forward and back-scattering geometries with light propagating along the normal to the sample surface. The resulting transient PL signal was detected by a Hamamatsu streak camera combined with a 0.5-m grating monochromator. Time resolution of the whole system was better than 2 ps. The second harmonic laser pulses tuned below the free exciton but in vicinity of bound exciton energies (3.326 - 3.361 eV) were used as a light source during time-of-flight measurements. The time origin was calibrated by carefully removing the sample out of the beam.

3 Results and discussion Characteristic transient PL images from the investigated Denpa and Cermet ZnO samples are shown in Fig 1(a, c) and 1 (b, d), respectively, measured at 5K and within the near-band-edge spectral range. Figure 1(a) and (b) show images measured in the conventional back-scattering geometry, whereas Fig.1(c)

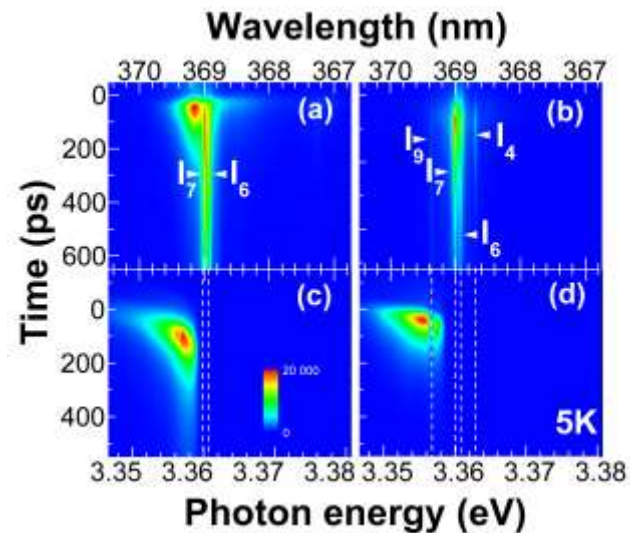


Figure 1 (Color online) Transient PL images measured at 5K within the near-band-edge spectral range from the Denpa (a, c) and Cermet (b, d) ZnO samples with the thicknesses of 0.55 and 0.25 mm, respectively. (a) and (b) show images measured in the conventional back-scattering geometry, whereas (c) and (d) present time-of-flight PL spectra obtained in the forward configuration. All spectra were measured with the light wave vector being parallel to the principal *c* axis of wurtzite ZnO.

and (d) present time-of-flight PL spectra obtained in the forward configuration. The corresponding time-integrated PL spectra are summarized in Fig. 2. The back-scattered PL spectra (denoted by the solid lines in Fig. 2) exhibit a fine excitonic structure with the dominant BX lines denoted as I_0 , I_4 , I_6 , I_7 and I_9 following the common notations, as well as weaker emissions from the upper (FX_A^u) and lower (FX_A^l) polariton branches of the FX-polaritons from the topmost A- valence subband. Relative contributions of these emissions vary between the samples, likely due to differences in residual contamination. The BX transitions exhibit fast rising after the excitation laser pulse and reach their peak intensity already within the first 50 ps, indicating fast trapping by donors. The trapping time is found to be comparable for all BXs resulting in the flat PL streak seen in Fig.1(a) and (b). From Figs. 1 and 2, PL spectra dramatically changed when they were recorded in the forward geometry, i.e. after transmission of the PL light through the ZnO media. First of all, complete quenching of PL intensity at photon wavelengths shorter than that of the dominant I_6 line can be observed due to strong light re-absorption by the corresponding BXs. Light absorption is also apparent for the I_9 transition, which is seen as a dip in the time-of-flight PL spectra of the Cermet ZnO. Most importantly, the PL streak in the forward geometry [Figs.1(c) and (d)] is no longer straight but instead exhibits a strong bending towards the absorption edge. The bending is pronounced only within the spectral range of the no-phonon DX transitions. It is no longer obvious for the transitions assisted by emission of longitudinal optical (LO) phonons, as can be seen from Fig.3, where the time-of-flight PL spectrum from the Denpa ZnO recorded within a wider spectral range is shown.

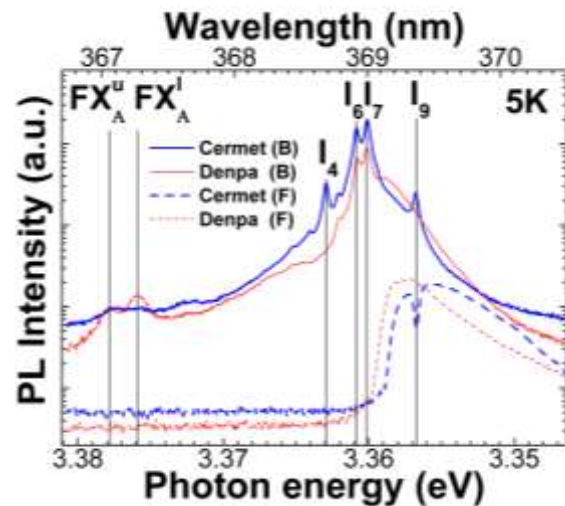


Figure 2 (Color online) Time integrated PL spectra measured at 5K from the Cermet and Denpa ZnO are shown by the thick and thin curves. The spectra measured in the forward (F) and back-scattering (B) geometries are shown by the solid and dashed lines, respectively. The spectra are displayed in the logarithmic scale.

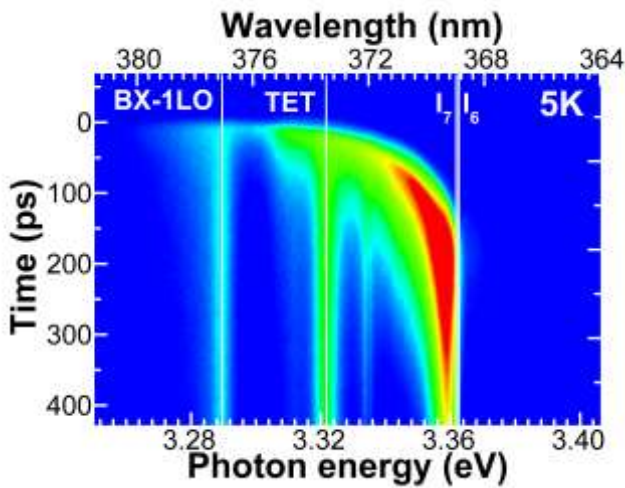


Figure 3 Transient image of the forward PL measured from the same Denpa ZnO as shown in Fig.1 but recorded within the wider spectral range covering the LO-assisted transitions. TET denotes two-electron transitions. The spectra are displayed in the logarithmic scale.

The observed bending of the PL streak means that the time required for the PL light to reach the back surface of the sample (to be referred below as time delay) critically depends on photon wavelength and increases when it approaches the region of the near-band-edge excitonic absorption. To quantitatively illustrate this effect, in Fig. 4 we compare temporal profiles of the forward PL intensity detected at different wavelengths. It is found that for the 0.55 mm-thick ZnO, the time delay experienced by DX in the vicinity of the I_6 transition (e.g. at 368.7 nm) is longer by about 200 ps as compared with that for the LO-assisted transitions. All delays times are about 2 times shorter in the 0.25mm-thick Cermet ZnO, i.e. the delay effect scales with the sample thickness. This can clearly be seen from Fig.5, where spectral dependences of the measured time delay are shown (the solid symbols). The time delays were calculated relative to the values measured at 381 nm, i.e. within the spectral range where the slow-down effect is marginal – see Fig.3.

Let us now discuss the origin of the observed effect. Two mechanisms could in principle contribute to the PL delay in the time-of-flight experiments. First of all, it could be partly related to delayed formation of the BX following expansion of electron-hole (e-h) plasma through the crystal from the front surface of the sample where it was initially excited. This mechanism could cause some time spreading of the PL light pulse, which mimics a spatial distribution of the excited electron-hole plasma, contributing to the overall delay in rising of the forward PL. The corresponding delay, however, is expected to be spectrally independent as it is simply related to the delayed excitation of the monitored PL. Secondly, the time delay should depend on the

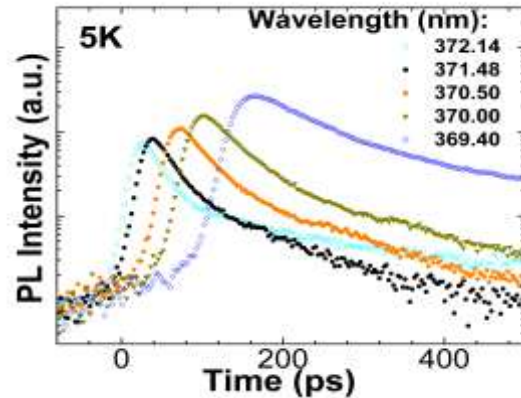


Figure 4 Temporal profiles of the transmitted PL light measured from the Denpa ZnO at the specified wavelengths.

time required for the PL light to propagate through the sample with a thickness L . The corresponding time delay T_d is directly determined by the group velocity of light (v_g) as $T_d = L/v_g$. The latter is defined as

$$v_g(\omega) = \frac{d\omega}{dk} \quad (1)$$

where k is the wave vector and ω is the photon frequency. T_d could be spectrally dependent due to spectral dispersion of v_g . In order to confirm that the main contribution to the observed strong delays in the BX light propagation is indeed caused by a decrease in the group velocity of light in the vicinity of the BX resonances, time-of-flight experiments were repeated using laser pulses instead of the PL light. This allowed us to exclude the possible contribution of e-h plasma expansion to the light delays. The corresponding results are shown by the open symbols in Fig.5 and are again calculated relative to the delay value at 381 nm, to allow direct comparison with the time-of-flight PL data. Apparently, the slow down effect is identical in both types of experiments which provides an unambiguous proof that it is determined by the spectral dispersion of v_g .

The observed spectral dependence of the group velocity can be understood within the polariton framework. It is well-known that strong exciton-photon coupling in ZnO leads to the formation of a mixed-mode exciton-polariton state that is now a true eigenstate of the system. In other words, the light wave entering the sample is converted into the polariton wave which then propagates through the ZnO media with the group velocity determined by the polariton dispersion

$$\frac{c^2 k^2}{\omega^2} = \varepsilon(\omega, k) \quad (2)$$

Here $\varepsilon(\omega, k)$ is a dielectric function given by [15]:

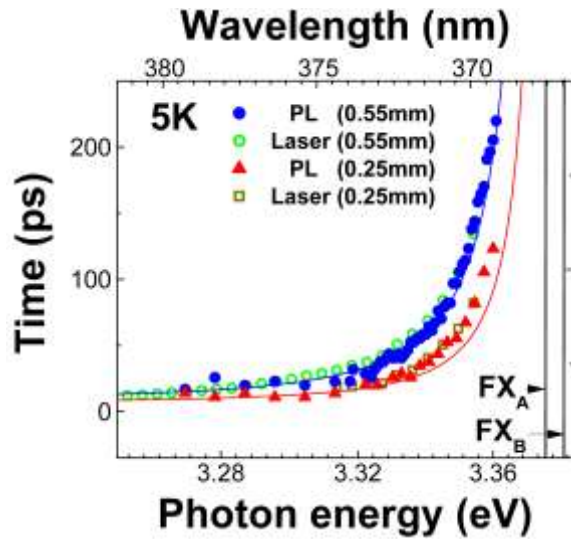


Figure 5 (Color online) Time delays caused by propagation of light through the ZnO media with the specified thicknesses. The time delays are plotted relative to the measured value at 381 nm, where the slow-down of light becomes only marginal. The filled (open) symbols are experimental data for the transmitted PL (laser) light. The solid lines represent results of the simulations performed by taking into account the FX excitons-polaritons but omitting contributions of all DX polaritons.

$$\varepsilon(\omega, k) = \varepsilon_{\infty} + \sum_i \frac{f_i \omega_{0i}^2}{\omega_{0i}^2 - \omega^2 - i\omega \hbar \Gamma_i} \quad (3)$$

where ε_{∞} is the background dielectric constant, f is the oscillator strength, ω_0 is the resonance frequency, and Γ_i is the exciton damping. The summation in the second term should be performed over all optically active resonances denoted by the subscript i . Equations (1) - (3) can be used to simulate spectral dependence of the polariton group velocity. The corresponding results are shown by the solid lines in Fig. 5 assuming that the dispersion is determined by the formation of the FX polaritons related to the A- B- valence band, which are allowed by selection rules in the used measurement geometry with the electric field vector \mathbf{E} of light being perpendicular to the principal axis c of wurtzite ZnO. Note that the simulated curves were obtained without any adjustable parameters, using the commonly accepted values of $\varepsilon_{\infty} = 6.69$ [16], $\hbar\omega_0 = 3.3758$ eV (3.3810eV) and $f = 0.0071$ (0.0404) for A (B) FX resonance [Fel! Bokmärket är inte definierat., 15]. The damping term $\hbar\Gamma_i$ for all resonances was assumed to be of the order of the PL linewidth of 0.5 meV. We see that the simulation results are in excellent agreement with the experimental data for the Denpa ZnO. This evidences that the observed decrease of the light velocity in the vicinity of the absorption edge is chiefly caused by the formation of free exciton-polaritons and is determined by their dispersion, contrary to the previous conclusions of Ref. 13. The

agreement is somewhat less satisfactory for the Cermet ZnO, especially in the close vicinity to the DX transitions, but can be further improved by including contributions from the DX-polaritons (not shown in Fig.5). This is not surprising and could naturally be attributed to a higher oscillator strength of DX in this sample caused by a higher concentration of residual donors. The latter was independently confirmed by the performed spin resonance measurements [17].

4. Conclusions We have observed significant delays of light propagating through ZnO media for photons with energies close to the absorption edge of the material. The observed delays were found to be identical during the time-of-flight experiments performed utilizing either PL or laser pulses. The observed slow-down of light is attributed to formation of free-exciton polaritons and strong spectral dependence of their group velocity in the vicinity of the excitonic resonance. It was also shown that the contribution of the bound-exciton polaritons in the observed slow-down is only essential in the direct proximity to the DX resonances and is enhanced with increasing concentration of the related donor impurities.

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