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Time-Resolved Photoluminescence Lifetime Measurements of the Gamma(5) and Gamma(6) Free Excitons in ZnO

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Time-resolved photoluminescence spectroscopy at 2 K was used to measure the radiative recombination lifetime of the allowed (Γ_5) and forbidden (Γ_6) free excitons in ZnO. The measurements were made on a sample containing internal strain, which altered the sample symmetry, and resulted in relaxed selection rules, allowing the Γ_6 exciton to be observed. A radiative recombination lifetime of 259 ps was measured for the Γ_5 exciton and 245 ps for the Γ_6 exciton. The decay of the free excitons was of single-exponential form, and the decay times were obtained using a least-squares fit of the data. © *2000 American Institute of Physics.* [S0021-8979(00)00316-9]

ZnO is a wide-band-gap material and recently has been recognized to have potential for optoelectonic applications. Some of the properties that support this assertion are as follows: (a) low-threshold power for optical pumping at room temperature;[1–3] (b) large exciton binding energy (60 meV), which may give rise to efficient UV laser applications; and (c) a tunable band gap from 2.8 to 4.0 eV.[4,5] A clear understanding of recombination mechanisms is important for optimization of device structures. Time-resolved photoluminescence (TRPL) is a unique way of studying materials because the temporal information combined with spectral data can elucidate the dynamics of carriers involved in optical transitions. We have shown in GaN that as the strain decreases the lifetime for both free excitons and donor-bound excitons increases.[6] This suggests that the factors contributing to strain also introduce recombination paths as well as nonradiative decay processes.

ZnO crystallizes in the wurtzite structure; in this structure the conduction band has Γ_7 symmetry while the top valence band has Γ_9 symmetry. The exciton symmetries associated with the optical transitions between these two bands are as follows:

$$\Gamma_7 \times \Gamma_9 = \Gamma_5 + \Gamma_6 .$$

The Γ_5 exciton is an allowed exciton while the Γ_6 is forbidden. In this communication, we report on the radiative lifetimes of these two free excitons in ZnO.

The sample used for this study was grown by a hydrothermal process. The apparatus consisted of an autoclave equipped with a free-standing sealed platinum liner in which the ZnO nutrient material, mineralizer, and seed plate were contained. The seeds were (0001) plates of ZnO from previous hydrothermal growth runs. At the growth temperature, the nutrient zone was at 355 °C with a temperature gradient of 10 °C, declining to the seed plate. Some of the crystals contained strains, which were evidenced by shifts in the free-exciton emission positions.[7] The strains also relax the selection rules by changing the symmetry of the sample. In a strained sample the Γ_6 unallowed exciton is clearly observed, permitting lifetime measurements to be made on both Γ_5 and Γ_6 excitons. The exciton lifetimes were determined from TRPL measurements made at low temperature (2 K) with a Hamamatsu model C1587 synchroscan streak camera. The excitation source was a frequency-tripled mode-locked Ti:sapphire laser producing pulses with a wavelength of about 2750 Å, and a nominal pulse width <1 ps.

The free-exciton emission spectra for an unstrained ZnO sample and for the strained sample are shown in Fig. 1. In the unstrained sample, only the Γ_5 exciton is observed since the Γ_6 is forbidden. In the strained sample, both the Γ_5 and Γ_6 excitons are clearly seen and are shifted to lower energies

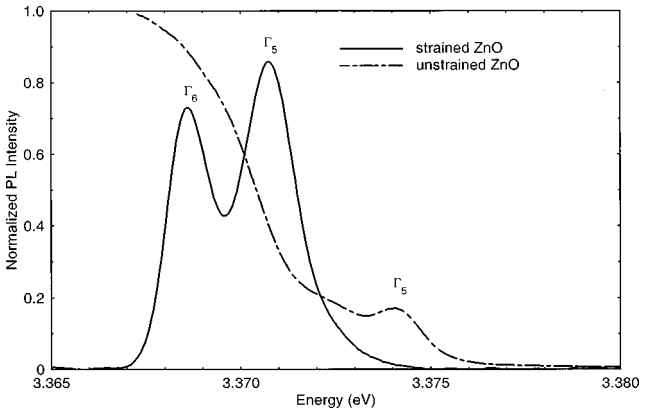

FIG. 1. Free-exciton emission spectra for strained and unstrained ZnO samples.

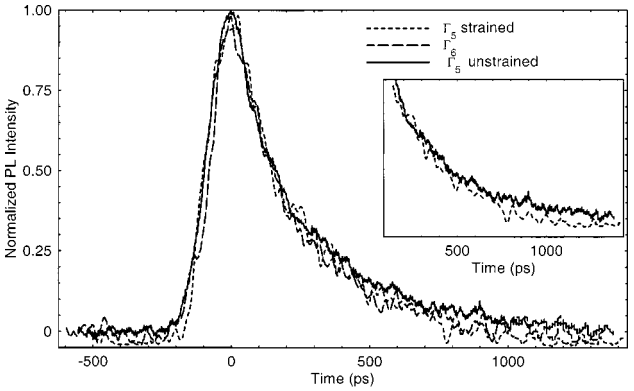

FIG. 2. Recombination lifetimes for the Γ_5 and Γ_6 free excitons in ZnO.

by ~0.0025 eV. This shift to lower energy reflects a tensile strain. The two excitons are well resolved, permitting accurate lifetime measurements with very little overlap. The time-resolved measurements are shown in Fig. 2. The decay time for the Γ_5 exciton in the unstrained sample is also shown in Fig. 2. The decay times for the Γ_5 excitons in the strained and unstrained samples are portrayed in the inset of Fig. 2. The decay times were obtained from a least-squares fit of the data to a single exponential. The lifetime of the Γ_5 exciton in the strained sample was determined to be 259 ps, while the lifetime of the same exciton in the unstrained sample was found to be 322 ps. The lifetime of the Γ_6 exciton was 245 ps. Note that free-exciton lifetimes are determined not only by radiative decay, but also by nonradiative decay and by capture processes (leading to bound excitons). Evidently, the dominant lifetime limiter affects the Γ_5 and Γ_6 excitons similarly.

In summary, we have measured the lifetime of the allowed Γ_5 and unallowed Γ_6 (allowed by incorporated strain) excitons in ZnO. In the unstrained crystal, there is room-temperature lasing potential via the Γ_5 free exciton due to its large binding energy. These exciton lifetimes will vary with crystal quality, becoming longer as the quality improves, as is demonstrated by the lifetimes of the Γ_5 exciton in strained and unstrained material. Radiative decay measurements are very helpful in analyzing materials for optoelectronic applications.

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