Exciton recombination dynamics in single ZnO tetrapods

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Exciton recombination dynamics in single ZnO tetrapods

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Abstract. We present the optical properties of individual ZnO tetrapods as a function of excitation power and temperature by time-integrated and time-resolved spectroscopy. At 10K, we identify the different excitonic transitions by both their characteristic energy and their excitation power dependence. When we increase the tetrapod temperature we observe that the emission intensity decrease and occur a red shift of the emission energies. Our time-resolved studies confirm the predominance of the radiative recombination at low temperatures (< 45 K). Increasing the temperature opens up the non-radiative channels, which are evidenced by a much faster decay time.

Keywords: ZnO nanotetrapods; photoluminescence.
PACS: 78.55.Et; 78.67.-n; 72.20.Jv

INTRODUCTION

ZnO is one of the most attractive wide band-gap emitters, with a direct band gap of 3.37 eV at room temperature and a large exciton binding energy (60 meV). This makes ZnO a potential candidate for optoelectronics applications, such as blue and UV light emitters and detectors[1,2]. Among the diverse ZnO nanostructures, tetrapods are known to be stable and tough[3]. They consist of four-shaped structures of ZnO joined at tetrahedral angles to a central core. One key exploitable advantage of tetrapods over nanocrystalline geometric forms is that they may spontaneously orientate with one *leg* directed normal to the plane of the substrate[4].

We study well-isolated single ZnO tetrapods deposited on a Silicon substrate. The typical *leg* dimensions are 2 microns long and few hundreds of nanometers diameter. Each individual tetrapod is optically excited with a 50× microscope objective, which focuses the laser beam (300 nm, obtained from the third harmonic of a pulsed Ti:sapphire laser) and collects the tetrapod photoluminescence (PL). The sample is mounted on a cold finger cryostat, where its temperature can be varied between 10 K and 300 K. The PL is detected either with a standard CCD camera to study the time-integrated (TI-PL) or with a streak camera for time resolved (TR-PL) studies.

RESULTS AND DISCUSSIONS

The TI-PL reveals the excellent quality of the ZnO tetrapods: we obtain a strong ultraviolet PL peak and an almost negligible green/yellow-band emission. At 10K, the PL spectrum is composed of several transitions identified by their characteristic energies and their pump power dependence. Figure 1 presents typical PL spectra at 10 K for increasing laser power.

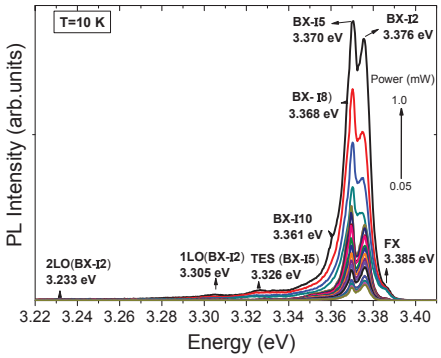

FIGURE 1. Near band edge emission of a ZnO tetrapod, measured at 10 K for different pump powers.

We resolve the free exciton (FX) at 3.385 eV and several bound excitons: (i) an excited rotator state (BX-I2) at 3.376 eV, (ii) two ionized donor states (BX-I5 and BX-I8) at 3.370 eV and 3.368 eV respectively, and (iii) a neutral acceptor (BX-I10) at 3.361 eV. In addition, the two electron satellite (TES) of the BX-I5 at 3.326 eV and the first and second

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longitudinal optical phonons (LO) replicas of the BX-I2 are observed.

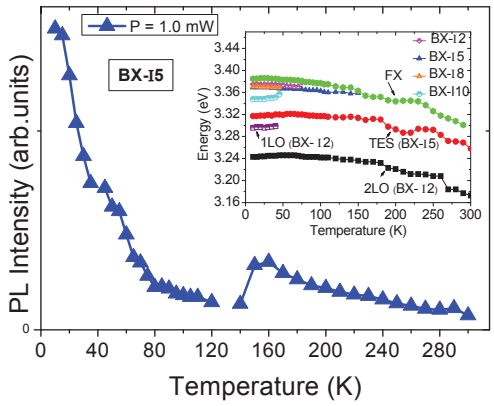

FIGURE 2. BX-I5 emission intensity versus temperature for 1 mW pump power. The inset shows the red shift of the different transitions with increasing temperature.

The temperature dependence of the PL intensity for one value of pump power is shown in Figure 2. The intensity decreases as the temperature increases until around 150 K. At this temperature, an abrupt increase of the intensity is observed. Above 150 K, the intensity keeps on decreasing up to room temperature. The intensity jump at 150 K may be explained in terms of the difference between the dilatation coefficients of the Si substrate and ZnO. At this temperature, the deformed ZnO crystal lattice relaxes the stress. The inset of Figure 2 shows that there is a red shift of the emission peaks as the temperature increases. At low temperatures (<45 K), BX-I8, BX-I10 and the 1LO (BX-I2) ionize quickly, following the BX-I2 and BX-I5 that ionizes around T =80 K and T=150 K, respectively. Above 150 K, only the FX, TES (BX-I5) and 2LO-BX-I2 are visible.

To study the recombination dynamics of each exciton, we have measured time-resolved PL. Figure 3 (a) displays a streak camera image of the tetrapod's emission at 10 K obtained with a pump power of 1.0 mW. It is possible to observe the FX, the BX-I2 and the BX-I5. Selecting these energies we can extract the time-evolution traces. The decay time of these traces is fitted with an exponential decay function giving a characteristic decay time as explained in Ref. 5.Figure 3 (b) shows the temperature dependence of PL decay constants for these transitions. For temperatures below 45 K, the evolution is characterized with a single decay (t_1) for both BX-I2 and FX. Above 45 K, the decay of the FX is better characterized by two decay times (t_1 and t_2) as well as BX-I5 from 10K, which evidence the contribution of non-radiative (NR) recombination.

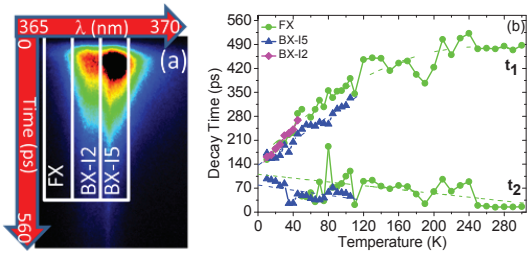

FIGURE 3. (a) Streak camera image of the tetrapod's emission at 10K and pump power of 1.0 mW, showing the FX, BX-I2 and BX-I5. (b) Temperature dependence of the decay times for the different transitions. Dashed lines are drawn as a guide to the eye.

CONCLUSIONS

In summary, we have shown that increasing the temperature, some transitions quench rapidly due to the thermal ionization. At 150 K, a jump of intensity occurs, which may due the different dilation coefficients of Si and ZnO. At this temperature, the ZnO crystal lattice is deformed and it releases stress.

Increasing the lattice temperature activates the non-radiative recombination channels, as evidenced by the bi-exponential decay observed in distinct excitonic transitions. The fast PL decay is attributed to non-radiative recombination and the slow PL decay is related to the radiative recombination.

ACKNOWLEDGMENTS

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REFERENCES

1. Nguyen ThiThucHien, Doan Manh Ha, Ngo Xuan Dai, Nguyen Thi Thu Huong, *VNU Journal of Science, Mathematics - Physics***24**, 2008, pp. 24-29.
2. Zhong Lin Wang, *Materials Today* **7**, June, 2004.
3. M. N. Jung, S.Y. Ha, S.H. Park, M. Yang, H.S. Kim, W.H. Lee, Y. Yao, J.H Chang, *Physica E* **31**, 2006, pp. 187-190.
4. M.C.Newton and, P.A.Warburton, *Materials Today*, **10**, 2007, pp. 5.
5. S.-K. Lee, S. L. Chen, D. Hongxing, L. Sun, Z. Chen, W. M. Chen, and I. A. Buyanova, *App. Phys. Lett.* **96**, 083104, 2010.