Refractive index of a single ZnO microwire at high temperatures

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(Received 11 January 2014; accepted 11 February 2014; published online 25 February 2014)

We report a study of refractive index of a wurtzite ZnO single crystal microwire at a temperature range from room temperature to about 400 K using optical cavity modes. The photoluminescence (PL) spectra of the ZnO microwire at different temperatures were performed using a confocal micro-photoluminescence setup. The whispering gallery modes observed in the PL spectra show a redshift both in the ultraviolet and the visible range as the temperature rises. The redshift is used to extract the refractive index of the ZnO microwire. The dispersion relations are deduced at different temperatures, and the results show that the refractive index increases with raising temperature for both transverse electric and transverse magnetic modes. The refractive index increases faster at a shorter wavelength, which is due to the fact that the shorter wavelength is closer to the resonance frequencies of ZnO microwire according to the Lorentz oscillator model. © 2014 AIP Publishing LLC.

Single ZnO microwire microcavities have attracted much attention for their potential applications, such as photoluminescence enhancement,1,2 polariton condensation,3 and ultraviolet (UV) lasers.4–10 Several types of cavity modes have been observed in ZnO micro structures, including whispering gallery modes (WGMs),11,12 quasi-WGMs,13–15 and Fabry-Perot modes (FPMs).16,17 The WGMs have higher quality factors (Q) as they are the resonances of the cavity by the total internal reflection,6,11,18–22 while the quasi-WGMs and FPMs formed from the partial reflection have lower quality factors.2,14,23,24 Due to the strong coupling between the excitons and the cavity modes, exciton-polariton has been observed in WGMs, quasi-WGMs, and FPMs, but the UV lasering was studied mainly in WGMs due to the higher quality factors.7,25–29

Since ZnO material has a large exciton binding energy of about 60 meV, exciton-polariton emission has been observed at room temperature or even higher.17,30 In order to obtain the energy-wavevector (E-k) dispersion relation of exciton-polariton, the dispersion relation of the refractive index must be obtained first. For bulk materials or thin films, the refractive indexes were characterized traditionally using methods, such as transmission, reflectivity, or ellipsometry spectroscopy.31,32 However, it is very difficult to use these methods to measure the refractive index of a single microwire. In addition, the refractive index of ZnO above the room temperature has been rarely studied. In this letter, the refractive indexes of ZnO at a temperature within the range of 300 K–400 K are reported. The WGMs at different temperatures above 300 K were mapped using confocal micro-photoluminescence (µ-PL) spectroscopy, and from the PL spectra the refractive indexes of a single ZnO microwire are extracted.

The ZnO microwires were grown by a vapor phase transport method using high-temperature tube furnace.33,34 A quartz boat filled with a mixture of ZnO and graphite powder (weight-ratio, 1:1) was placed at the end of a slender one-end sealed quartz tube, and several cleaned Si substrates on a quartz wafer were placed in the quartz tube about 10 cm away from the quartz boat. The furnace was pre-heated and maintained at 950 °C, the quartz tube was then pushed into the furnace for a 8-h reaction. After that the tube was pulled out and cooled down to the room temperature at a rate of 30 °C/min. The Si substrates were then covered with a lot of crystal whisker which was confirmed to be the wurtzite structured ZnO microwires using scanning electron microscope (SEM) and X-ray Powder Diffraction. For the PL studies, a single hexagonal ZnO microwire was transferred to a Si substrate, and the sample was placed in a continuous-flow cryostat with a pressure under 10−3 millibars and a temperature within the range of 300K–400 K. A continuous wave He-Cd laser at 325 nm was used as an excitation source. The pump laser light was focused by a 36× reflective microscope objective with a spot size of about 2 μm in diameter. The PL from the ZnO microwire was collected by the same objective and dispersed through a 0.55 m monochromator, then detected by a nitrogen-cooled, back-illuminated charge-coupled device (CCD) camera. The transverse electric (TE, E//c-axis) and transverse magnetic (TM, E//c-axis) polarized PL spectra were separated by placing a Glan-Taylor polarizer in front of the monochromator.

Figure 1(a) presents a SEM image of the ZnO microwire studied in this work. The diameter of the ZnO microwire is about 9.5 μm. The TE and TM polarized PL spectra of the ZnO single microwire are shown in Fig. 1(b). For the TE polarized PL spectrum, two main peaks in the UV range are centered at about 380 nm and 391 nm with a full width at half maximum (FWHM) of 5 nm and 20 nm, respectively. The PL in the UV range is due to the emission of excitons in the ZnO microwire.35 The wurtzite ZnO conduction band is s-like with a Γ7 symmetry, while the valence band is p-like state and split into three bands due to the crystal-field and the spin-orbit interaction induced splitting. The excitons corresponding to the three valence bands are usually denoted by A, B, and C, with the symmetries of Γ9, Γ7, and Γ7,
respectively. According to the selection rules of transitions, all three exciton transitions are allowed in the \(\pi\) polarization (\(E \parallel c\) axis, and \(k \parallel c\) axis), but C exciton is quite weakly to be observed. The C excitonic transition is strongly allowed in the \(\pi\) polarization (\(E \parallel c\), \(k \parallel c\)), while the transitions for A exciton is forbidden and the B exciton is only weakly observable in this geometry. As a result, the TE polarized PL intensity is stronger than that of TM in the UV range. In addition, the broad peak in the visible range from 430 nm to 730 nm is centered at about 600 nm with a FWHM of about 240 nm, which is due to the defect-related emission. In this range, the TM polarized PL is stronger than TE, as the WGMs in ZnO microwires are preferentially TM polarized.

On top of the main peaks in the PL spectra, periodically spaced small peaks can be observed clearly from the UV to the visible range, which are ascribed to the WGMs, as sketched in the inset in Fig. 1(a). In the visible range the WGMs can be clearly observed in Fig. 1(b), and in the UV range they appear very densely but still can be resolved. Figure 1(c) shows the enlarged spectra in the UV range. The peak intervals of WGMs become larger as the wavelength increases, which are similar to what have been observed before.

Figs. 2(a) and 2(b) show the temperature dependent PL spectra of TE polarized modes in the UV and the visible range, respectively. The TM polarized PL spectra at different temperatures are similar to that of TE, and not shown here. The excitonic peaks and the optical WGMs shift to red as the temperature increases from 299.7 K to 399.8 K. A difference is that exciton energy red shifted by 75 meV, while the WGM at 402 nm only shifted about 27 meV for the TE polarized PL as marked in Figure 2(a). The redshift for the main peak in the UV range is due to the band gap narrowing of ZnO, while that for the optical WGMs is due to the refractive index increase of ZnO microwire when the temperature rises. From the redshift of WGMs, the temperature dependent refractive indexes of ZnO microwire can be extracted precisely. The mode equation for the WGMs in a regular hexagonal cavity is

\[
R = \frac{\lambda}{3\sqrt{3}n} \left[ N + \frac{6}{n} \arctan(\beta\sqrt{3n^2 - 4}) \right],
\]

where \(R\) is the side length of the hexagonal cavity, \(\lambda\) is the resonance wavelength, \(n\) is the refractive index, and \(N\) is the mode number. The factor \(\beta\) is related to the polarization of the spectrum, \(\beta = n\) for TE polarized modes and \(\beta = 1/n\) for TM. At room temperature, the mode number \(N\) of WGMs is determined by the refractive index from the reference. When the temperature rises from 300 K to 400 K, the WGMs shift to the lower energy and keep the same mode number. The thermal expansion of the microwire can be neglected; therefore, the side length \(R\) can be considered as a constant. The resonant wavelengths can be read from the sharp peaks in PL spectra from Fig. 2, which results in that the refractive index can be calculated with Eq. (1).

It is well known that ZnO is a birefringence material, and the refractive indexes of TE and TM modes are different. The refractive indexes as a function of wavelength at different temperatures for TE polarized PL (\(n_o\)) and the TM polarized PL (\(n_e\)) are shown in Fig. 3. In Figs. 3(a) and 3(c), the refractive index of TE mode is greater than that of TM mode, namely, \(n_o > n_e\). This means that it is a negative uniaxial crystal in the UV range. However, in Figs. 3(b) and 3(d), the refractive index of TM polarized PL is greater (\(n_o < n_e\)), indicating a positive uniaxial crystal in the visible range.
range. It can be seen that the ZnO single crystal microwire is not always a positive or negative uniaxial crystal, but depends on the wavelength.\textsuperscript{13} In addition, the refractive index in UV range is greater than that in the visible range for both TE and TM polarized PL spectra. The dispersion curves for TE and TM polarized PL spectra move up monotonically, providing a refractive index increase of ZnO microwire with increasing temperature.

From the refractive index change in Fig. 3, the temperature dependent refractive index at fixed wavelengths can be deduced using cubic spline interpolation. Figure 4 shows that the refractive index increases at fixed wavelengths when the temperature increases from 299.7 K to 399.8 K. The refractive index increases faster in the UV range than that in the visible range for both TE and TM modes. While in the visible range, the refractive index increase is about 0.013, which is around 1/3 of that in the UV range for both TE and TM modes. The refractive index \( n(\omega) \) is related to the relative dielectric constant \( \epsilon_r(\omega) \) derived from the Maxwell’s equations: \( n(\omega) = \sqrt{\epsilon_r(\omega)} \). For the ZnO material, the permittivity can be expressed by the Lorentz oscillator model.\textsuperscript{32} The optical dielectric function \( \epsilon(\omega) \) is given by the following expression:

\[
\epsilon(\omega) = \epsilon_0 + \frac{\epsilon_0^2}{\epsilon_0 m} \sum_n \left( \frac{N_{\epsilon b,n}}{\omega_n^2 - \omega^2 - i\gamma_n \omega} \right),
\]

where \( \omega \) is the angular frequency, \( N_{\epsilon b,n} \) is the concentration of electrons, \( \omega_n \) is resonance frequency, \( \gamma_n \) is the frictional constant, \( \epsilon_0 \) is the permittivity of vacuum, \( e \) and \( m \) are the charge and mass of a single electron. \( \epsilon_0 m \) represents the contributions to \( \epsilon \) from electronic resonances with \( \omega_n \) at a high frequency range, which equals to 1 here. When the temperature is the only variable, the dielectric function in the Lorentz oscillator model can be simplified as \( \epsilon(\omega) \sim 1/(\omega_n^2 - \omega^2) \). The resonance frequency \( \omega_n \) corresponds to the exciton energy, which shows a redshift as the temperature rises, as aforementioned. As a result, the permittivity \( \epsilon(\omega) \) increases as the temperature rises. The UV light frequency is closer to resonant frequency than the light in the visible range, which results in that the refractive index changes faster with increasing temperature. As the other parameters in Eq. (2) are not determined accurately, the refractive index changes as a function of temperature can only be explained qualitatively here.

In summary, the refractive indexes of wurtzite ZnO single microwire of TE and TM polarized PL were extracted precisely according to the redshifts of the WGMs in a temperature range from 300 K to 400 K. The birefringence properties of the single ZnO microwire depend on the wavelength range. With increasing temperature, the resonance frequencies red shift as the energy gap narrowing in ZnO microwire. According to the Lorentz oscillator model, the refractive index of ZnO increases as the temperature rises. The refractive index increases more in UV range, which is due to these cavity modes are close to the resonance frequencies. The refractive index of ZnO microwires in this work provides a fundamental parameter to understand the microstructure-based strong coupled cavities, UV lasers and nonlinear optics at high temperatures.

This work was supported by the National Basic Research Program of China under Grant Nos. 2013CB328706, 2014CB921003, and 2013CB632704; the National Natural Science Foundation of China under Grant Nos. 11174356 and 61275060; the Hundred Talents Program of the Chinese Academy of Sciences; and the China Postdoctoral Science Foundation under Grant No. 2013MS540155.