Single nanowire waveguides and lasers

Justin C. Johnson\textsuperscript{a}, Haoquan Yan\textsuperscript{b}, Heon-Jin Choi\textsuperscript{b}, Kelly P. Knutsen\textsuperscript{a}, Poul B. Petersen\textsuperscript{a}, Matt Law\textsuperscript{b}, Peidong Yang\textsuperscript{b}, Richard J. Saykally\textsuperscript{a,*}

\textsuperscript{a}Department of Chemistry, University of California, Berkeley; \textsuperscript{b}Physical Sciences Division, Lawrence Berkeley Laboratory

ABSTRACT

Quasi one-dimensional nanostructures are unique probes of cavity quantum electrodynamics because they are capable of exhibiting photonic and/or electronic confinement in two dimensions. The near-cylindrical geometry and sharp end facets of zinc oxide (ZnO) nanowires enable the realization of active nanoscale optical cavities that exhibit UV/blue photoluminescence (PL) waveguiding and lasing action at room temperature under appropriate optical pumping conditions. Study of individual nanostructures is crucial for isolating geometry-dependent effects, and here it is achieved through both near- and far-field microscopies. The polarization of the emitted PL or lasing from individual nanostructures characterizes the coupling of the spontaneous emission to cavity modes, depending both on the wavelength of the emitted light and the nature of the emitting species (i.e., excitons and intrinsic defects in various charge states). In addition, the spectral evolution of the lasing/PL as a function of the pump fluence indicates both exciton and electron-hole plasma dynamics. Variations of size, geometry, and material on the prototypical cylindrical ZnO nanowire lead to further observation of unique photonic and/or carrier confinement effects in novel nanostructures.

Keywords: nanowire, laser, stimulated emission, photoluminescence, near-field, microscopy, ultraviolet, zinc oxide, gallium nitride

1. INTRODUCTION

Until recently, experimental nanowire optical physics has lagged behind investigations of 0-dimensional and 2-dimensional nanoscale systems (i.e., quantum dots\textsuperscript{1} and boxes/wells\textsuperscript{2,3}). Recent improvements in fabrication techniques for wire and rod-like semiconductor structures have engendered a new generation of experiments on these structures\textsuperscript{4-13}, which are unique because they are capable of exhibiting photonic and/or electronic confinement in two dimensions. Optical and electronic phenomena such as single nanowire logic gates\textsuperscript{4}, photodetectors\textsuperscript{5,6}, photochemical sensors\textsuperscript{7}, photonic wire lasers\textsuperscript{8}, and electron-injection lasers\textsuperscript{9} have recently been reported. Initial studies of lasing in nanowire arrays\textsuperscript{10} and single nanowires\textsuperscript{11,12} have provided insight into the phenomenon of confined stimulated emission in these structures, although much of the detailed optical physics remains to be fully explored. Recent efforts in our lab have been addressed the nature of the PL waveguiding in individual ZnO nanowires through the use of microscopy and spectroscopy, and the optical and material aspects of the transition from spontaneous to stimulated emission via its dependence on the cavity geometry.

Zinc oxide is a wide-band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV). The bulk PL from crystalline ZnO has been well-characterized over the years, and it has been attributed primarily to free and/or bound exciton recombination under low and moderate optical excitation conditions. Recent investigations of highly excited ZnO thin films have revealed stimulated emission at room temperature, the mechanism of which is thought to be either exciton-exciton (ex-ex) recombination or radiative decay of a dense electron-hole plasma (EHP).\textsuperscript{13-15} Despite some experimental results exhibiting characteristics of EHP or exciton behavior, the transition between the two types of excited carrier dynamics and how it affects stimulated emission in the ZnO crystal remains somewhat unclear.

\begin{small}\textsuperscript{*}saykally@uclink.berkeley.edu: 510 642-1047; fax 510 642-8566; http://www.cchem.berkeley.edu/rjsgrp; Univ. of California, Berkeley, Dept. of Chemistry, D33 Hildebrand Hall, Berkeley, CA, USA 94720-1460.\end{small}
One method for identifying EHP and exciton dynamics is to observe the lasing spectrum from a well-defined cavity. Stimulated emission in thin films is often identified by a narrowing of the PL spectrum and a superlinear increase in the PL intensity with respect to pumping power. Occasionally, fortuitous cavities are formed in disordered polycrystalline samples, leading to narrow cavity modes. However, analysis of this “random lasing” is nearly impossible due to the inherent uncertainty in the exact cavity parameters. In contrast, single ZnO nanowires have a well-defined cavity geometry that has been shown to be the source of a set of longitudinal cavity modes that are emitted in a cone from the nanowire ends. The approximate spacing of these modes is given by

\[
\Delta \lambda = \frac{\lambda^2}{2 L (n - \lambda \, \frac{dn}{d\lambda})},
\]

where \( L \) is the cavity length, \( n \) is the refractive index of ZnO (2.45), and \( \lambda \) is the emission wavelength. The sensitivity of the mode spacing to the material refractive index leads to the possibility of observing several effects. One of these effects is the increase of refractive index with increasing temperature induced by high pump fluence. In addition, \( n \) can decrease with pump fluence due to the saturation of exciton absorption, which can be envisioned with a Kramers-Kronig transformation of the imaginary refractive index. Loss of the exciton species indicates that the carrier density has increased beyond a critical level (Mott density), and the EHP state becomes favored. The competition between these two effects at high pump fluence determines the shifting of the cavity modes, as is shown in the data presented in the next section.

The issue of lasing properties versus nanowire diameter can be understood qualitatively by considering the electromagnetic field intensity per waveguide mode as a function of the wire diameter

\[
\eta = 1 - (2.405 \exp[-1/V])^{1/2},
\]

where \( V = k r (n^2 - 1)^{1/2}, k = 2\pi/\lambda \), and \( r \) is the wire radius. Clearly, nanowires with diameter much smaller than 100 nm have minimal EM intensity inside the wire, thus strongly reducing the possibility for gain. However, utilization of a core/shell structure leads to the possibility of observing lasing with an active material diameter of \(<60\) nm and a transparent, lower index shell with diameter near \(200\) nm. An AlGaN/GaN core/shell nanowire system that exhibits this behavior is discussed below. As the nanowire diameter increases above \(100\) nm, significant gain again becomes possible, and a single transverse mode is observed. For larger diameters \(>130\) nm, higher-order transverse modes are possible, much like conventional optical resonators. These modes contain polarization, linewidth, and spacing information that allows for their identification based upon the approximate cylindrical symmetry of the nanowire cavity.

The relatively high gain (>10^4 cm^-1) achieved in optically-pumped ZnO has allowed for the observation of lasing in a variety of other single nano and microstructures, including structures that are not quasi one-dimensional. These include nanoribbons, which contain approximate axial symmetry, but have a transverse dimension that is several times larger than the light wavelength. Due to the relaxation of strict photon confinement in this direction, the lasing modes are similar to whispering gallery modes (WGM), commonly observed in micron-sized spherical and circular structures. High quality end facets are no longer requisite in these structures, since multiple reflections can occur at non-normal incidence with respect to the side faces, leading to a variety of possible resonator geometries. In some cases, the axial directionality observed in nanowires is lost, leading to a complicated emission pattern.

2. EXPERIMENTAL

Nanostructures were synthesized according to procedures previously described and then typically sonicated to remove them from the growth substrate and dispersed onto either Si or sapphire to achieve a density of approximately 100 wires/cm^2, which is a suitable density for doing single wire measurements. The far-field microscope consists of a 0.7 NA objective used to collect the PL or lasing from single wires, which is then imaged on a video camera. The wire emission can also be directed to an optical fiber, which is coupled to a 0.3 m spectrograph and liquid nitrogen cooled CCD for spectra collection.

The near-field scanning optical microscopy (NSOM) setup (Topometrix, Lumina) utilizes a shear-force feedback mechanism to maintain a chemically-etched single mode optical fiber at a constant distance from the sample.
substrate. In this manner, simultaneous topography and optical images are obtained (200 x 200 pixels). The tip can be positioned at any point on the image and the emission can also be routed to the spectrograph for spatially-resolved spectroscopy. Typical spatial resolution for the NSOM system is 100 nm, using uncoated, chemically-etched tips.\textsuperscript{22}

The excitation laser is a home-built Ti:sapphire oscillator and commercial regenerative amplifier (Spectra-Physics, Spitfire). The pulses at 800 nm (2 mJ, 75 fs, 1 kHz) are spectrally converted using an optical parametric amplifier (OPA) and frequency doubling crystals for tunable excitation from 290 nm – 360 nm, appropriate for ZnO band-gap excitation. Photoluminescence measurements were made using a continuous wave He-Cd laser, operating at 325 nm.

Correlation of optical measurements with nanowire size and geometry was done using scanning or transmission electron microscopy (SEM, TEM). The individual structures were identified on the patterned substrate using the optical setup and taken to the National Center for Electron Microscopy (NCEM) for high-resolution structural characterization.

Figure 1. (a) Experimental apparatus used for far-field spectroscopic measurements. (b) Illustration of the near-field geometry for NSOM measurements.

Figure 2. Shapes and high-resolution electron micrographs of (a) ZnO nanowires, (b) ZnO nanoribbon, and (c) GaN/AlGaN core/shell heterostructure.
3. RESULTS

3.1 Nanolaser spectrum

Although the diameters of most nanowires cannot be fully spatially resolved by far-field optical microscopy, variation of optical emission along the length (2-10 µm typically) is easily observable. In a waveguiding system such as a nanowire, a high intensity of PL is expected near the ends where the emission leaves the cavity. Imaging in both far- and near-field shows this effect clearly, with contrast levels of approximately 5:1 from the end to the center of the nanowire. In the low pumping regime, emitted photons are waveguided but are not amplified due to the lack of sufficient gain from the excited carrier population. However, increased pumping leads to a dramatic change in the image (as shown in Figure 3), if the nanowire also provides requisite optical feedback inside the cavity. Contrast levels from these wires now increase to >1000:1 from end to middle. Nanowires that do not have sufficient resonant feedback may still have high carrier density (and thus high optical gain) but are unable to support stable lasing due to high loss resulting from structural defects. The emission pattern observed for lasing wires has a roughly Gaussian intensity profile across the cone emitted from each end. However, considerable structure can be seen with some wires, indicating multimode behavior and/or diffraction at the end faces. Multimode behavior leads to angular maxima and minima due to the higher-order Gaussian nature of the EM field for non-fundamental waveguide modes. An effect that is not easily demonstrated in still figures is the dynamic nature of the nanowire lasing. Because of the extreme sensitivity of the lasing to the exact pulse energy near threshold, fluctuations in pump fluence of only a few percent can cause drastic changes in the nanolaser spectrum and emission pattern.

![Figure 3](https://example.com/figure3.png)

Figure 3. (a) Topographic and (b) optical NSOM image of a single ZnO nanowire waveguide. Image size is 10 µm x 10 µm. (c) Far-field emission from a nanowire laser. Image size is 20 µm x 20 µm. (d) Near-field pattern of emission from the nanowire end. Image size is 5 µm x 5 µm.

The multimode behavior of the nanowire lasers is also evident in the emission spectrum. Wires with diameters > 130 nm can, in principle, show multiple transverse modes, but this is not always observed. Fundamental modes have the lowest threshold, but higher order modes can have comparable intensity at higher pump fluence. The different transverse modes can be identified both by their power-dependent behavior and by their polarization. For the case of ZnO wires, the approximate cylindrical symmetry produces a fundamental mode (HE_{11}) that is linearly polarized, and the detected signal can be maximized or minimized by using a polarization analyzer (Figure 4a). Higher order modes (TE, TM) should have less distinct polarization behavior. Figure 4b shows emission from a single nanoribbon at two different pump fluences. Lower pump fluence produces a single set of longitudinal modes (bottom), whereas a higher-order mode is also observed with higher pump fluence (top). For the ribbon with the approximate infinite planar structure, TE and TM modes are the distinct progressions expected in the spectrum (Figure 4b).
Figure 4. Nanolaser spectrum acquired with orthogonal detected polarizations, showing two distinct transverse modes. The values near each mode are the values of \( \rho = (I_x - I_y)/(I_x + I_y) \), where \( I_x \) and \( I_y \) are intensities at orthogonal polarizations. (b) Spectra taken from a nanoribbon laser, showing the occurrence of an additional set of longitudinal modes with increased pump intensity. One set of modes is indicated by the arrows. Inset: far-field image of the nanoribbon laser with length of about 35 \( \mu \text{m} \).

Multimode behavior produces a spectrum that is often quite complicated due to the large density of possible modes within the gain profile of the ZnO wire. However, at relatively low pump fluence, a single set of longitudinal modes can usually be identified. An example of this is shown in Figure 5. The spacing of the modes can be fit quite well with Eqn 1, with the term \( dn/d\lambda \) typically taking values near 1.0 through most of the gain profile (385-400 nm), which is predicted from the empirical Sellmeier model. The slight narrowing of the mode spacing on the blue edge of the observable lasing spectrum probably occurs due to increased dispersion of the refractive index, which is evident as the emitted photon energy approaches the ZnO band gap (3.37 eV) and exciton bands. For example, the spectrum in Figure 5a is from a 10 \( \mu \text{m} \) long nanowire, which shows approximately 2.2 nm average spacing for \( \lambda > 385 \text{ nm} \) but exhibits spacing near 1.2 nm for the bluest modes.

The length in Eqn 1 for nanowires can be taken to be equal to the length of the nanowire as determined by microscopy, and the mode spacing usually fits quite well with the Fabry-Perot axial resonator model, if a single progression of longitudinal modes can be identified. However, ribbon-like structures with significantly large transverse dimension can produce modes with non-axial character. Structures with low aspect ratio show emission patterns that exhibit behavior of WGM mode lasers (Figure 5b). Modifying the cavities of such ribbons facilitates the elucidation of the internal modal structure. We have utilized focused ion beam (FIB) etching to controllably alter the length of various nanoribbons to observe change in the lasing spectrum. The results of this procedure are shown in Figure 5d. The spacing of the longitudinal modes clearly show a linear trend with the reciprocal length of the structure, however, the magnitude of the mode spacing suggests a cavity length that is approximately 2-3 times longer that the actual measured length. The modes in the spectrum exhibit the properties of a single progression (Figure 5c), however these modes are apparently non-axial. With flat, intact side facets (0001 face), oblique reflection can produce a higher overall quality factor for strictly axial propagation, leaving the effective cavity length to be longer that the observed length of the structure. In general, structures that have width > 500 nm exhibited this behavior, and modes from ribbons with width < 500 nm often retained the Fabry-Perot character. However, the behavior was found again to be highly dependent upon the exact nature of the cavity geometry and quality.
Figure 5. (a) Nanowire emission spectrum near and above lasing threshold. (b) Far-field image of a nanoribbon laser (scale bar = 5 µm). (c) Series of lasing spectra from a single ribbon taken at several ribbon lengths (from bottom up, 18, 13, 10, 4.5 µm). (d) Plot of ribbon laser mode spacing vs. measured length. Inset: SEM image of ZnO ribbon after a single etch using the FIB.

The exciton Bohr radius, or the critical radius for observing quantum effects, for ZnO is approximately 1.7 nm. Due to diffraction loss, wires with such a small diameter are not likely to exhibit stimulated emission behavior. Therefore, simultaneous excitonic confinement and lasing is unlikely for ZnO. However, GaN has an exciton Bohr radius of approximately 11 nm, and wires with diameter of < 20 nm can be routinely synthesized. The problem of photonic confinement at this length scale is still significant, therefore we have designed a core/shell structure, which is capable of guiding the emitted light in the shell while retaining a small core that could show quantum effects. The core of the structure is pure GaN (n = 2.54), which is cladded with a Al_{0.75}Ga_{0.25}N (refractive index 2.25) sheath (Figure 6b, inset). Figure 6a shows PL spectra from wires of varying diameter, showing a blue shift of the emission maximum as the diameter decreases below 30 nm. Figure 6b shows the lasing properties of a core/shell nanowire with 52 nm core. The lasing properties of this wire do not show significantly different behavior from that of larger pure GaN wires, probably due to the relatively large size of the core with respect to the exciton Bohr radius.
3.2 High excitation effects

The pump fluence required to excite lasing in single wires has been determined to depend greatly on the geometry and quality of the individual nanowire cavity. High quality wires with good end facets and diameter of 130 – 250 nm typically have a lasing threshold near 100 nJ/cm². Wires with diameters of < 130 nm can show some lasing behavior, but usually at much higher pump fluence. The position of the nanowire with respect to the supporting substrate also affects the lasing threshold. Wires that have limited contact with a relatively high index substrate (n = 1.6-1.8) show the lowest lasing threshold, similar to what is observed in wires in a vertical array. Wires on a mesoporous silica substrate (n = 1.2) show a similar threshold, with a much smaller dependence on the amount of substrate contact. Coupling of the electromagnetic field into the substrate is largest with similar refractive indices between the wire and substrate and with the largest area of contact. Thus, the minimum lasing threshold is observed for wires that have a geometry that minimizes such coupling.

The transition from spontaneous emission to lasing is best characterized by observing the spectrum from a single wire. Figure 7a demonstrates this transition quite clearly, in which the linewidth of the nanowire emission is reduced from > 20 nm to < 1.0 nm with a change of only 1% of pump fluence. The spontaneous emission is still evident just above the lasing threshold, but at higher pump fluences the emission spectrum is dominated by the lasing modes of the nanowire cavity. As discussed previously, the spacing of the longitudinal modes depends on the refractive index roughly as 1/n. A slight red shift can be observed in the individual laser modes of single nanowires of both GaN and ZnO, attributed to an increase of the lattice temperature upon excitation. In Figure 7b, this shift is plotted as a function of the pump fluence for a single GaN wire. Figure 7c shows a similar plot for a ZnO wire. In this case, the individual modes initially show a blue shift upon excitation above the lasing threshold, which is thought to be due to the destruction of excitons due to the high carrier density. The carrier density excited near threshold is 1*10¹⁹ cm⁻³, which approaches the Mott density (2-4*10¹⁹ cm⁻³). Above the Mott density, the red shifting due to the rise in lattice temperature dominates the mode shifting. The overall spectral emission energy also shifts to the red upon increasing excitation, attributable to the formation of the EHP. A high density of carriers causes band-gap renormalization (BGR) in ZnO, which is especially apparent once the material enters the EHP phase. Excitonic emission typically shows a much smaller red-shift due to compensation of BGR by an increase in the exciton kinetic energy through scattering. Once the excitons become destabilized, the red shift dominates.
Figure 7. (a) PL (bottom, x 10) and lasing spectra (middle, upper), of a single ZnO nanowire.  (b) Plot of the shift of individual modes and overall gain profile of a single GaN wire.  (c) The spectral position of two longitudinal modes (A, B) in a single ZnO wire as a function of pump fluence.

The overall power dependence of the PL/lasing intensity in single wires also provides evidence for ex-ex to EHP transition.  For a typical wire, the power dependence is linear below the lasing threshold (Figure 8a).  Once the threshold is reached, the power dependence shows superlinear (quasi-exponential) behavior, as shown in Figures 8b,c.  However, at a pump fluence of only 2x - 5x above the threshold, the emission becomes damped and shows linear or sublinear behavior before complete saturation occurs.  This saturation of the gain is primarily attributed to the lower efficiency of the EHP vs. ex-ex process of stimulated emission.  Under continuous-wave excitation, there is no stimulated emission, and the single ZnO wires show two types of emission: spontaneous exciton recombination and defect emission.  As shown in Figure 8a, the UV PL is linear with power in this regime, however the broad defect emission (centered at 510 nm) is highly saturated at pump powers above 2 W/cm².  The defects likely to be responsible for the green emission in ZnO are singly-ionized oxygen vacancies.  There are a limited number of these vacancies in the nanowire, thus a sufficiently large carrier density will cause the sites to be filled, resulting in a sublinear increase (saturation) in emission with power.

Figure 8.  Power dependences of (a) defect and CW-pumped exciton PL emission.  Lasing emission (b) above and (c) near threshold.
4. CONCLUSIONS

The results presented here demonstrate the unique characteristics of single nanowire, nanoribbon, and core/shell lasers of ZnO and GaN. It is possible to probe these processes in single structures by combining ultrafast UV pulsed excitation and high-resolution microscopy. The nature of the transition from spontaneous to stimulated emission is characterized by examining the defect, exciton, and electron-hole plasma emission. The spectrum of the nanolaser provides much information about the processes involved in the lasing phenomenon.

The previous results represent indirect methods of measuring the dynamic processes associated with the onset of stimulated emission in the nanostructures, although an additional advantage of ultrafast excitation is the possibility of directly obtaining information on the transient behavior of the lasing action. Present and future efforts are aimed at utilizing pump-probe and other ultrafast transient spectroscopies to examine the characteristic charge carrier behavior in single structures immediately following ultrafast excitation.

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REFERENCES