Resolving Stable Axial Trapping Points of Nanowires in an Optical Tweezers Using Photoluminescence Mapping

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Supporting Information

ABSTRACT: Axially resolved microphotoluminescence mapping of semiconductor nanowires held in an optical tweezers reveals important new experimental information regarding equilibrium trapping points and trapping stability of high aspect ratio nanostructures. In this study, holographic optical tweezers are used to scan trapped InP nanowires along the beam direction with respect to a fixed excitation source and the luminescent properties are recorded. It is observed that nanowires with lengths on the range of 3−15 μm are stably trapped near the tip of the wire with the long segment positioned below the focus in an inverted trapping configuration. Through the use of trap multiplexing we investigate the possibility of improving the axial stability of the trapped nanowires. Our results have important implication for applications of optically assisted nanowire assembly and optical tweezers based scanning probes microscopy.

KEYWORDS: Semiconductor nanowires, photoluminescence, optical tweezers, spatial light modulator

Optical tweezing of nanowires and other elongated nanostructures has provided a model system for interrogating a diverse range of trapping dynamics not normally observed in conventional optical tweezers experiments. In particular, properties of equilibrium trapping orientations and stability, trapping asymmetry, and rotational dynamics have all been strongly linked to physical parameters such as length, diameter, shape, and refractive index.1−3 From a practical perspective, optical trapping of nanostructures is of considerable interest for both unconventional nanoscale assembly techniques4−6 and photonic microscopy applications.7−9

Optical trapping of micrometer scale objects with high aspect ratios has received growing attention as potential probe tips in high-resolution scanning probe microscopy.7 The appeal of these objects is that an elongated tip has a very small footprint, which can provide high spatial resolution and enable interrogation of surfaces that are otherwise inaccessible to other scanning probe techniques.5,10,11 In particular, tapered probes that have been fabricated using two-photon polymerization have been used to produce complex three-dimensional shapes that may be tailored for maximum stability and flexibility in orientation and force application.12,13 Semiconductor nanowires, being characterized by a cross-sectional dimension of the order of tens of nanometers and an aspect ratio of greater than 100, have the potential for creating even higher-resolution scanning probe tips. In addition, nanowires composed of optically active materials can exhibit room-temperature photoluminescence when trapped in an aqueous environment as well as strong second harmonic generation.14 This functionality provides additional possibilities in terms of probing methods. Despite these desirable properties, optical scanning probe microscopy based on trapped nanowires has yielded resolutions considerably poorer than that of conventional light microscopy.7 Ultimately, a more detailed study is needed to understand and overcome the fundamental limitations of nanowires based optical scanning microscopy.
The use of adaptive optics has proven to be indispensable in the area of optical micromanipulation. In particular, spatial light modulators (SLM) allows for the introduction of aberration correction, which can improve the trap stiffness, and enable trapping within complex scattering media. Advanced beam shaping, such as Bessel beams and Laguerre Gaussian beam, and Airy beams, can be generated, which in turn provides more novel trapping. Using holographic optical tweezers video rate dynamic control of single and multiple micro-particles and nanoparticles in three dimensions. Applications of holographic optical tweezers for nanowire manipulation have focused on in-plane reorientation, registration, and assembly on substrates, however, dynamic manipulation afforded by SLM is crucial for probing both the luminescence and trapping properties of semiconductor nanowires.

In this work, we utilize dynamic optical tweezers to map the luminescence properties of mixed phase InP nanowires along the axis of the nanowire. This is also used to map the position of trapped nanowires with respect to the laser focus in the axial direction, resolving such axial position information is not usually possible as the nanowires extend well outside the depth of focus for the high numerical aperture trapping objective. We find that nanowires of a range of lengths are trapped in a highly asymmetric configuration with the equilibrium trap position near the end of the wire and with a strong orientation preference for with respect to tapering. Using trap multiplexing we study the effect of including multiple traps along the length of the nanowire for improving axial trapping stability.

**Experimental Methods.** Figure 1 depicts the experimental setup used for direct mapping of luminescent properties of optically trapped InP nanowires; the arrangement comprises a dynamic holographic optical tweezers ($\lambda = 1064$ nm) integrated with a microphotoluminescence ($\mu$-PL) spectroscopy setup. Full details of the instrumentation and sample growth conditions may be found in the Supporting Information section. With this experimental arrangement 3D (translational) manipulation of InP nanowires can be achieved where the long axis of the nanowire is aligned to the laser propagation direction. Axial displacement is achieved by applying different Fresnel lens patterns (Figure 2b) to the spatial light modulator to control the convergence or divergence at the back aperture of the objective. $\mu$-PL mapping of the trapped nanowire, as depicted in Figure 2a, involves axially displacing the trapping beam (labeled by red) with respective to the fixed excitation beam (labeled by green); the $\mu$-PL spectrum is then recorded from the region of the nanowire within the excitation volume ($\lambda = 514.5$ nm). Typical excitation powers for the $\mu$-PL measurements are 489 $\mu$W; optical trapping powers are of the order of 50 mW.

The spatial resolving power in the axial direction is an important consideration in the study and the procedure for measuring is depicted in Figure 2c. Using different Fresnel lens patterns applied to the spatial light modulator, an optically trapped $1 \mu$m fluorescent microsphere is displaced along the beam axis and the $\mu$-PL ($\lambda_{\text{peak}} = 650$ nm), excited through two-photon absorption of the trapping laser, is measured at different positions. In Figure 2c, the integrated fluorescence intensity is plotted as a function of particle displacement; from this measurement the axial resolution of collection optics is estimated to be 1.9 $\mu$m. The position of the origin in Figure 2c corresponds to zero axial displacement (no Fresnel lens), which is optimized for maximum collection efficiency. The axial resolution of the $\mu$-PL, as defined by the depth of focus of the excitation source, is probed by measuring the directly excited luminescence from the trapped microsphere as it is translated through the fixed focal position of the excitation laser. The depth of focus of the $\mu$-PL system is experimentally estimated at 0.95 $\mu$m. On the basis of vector diffraction calculations the theoretical axial resolution is 0.73 $\mu$m; the discrepancy may be accounted for by the size of the test particle (1 $\mu$m). The axial $\mu$-PL mapping resolution can be further improved using a smaller pinhole, however this will decrease the collection efficiency of the optics, necessitating a high excitation power,
which may yield sample heating, annealing and other deleterious effects.

Results and Discussion. In Figure 3, a typical data set for a trapped nanowire (NW11) is presented. In the figure, the imaging focal plane defines the origin: as the tweezers are in an inverted configuration the positive scale represents a height above the focus and the negative scale corresponds to positions between the objective and the focal plane. An initial estimate of the nanowire length is measured from bright field imaging (Figure 3b). By measuring the μ-PL intensity distribution (Figure 3a) along the trapped nanowire, the length of nanowire can also be measured since the PL intensity signal drops off rapidly as the nanowire is moved outside the depth of focus. Figure 3c shows the μ-PL spectrum for four different positions along the nanowire. Because of the changes in crystal phase for the different probed positions, each spectra has a distinct intensity, peak wavelength, and spectral profile; a clear example of this is seen when comparing spectra for position −2.4 and −9.4 μm. On the basis of previous research, the peak wavelength can be accounted for by considering the density of the two different InP crystal poly types that are present within the excitation volume. The peak wavelength for the pure wurtzite (WZ) crystal phase is 865 nm and pure zinc blende (ZB) is 923 nm. It is known that the frequency of twinning defects, which leads to crystal phase changes, is strongly dependent on the growth conditions and can vary during the growth of the nanowires. In Figure 3d, the peak wavelength is observed to shift from 895 to 867 nm then increase again along the length of the wire. The interpretation based on these shifts is that a predominantly ZB crystal phase is present at the bottom and top of the wire with a predominantly WZ phase in the middle. In Figure 3a, we observe that the WZ phase generally provide higher PL intensity than ZB phase. In Figure 3e, the wire is represented as a false-color map where the scale represents the peak wavelength.

Applying the above method, the compositional variation along the nanowire axis can be probed. The μ-PL mapping results for 15 different nanowires with different length is shown in Figure 4, where the color bar is the same as in Figure 3e and the orange error bar indicates the uncertainty in the nanowire length. For NW1 to NW12, the base of the nanowire is oriented above the trap, while for samples NW13 to NW15 the tip of the nanowire is above the focus. From the spectral data in Figure 4 we observe two types of nanowires in the sample: (1) long nanowires with both ZB and WZ crystal phase (NW10–13), where the base shows more ZB crystal phase while in the middle of nanowire the density of WZ crystal phase is higher, and (2) shorter nanowires exhibiting uniformly ZB crystal phase (NW2–5 and NW14–15). We note that due to the preparation method for dispersing the nanowires in solution (sonication) we do expect to see fragments of nanowires, for example NW6, which are shorter, but have a composition similar to the longer nanowires. SEM images of this sample-set also reveal two populations of nanowire: (i) short nanowires (3–7 μm) with diameters in the range of 165–220 nm and

Figure 3. (a) The μ-PL intensity distribution from trapped nanowire (NW11) along axial direction. Origin of axis is the fixed focal position of excitation laser and the initial focal position of the trapping laser. The laser propagation direction is from negative (below the focus) to positive (above the focus). The positive value stands for length of nanowire above focus. (b) The bright-field image of free nanowire used for estimating the length. (c) μ-PL spectra in for trapping positions of −11.4, −9.4, −5.4, and −2.4 μm, where both position of peak wavelength intensity amplitude have noted difference. (d) The distribution of peak wavelength at different positions along the nanowire. (e) False-color map of nanowire representing the peak wavelength and crystal phase density; deep blue (865 nm) is pure WZ crystal phase and deeper red (925 nm) is pure ZB crystal phase. The orange error bar indicates the uncertainty in the nanowire length.
average taper angle 0.28°, and (ii) longer nanowires (10–15 μm) where the diameter varies from 50 to 236 nm and exhibits a taper angle of 0.37°. Note that while the extent of tapering is quite small, over the total length of the nanowire the diameter of the nanowire changes by up to a factor 4.

Another important observation made possible with the axial μ-PL mapping is the determination of the equilibrium trapping position for the nanowires. As the distance between the trapping focus and fixed excitation focus is known, the separation between the points where the μ-PL intensity vanishes can be used to define the end points of the nanowire. In Figure 4, the red line represents the stable trapping position for all of the nanowires measured. We observe that for the majority of cases the nanowire is trapped near one end with the major segment of the length sitting below the trap; note the orientation of the nanowire is with the base above the trap (NW1–NW12). This trapping position is neither at midpoint nor center-of-mass position when tapering is taken into account, and gravitational forces acting on the nanowire are too small to account for the displacement in the axial direction, indicating that this is the equilibrium position where the optical forces are balanced.

The equilibrium trapping position does vary between trapped nanowires. The fraction of the length sitting above the trapping focus varies between samples from 0.10 to 0.36 and does not correlate well with the length of the wire. Full, tabulated data is provided in Table 1. Wires may also be trapped in the inverted configuration with the tip above the trap (NW13–NW15) and in this instance the equilibrium trapping position is much higher with 0.40 to 0.75 of the wire length above the trap. For a perfectly cylindrical, nanowire aligned axially to an optical trap one may rationalize why the equilibrium trapping position is at the end of the trap. As the objects extend 10 to 20 times beyond the depth of focus, displacement along the axis, on the scale of the Brownian motion (typically less than 100 nm), will yield no change in the scattered field in the vicinity of the focus. As optical forces arise from a change in the scattered field (momentum change) the nanowires experience negligible axial optical forces, leading to free diffusion in this direction. Only at the ends of the nanowire, where the translational symmetry is broken, will the wires experience any kind of optical restoring force.

The presence of tapering modifies the axial trapping dynamics and ultimately governs the detailed nature of equilibrium trapping position. Theoretical calculations have been performed by S.H. Simpson et al.,27 where the stable trapping position and optical forces of high aspect ratio nanoscale objects with different taper angle are calculated. In their paper, the tapered nanowires can be trapped with two orientations. For the orientation with the base above the trapping focus, the trapping position is close to the end and the bulk of the nanowire is beneath the trapping focus. For the inverted orientation the trapping position is closer to the midpoint with the bulk of nanowire above trapping focus. For both orientations, either larger tapered angle or higher refractive index will push the base of the nanowire closer to the trapping focus. It is important to mention that the paper also shows (i) the base of the taper is subjected to more trapping force than tip; (ii) the disparity between the trapping force for the two orientations increases as the refractive index of the objects increases.

Our results are qualitatively consistent with their predictions, despite the discrepancy between key modeling parameters, such as refractive index and taper angle. One possible reason for this correspondence is that while our tapering angle is smaller than those used by Simpson et al., our refractive index values are substantially higher and this should lead to an enhancement of the effect of tapering with respect to optical forces. On the basis of SEM data the long nanowires show the strongest tapering.
and hence these wires are trapped closer to the end with the base. Because of stronger radiation pressure, the base will be close to the trapping focus, and for the inverted orientation the stronger radiation pressure of base again displaced the trapping position toward the base and away from the tip. NW7 and NW15 are in fact the same wire trapped in the two alternate orientations and we observe two distinct trapping points. Most of the nanowires interrogated can only be trapped in one orientation, which indicates that orientation with the base of the nanowire above the trap is the most stable; this result is consistent with the calculations of Simpson et al.  

In order to investigate the possibility of multitrapping points for nanowires we create two focal spots (dual trap) using the SLM and monitor the axial trap stiffness as the position of the second spot is varied along the length of the nanowire. The trap stiffness is then compared against a single trap with the same total intensity. The assumption made for these measurements is that the contribution of the two trapping points on the position sensitive detector is equivalent to the single trap case. While in general this may not be the case, for a rigid body aligned axially between two traps the resulting signal on the PDS for each trapping center should yield the same response. Figure 5 shows the comparison between trapping with one and two focal points. For a short nanowire (NW7), the initial trapping position is 1.8 μm away from upper end (shown in Figure 5a) and the optimized second trap is 5 μm away from initial trapping spot. Figure 5c shows the power spectrum29 for a single trapping spot (red line) with a total trapping power of 5.5 mW, compared with the dual trap case (black line), where each trap has a power of 27.5 mW. The corner frequency for two spot trapping in this instance is observed to be higher, providing a trap stiffness of 16.1 pN/μm, while the value for one spot trapping is 11.3 pN/μm. Here the Stokes’ drag used to calculate axial trap stiffness is developed by Tirado and Torre.30 For a cylinder with radius, r, length, l, and surrounding viscosity η, the drag coefficient in axial direction can be written as

\[ \gamma_\parallel = \frac{2\eta r l}{\ln\left(\frac{1}{5}\right)} + \gamma_\parallel^{0} \]

where \( \gamma_\parallel^{0} \) is a correction constant for the ends of the nanowire, which is calculated to be -0.2. The axial position distribution of the above two cases can be calculated from axial trap stiffness by using a straightforward extension of the Equipartition Theorem. The probability for the axial displacement of trapped nanowire is

\[ P(x) \propto \exp\left(-\frac{U(x)}{k_{B}T}\right) = \exp\left(-\frac{k_{B}T}{2k_{B}T}\right) \]

where \( U(x) \) is the potential energy, \( k_{B} \) is the axial trap stiffness and \( k_{B}T \) is the thermal energy. The calculated Gaussian distribution is shown at Figure 5d, where the moving range 22.6 and 27.1 nm are calculated for two spots trap and one spot trap, respectively. This result shows that by splitting the trap spot into two, the axial trap stiffness can be enhanced thereby producing a more stable trapping configuration for nanowires in the axial direction. 

Further measurements on dual trapping for a number of other nanowires are presented in Figure 6. The schematic indicates the lengths of the nanowires measured, their stable trapping position relative to the fixed trap position (dotted red line) and the height of the secondary equilibrium trapping positions (dotted pink, green, and blue lines). Each of the nanowires was oriented with the base above the trapping position. The changes in trap stiffness for individual nanowire for different position of the second trap are shown at the bottom of Figure 6. Generally, the effect of the second trapping site can be grouped into two types of responses: (i) the trap stiffness is reduced at all points along the nanowire with a small increase in the trap stiffness when the trap is placed near the end of the nanowire (Figure 6a–c), and (ii) similar to the first case but where the enhancement exceeds the trap stiffness for the single trapping case (Figure 6d–f).

The physical interpretation of the above effect is again related to the taper angle. On the basis of calculations presented in Figure 5 of Simpson et al.27 for larger taper angles and higher refractive index values, two distinct positions are present where stable trapping occurs, that is, the optical field produces an anharmonic restoring force. At other points along the nanowire axis, there is an additional optical force, which can be attributed to a destabilizing scattering force. When the two focal points in the dual beam trap are positioned over the stable trapping sites, then the axial trapping improves. Depending on the tapering angle this can be more or less than the single trap case. If the second trap is positioned off the second stable trapping position, there is a marked decrease in the trap stability indicating that multiple trapping sites do not necessarily equate to improvements in the stability of the trapped nanowire.
In the context of using optical trapped nanowire in a scanning probe microscope, these results have some interesting implications. First, given the relative position of the nanowire probe with respect to the focal position, the end of the nanowire closest to the surface will be the most stable point on the probe. However, as the trapped end of the nanowire represents a fixed pivot point around which the nanowire can rotate, the angular pointing stability of the probe could be a significant factor. If the dual trap configuration is utilized, the rotation can be significantly suppressed. Finally, as the thicker end of the nanowire is the most stable, a compromise between probe dimensions and nanowire stability.

In conclusion, we have demonstrated a method for mapping μ-PL properties of length of the semiconductor nanowire using dynamic optical tweezers. We have used this technique to investigate the axial trapping dynamics and stability points along the axial direction. We find that nanowires are trapped in a highly asymmetric configuration with the equilibrium trap position near the end of the wire with the most stable orientation with base closest to the focus. Using trap multiplexing we investigate the effect of including multiple traps along the length of the nanowire for improving axial trapping stability.

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ABBREVIATIONS

SLM, spatial light modulator; PL, photoluminescence; μ-PL, microphotoluminescence; WZ, wurtzite; ZB, zinc blende; AOD, acousto-optic deflector; CCD, charge-coupled device; TPA, two-photon absorption; SEM, scanning electron microscope; InP, indium phosphide

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