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Lasing in Single Cadmium Sulfide Nanowire Optical Cavities

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ABSTRACT

The mechanism of lasing in single cadmium sulfide (CdS) nanowire cavities was elucidated by temperature-dependent and time-resolved photoluminescence (PL) measurements. Temperature-dependent PL studies reveal rich spectral features and show that an exciton–exciton interaction is critical to lasing up to 75 K, while an exciton–phonon process dominates at higher temperatures. These measurements together with temperature and intensity dependent lifetime and threshold studies show that lasing is due to formation of excitons and, moreover, have implications for the design of efficient, low threshold nanowire lasers.

Semiconductor nanowires (NWs) are emerging as versatile nanoscale building blocks for the assembly of photonic devices,[1−4] including polarization sensitive photodetectors,[2] light emitting diodes,[3] and electrical injection lasers.[4] Progress on such nanophotonic devices will require developing a detailed understanding of how confinement of charge carriers and photons affects optical properties and/or gives rise to interesting phenomena.[4−6] For example, single NWs have recently been shown to function as optical waveguides and Fabry−Perot cavities.[4,7] Intense optical excitation of single NWs has produced stimulated emission and lasing,[4,8,9] and, significantly, lasing has also been obtained from cadmium sulfide (CdS) NW electrical injection devices.[4] The mechanism of lasing in these confined NW cavities is unclear, although critical to the rational development, for example, of ultralow threshold NW lasers.

CdS nanowires are particularly interesting since optical excitation and electrical injection have been used to exceed the threshold for lasing.[4] In bulk CdS, three different mechanisms are known to produce significant gain: exciton−exciton scattering; exciton−logitudinal optic (ex-LO) phonon scattering; and exciton−electron scattering.[10−13] The geometry and quality[14] of the bulk CdS materials have been found to affect the mechanism yielding the highest gain and lasing, and, importantly, it is expected that geometrically confining cavities might also significantly affect the gain mechanism and lasing.[6,15] In this letter we report detailed temperature-dependent and time-resolved PL measurements that define the mechanism of lasing in single nanowires for the first time. PL studies of CdS NW optical cavities, which have diameters smaller than the wavelength of light but large enough to sustain a single optical mode, demonstrate that exciton−exciton scattering is critical to lasing up to 75 K and that an exciton−phonon process dominates at higher temperatures. These measurements together with intensity dependent PL, lifetime, and threshold studies imply that lasing is due to the formation of excitons and not an electron−hole plasma at all of the temperatures and intensities studied.

Single-crystal CdS NWs with diameters from 80 to 150 nm and lengths up to 100 μm were prepared by a metal nanocluster catalyzed vapor−liquid−solid growth,[16] and subsequently dispersed on Si/SiO_2 substrates (600 nm thermal oxide) with an average separation of 100 μm. PL experiments were carried out by exciting the NWs using frequency doubled Ti:sapphire laser pulses (~405 nm, 350 fs fwhm) focused to a diameter of ~75 μm. PL spectra from individual NWs were recorded from the ends of the NW cavity as illustrated schematically in Figure 1a using a home-built epifluorescence microscope (60×, 0.7 NA objective) with a spectral resolution ca. 0.15 nm. A typical PL image of a NW excited by a tightly focused laser (Figure 1b) exhibits emission from the excitation region and 20 μm away at the NW end, thereby demonstrating excellent waveguiding of the CdS NWs. Below we focus on the emission from the NW ends.

PL spectra recorded at 4.2 K from a 40 μm long, ca. 100 nm diameter CdS NW as a function of excitation power are shown in Figure 1c; similar results were observed for NWs with 80−150 nm diameters and 30−50 μm lengths. The PL spectrum recorded at low excitation intensity of 0.6 nJ/cm2 (Figure 1c) reveals a number of well-defined and reproducible features in the 488 to 530 nm range, with peaks at 488.8,

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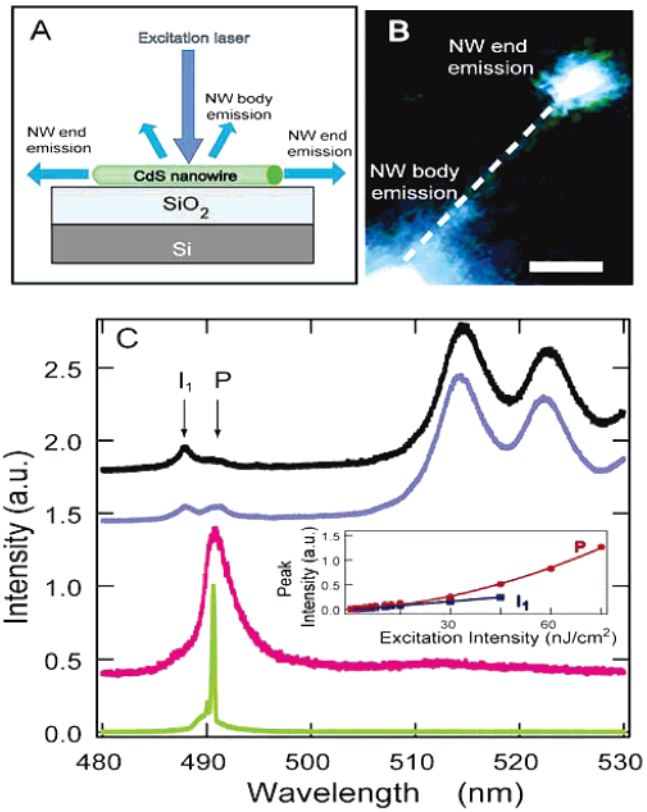

Figure 1. (A) Schematic of single NW optical experiments. (B) PL image showing luminescence from the excitation area (lower left) and one end (upper right) of a CdS NW. The NW was excited with a focused beam (~5 μm diameter) with a power of 10 nJ/cm^2; scale bar, 5 μm. (C) PL spectra of CdS NW end emission recorded at 4.2 K with excitation powers of 0.6, 1.5, 30, and 240 nJ/cm^2 for the black, blue, red, and green curves, respectively. Inset shows peak intensity of I_1 (black squares) and P (red circles) bands vs incident laser power. Solid lines are fits to experimental data with power exponents of 0.95 for I_1 and 1.8 for P.

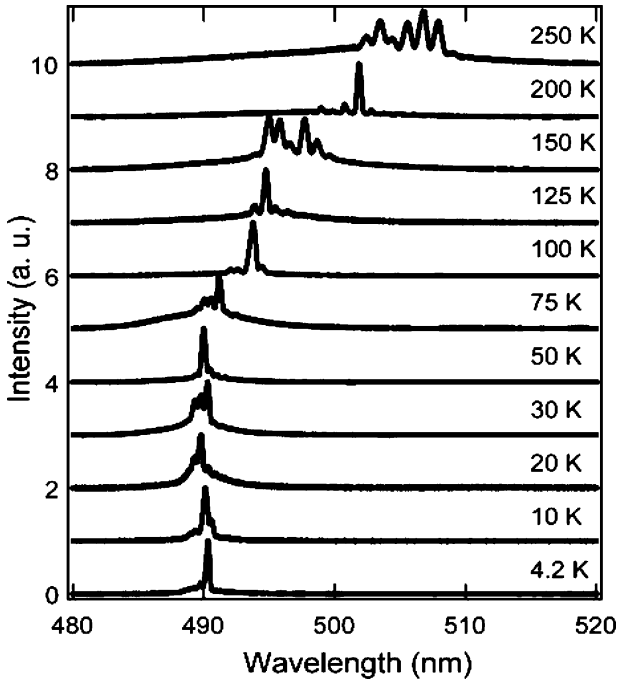

Figure 2. Temperature-dependent spectra recorded from a single CdS NW above the threshold for lasing. The temperature values are given next to each spectrum. The excitation power ranges from 0.24 μJ/cm^2 at 4.2 K to 3.3 μJ/cm^2 at 250 K.

490.5, 513, 522, and 530 nm. Comparison to previous studies of bulk CdS crystals suggests that the peaks at 488.8 (I_1), 490.5 nm (P), 513, and 522/530 nm correspond to neutral acceptor bound excitons,[17] exciton−exciton scattering,[18] free electron-bound hole radiative recombination, and the LO phonon progressions of the free electron-bound hole transitions,[19] respectively.

Excitation power dependent measurements (Figure 1c) show that the P-band intensity increases rapidly and becomes dominant at higher excitation powers. Analysis of the P-band data shows an intensity increase of ~1.8, where I is the excitation intensity (inset, Figure 1c), while the I_1 band increases with an exponent near unity (0.95). These exponents are close to the values expected for 2- and 1-exciton processes.[10,18] At higher excitation intensities the P-band is the dominant feature in PL spectra (Figure 1c) and furthermore shows a superlinear increase in the PL intensity above a threshold pumping power of 200 nJ/cm^2. Above this threshold the PL spectrum collapses to a narrow peak at 490.5 nm with a line width of 0.3 nm, indicative of lasing. The position and the power dependence of the PL spectrum strongly suggest that the mechanism of lasing in CdS NWs at 4.2 K is due to an exciton−exciton process. Although previous studies reported line narrowing at 490 nm,[4] these studies did not identify the origin of the lasing peak.

Temperature dependent spectra, which were recorded to probe further the mechanism of lasing in the CdS NWs, show that the lasing line at 490.5 nm is temperature independent from 4.2 to 75 K, while the spectral features associated with lasing exhibit a pronounced red-shift at high temperatures (Figure 2). A summary of these temperature dependent results (Figure 3a) shows clearly the temperature independence of the 490.5 nm peak above threshold at low temperatures, and the subsequent monotonic red-shift at 0.083 nm/K above ca. 100 K. Below the threshold for lasing the main PL peak at 490.5 nm was also found to be temperature independent up to ca. 100 K. Above 100 K the PL peak shifts to ca. 494 nm and then further red-shifts at a rate similar to that observed above threshold. The peak at 494 nm has been assigned previously to an exciton-LO band.[11−14] The laser threshold temperature dependence (Figure 3b) shows that the threshold power increases very slowly until 50 K (4.5 nJ/cm^2/K) and then increases at a ~3× higher rate of 14 nJ/cm^2/K.

The observation of the dominant lasing line at 490.5 nm up to 75 K shows that exciton−exciton scattering is the key gain mechanism for CdS NW optical cavities in this lower temperature regime. This temperature independence is consistent with the ca. 20 meV separation between the $n = 1$ ground state and $n = 2$ state.[12] Hence, $n = 2$ and higher exciton states are not significantly populated over this temperature range, and the dominant lasing line should not vary strongly with temperature as we observe. In addition, measurements of the threshold power dependence for our CdS NW system (Figure 3b) show little temperature depen-

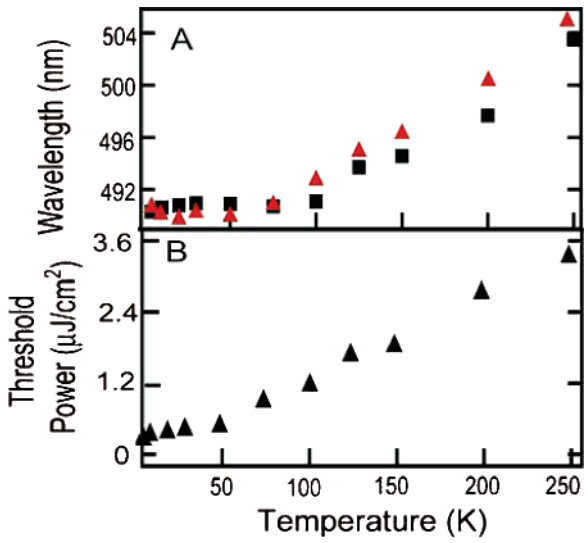

Figure 3. (A) Temperature dependence of key spectral features above and below the threshold for lasing. Red triangles correspond to the temperature dependence of the most prominent lasing peak (for multiple peaks of comparable intensity the central peak). Black squares correspond to temperature dependence of the PL peaks that lead to lasing. These latter data were recorded at low excitation powers, ranging from 25 nJ/cm^2 (4.2 K) to 125 nJ/cm^2 (250 K). (B) Temperature dependence of laser threshold power.

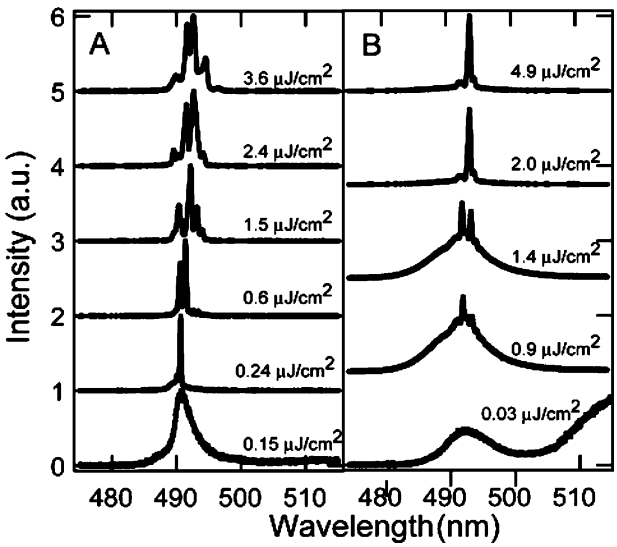

Figure 4. Spectra recorded above the lasing threshold for a CdS NW at different pumping powers at 4.2 K (A) and 100 K (B). The bottom spectrum in both the panels is the PL recorded below the threshold for lasing.

dence below 75 K, which is also consistent with our assignment of lasing from $n = 1$ excitons.

At temperatures above 75 K, higher exciton states become thermally populated and lead to increases in the lasing threshold for the exciton−exciton process. Exciton scattering by LO phonons can contribute more to gain at these temperatures since the LO phonon energy, 38 meV, is larger than the available thermal energy.[11−13] Significantly, at temperatures >75 K the PL band and laser lines occur in the region of the ex-LO phonon scattering band, 493 nm.[12,13] Temperature-dependent measurements (Figure 3a) further show a red-shift, 0.083 nm/K, consistent with that observed in bulk CdS,[13] 0.086 nm/K, for the ex-LO phonon band. Therefore, at temperatures higher than 75 K the lasing mechanism of CdS NWs can be assigned to ex-LO phonon scattering process.

In contrast, lasing in bulk CdS crystals has been primarily attributed at higher temperature to an exciton−electron scattering process.[10−13] The exciton−electron scattering band appears at ∼494 nm at 70 K and exhibits a large red-shift of ca. 0.147 nm/K.[12,13] The temperature-dependent red-shift we find for CdS NWs, 0.083 nm/K, is much smaller than this but agrees with the ex-LO process (see above). We believe that the difference between previous bulk studies and these new NW lasers arises from the small modal volume of the laser cavity.[20] To understand this unique difference a simple model based on the density of states of electrons and excitons at equilibrium was used to calculate the ratio of free carriers to the total injected carriers in the cavity as a function of temperature (Figure S1, Supporting Information). These results show that at 150 K temperatures and low carrier densities (10^{15}−10^{16} cm^{-3}) > 80% of the carriers exist as free electrons, whereas at higher densities (10^{18} cm^{-3}) the free carriers do not exceed 40%. The small volume of the NW laser cavity can effectively yield large carrier densities, and hence the portion of free carriers is smaller than in bulk samples, thus reducing contributions from exciton−electron scattering.

In addition, we find that the laser threshold power for CdS NWs is 5−10 times less sensitive to temperature than reported for bulk CdS crystals.[21,22] The linear increase of the lasing threshold power with temperature due to ex-LO mechanism of lasing cannot be explained by a simple model based on the temperature dependence of the occupation of the phonon states as this model predicts an exponential increase in the threshold. We believe this disagreement can be attributed to the strong confinement of the optical mode in the CdS NW cavity, where there is ∼50% mode confinement due to strong dielectric mismatch between the wire and its surroundings.[23] Strong mode confinement in optical cavities leads to much better overlap of the optical mode with excitons, where the modal volume of the NW cavity is of the order of ($3\lambda^3$).[20] This observation is similar to the reduced magnitude and lower temperature dependence of the laser threshold observed in double heterostructure planar semiconductor lasers,[24] although the mode confinement is typically only a few percent. Future theoretical analysis, which includes the effect of strong optical confinement[15] along with the exciton-LO scattering mechanism for gain, will be required to explain the weak temperature dependence of lasing threshold observed for CdS NWs.

We have also investigated the possibility of lasing from an electron−hole plasma, which can form due to screening of excitons at high carrier densities ($n \sim 2.1 \times 10^{18}$ cm^{-3})[25] by recording spectra as a function of different pumping powers above the threshold for lasing. Significantly, no red-shift of the lasing line was observed at either 4.2 or 100 K while increasing the excitation intensity approximately an order of magnitude (Figure 4). An estimate of the carrier

density based on laser pump intensity (5 μJ/cm^2), CdS NW dimensions (40 μm length, 100 nm diameter), CdS absorbance at 400 nm $\sim 10^5$ cm^{-1}) gives a value of $n \sim 1.0 \times 10^{18}$ cm^{-3}, which is close to the threshold reported[25] to yield dissociation into an electron−hole plasma.

Formation of electron−hole plasma is generally accompanied by a strong red-shift of the spectrum due to band-gap renormalization effect[13,26] and has been suggested for GaN nanowires.[7] The absence of a red-shift with increasing excitation intensity is a further proof of lasing by excitonic mechanism in the range of the excitation intensities used in our study. In addition, excited state PL lifetime measurements (data not shown) did not show significant pump intensity dependence. The lifetime at 4.2 K was observed to be 1.2 ns (90% amplitude), which rapidly dropped to 400 ps at 50 K and then decayed very slowly to ~350 ps at room temperature. However, neither the amplitude nor the time scale of the PL lifetime changed more than 10% with 10× (4.2 K) or 5× (100 K) increase in pump intensity. In contrast, previous studies of highly excited bulk CdS samples showed a rapid 200 ps (5 K) lifetime that was attributed to the decay of an electron−hole plasma into excitons.[27] The absence of a fast component in our experiments, even at very high pump powers, further rules out the formation of an electron−hole plasma in the CdS NW lasers.

In summary, the mechanism of lasing in single CdS NWs was elucidated by temperature-dependent spectroscopic studies. Our data show that the mechanism is exciton-based: exciton−exciton scattering from 4.2 to 75 K and exciton-LO scattering at higher temperatures. Similar detailed optical studies would be useful for other NW optical cavities, such as ZnO[5] and GaN,[7] to enable determination of the lasing mechanism, since the mechanism will depend on factors including the crystal properties, cavity configuration, losses, and excited-state lifetimes. We believe our results will help in modeling[6] the lasing behavior in these novel nanostructures, and also aid in the design of ultralow threshold NW lasing devices. For example, the excitonic mechanism of lasing could be enhanced through of NW laser cavities based on radial NW heterostructures.[1] Specifically, small diameter NWs coated by a larger band-gap material might be used as efficient nanoscale lasing structures, where the small diameter NW provides a low threshold active medium due to exciton confinement, and the outer shell would facilitate waveguiding within a small modal volume optical cavity.

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Supporting Information Available: Calculated fraction of free carriers/total carriers in a bulk CdS crystal for different carrier densities as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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