Stimulated emission behaviors from Excitons in CdS nanoribbons

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Abstract. Semiconductor nanowires show promising properties in nanoelectronic and nanophotonic devices. The nearfield photoluminescence spectra of CdS nanoribbon indicated the luminescent light waveguide behavior. The stimulated emission from the two-phonon bound excitons was also observed at room temperature in this nanoribbon with intense ns laser pumping.

1. Introduction
Semiconductors nanowires (NWs) and nanoribbons have received considerable attention owing to their special properties and potential applications in sensors, optoelectronics, spintronic devices and the assembly of integrated nanosystems [1-11]. Single-crystalline ZnO and ZnS NWs or nanoribbons have been found recently that they can serve as nanoscale lasers, where the high refractive index contrast between the nanostructures and the surroundings defines a subwavelength sized optical cavity [12-16]. As a direct wide band gap (2.42 eV) semiconductor, CdS is an excellent material for a host of applications in optoelectronics, such as nonlinear optical devices, light-emitting diodes. Recent works by Lieber’group have demonstrated that CdS nanowires are good optical waveguides [17] and can function as highly optical confined cavities for stimulated emission or lasing [18,19]. That is to say, to realize the stimulated emission in 1D semiconducting nanostructures, good optical waveguide is fundamentally needed. However, the optical waveguide in CdS nanoribbons has not been reported. Compared to highly transverse optical confined NWs, quasi-1 dimensional nanoribbons own much large cross-sections which are comparable to the optical wavelength, may be another good choice for lasing. Recently lasing in CdS nanoribbons at room temperature was observed by Lee’ group [20] with multimode at room temperature by using a picosecond laser pumping. They also assigned the lasing to the Fabry-Preot oscillation in nanribbon. In this work, uniform and single-crystalline CdS nanoribbons were prepared through the physical evaporation of CdS nano-powder in the presence of an Au catalyst. The optical behavior of these ribbons was investigated using the near-field scanning optical microscopy (SNOM). The results indicate that the CdS nanoribbons can be good optical waveguide cavities under excitation. We also observed the stimulated emission of these nanoribbons at
both room temperature and low temperature (77K) under the nanosecond light excitation. Their different mechanisms of stimulated emission were discussed.

2. Experiment section
CdS nanoribbons were synthesized based on the physical evaporation of CdS nano-powder in the presence of an Au catalyst. An appropriate amount of CdS nanocrystals (~7 nm), preliminary prepared according to reference [21], was placed onto a ceramic plate in the center of a quartz tube, which was inserted into a horizontal tube furnace. Next to the ceramic plate, several pieces of silicon slices coated with a thin Au film (~20 nm) were placed downstream of the gas flow. Prior to heating, high-purity He was introduced into the quartz tube with a constant flowing rate (0.3 sccm) to eliminate the O2 inside. After 60 min, the furnace was rapidly heated to 760 °C and maintained for 60 ~100 min without changing the conditions. Then the power was switched off and the quartz tube was cooled down to room temperature in furnace. Yellow spongelike products deposited on the surface of the silicon slice which was 14 cm away from the center of the quartz tube.

The scanning electron microscope (SEM) images and the energy dispersive spectroscopy (EDS) were achieved on a Scanning Electron Microscopy (SEM, Hitachi S-4200). The transmission electron microscopy (TEM) observations were carried out on a Hitachi H-800 microscope with an accelerating voltage of 200 kV. Optical waveguide was investigated using a commercial scanning near-field optical microscopy (NSOM) from RHK Technology (USA). During the experiment, the continuous wave laser beam (Ar+, 488 nm; power, 10-200 mw) was focused onto a spot size of ~500 µm in diameter to ensure uniform illuminating of the examined CdS nanoribbons which were pre-dispersed in a silicon substrate with a 500 nm thick thermally grown SiO2 layer, and a very small aluminum-coated single-mode cantilevered fiber tip (~ 50 nm) scanned near the surface of the ribbon to achieve high spatial resolution near-field optical images. A white and black CCD through an objective lens was used for collecting the far-field optical image of the excited nanoribbons. Stimulated emission measurements were done using the third harmonic of a Nd:YAG laser (355 nm; spot size, ~0.5 mm2) with pulse width 6 ns as the excitation source. The PL was detected by the spectrometer (Acton Research Corp. Spectra Pro 500i) and a liquid N2-cooled charge coupled device (CCD) camera (Roper Scientific), with an expected spectral resolution of ~0.2 nm. Micro-Raman experiments were conducted in a Raman scattering spectrometer (LABRAM-HR, JY, France), with the 514.5 nm line of an Ar+ laser as the excitation source.

3. Results and discussion
From the SEM observations, the nanoribbons possess fairly uniform rectangular cross sections with a length of a few hundreds of microns, width of around 1 µm, and a thickness of 60–400 nm. The in-situ energy-dispersive X-ray spectrum (EDS) indicates that the nanoribbons contain only element Cd and S and the atomic ratio is very close to 1, indicating the stoichiometric composition of CdS. The TEM examination of a representative single CdS nanoribbon shows that the nanoribbons are straight, with a very uniform width along its long axis. And the selected-area electron diffraction (SAED) pattern of the ribbon indicates that the nanoribbons are single crystalline wurztite structure and grow along the [100] direction.

The light emission of the CdS nanoribbons under Ar+ laser excitation was so strong that it could be imaged easily with a CCD camera and was visible to the naked eye through the objective lens of the SNOM. Through the CCD imaging, only part of a single ribbon can be detected each time, since its length is beyond the vision field of the CCD. However, the entire image of a ribbon can be obtained through adjusting the position of the object stage. From the far-field observation, strong emission was found from both ends of the ribbons and almost no signal can be detected from the side surfaces. A typical amplified far-field emission image for the end emission of an excited CdS nanoribbon is shown in figure 1(A), which exhibits a bright emission spot at the end of one nanoribbon. The result clearly indicates waveguide emission by the nanoribbon itself.
Figure 1. (A) shows a typical far-field emission image of a single CdS nanoribbon excited with the Ar$^+$ laser. (B) is the three-dimensional near-field morphology image of one end of the nanoribbon. (C) and (D) is the corresponding near-field optical image of the ribbon excited with the maximum power (100 mw) and the minimum power (10 mw) of the Ar$^+$ laser, respectively.

To further investigate the waveguiding characteristics of the ribbons, we obtained the high-resolution SNOM images of the ribbon under different illumination power. Figure 1(B) is the three-dimensional near-field morphology image of one end of the nanoribbon, which demonstrates that the ribbon owns highly uniform width (~1 µm) and depth (~100 nm), and a nearly perfect rectangular terminal face. Figure 1(C) is the corresponding near-field optical emission image of the ribbon excited with the maximum power (100 mw) of the Ar$^+$ laser, showing clearly a spatial map of the emission intensity with a maximum at the tip of the nanoribbon, while with relatively very weak emission at both edges of the ribbons. Figure 1(D) shows the near-field optical image of the same nanoribbon when excited with the minimum power (10 mw). Interestingly, the spatial distribution of the emission intensity show great difference to that excited with the maximum power. The end and edges show comparable intensities of emission, in contrast to the case under high power excitation. Clearly the optical waveguide or gains along the long axis of the ribbons was preferred at high power excitation. All of the results indicate that the nanoribbons can serve as active medium as well as potential optical waveguides/resonant cavities and stimulated emission is expected once the optical pumping intensity exceeds the threshold power.

Figure 2. (a) the excitation power-dependent PL spectra of the nanoribbons excited by a nanosecond pulse (Nd:YAG, 355 nm) at 77 k; the inset show the plots of emission intensity and FWHM vs excitation power for the PL spectra. (b) the excitation power-dependent PL spectra of the CdS
nanoribbons at room temperature; the inset plots the excitation power dependence of the emission intensity for spectral position at 503 nm and 518.6 nm, respectively.

As to realize stimulated emission of the CdS nanoribbons, we turn to use the pulsed laser as the excitation source. Figure 2(a) shows the excitation power-dependent PL spectra of the nanoribbons excited by a nanosecond pulse (Nd:YAG, 355 nm) at 77 K. Only one sharp peak appeared at ~492 nm in the emission spectra. The inset show the plots of emission intensity and FWHM vs excitation power for the PL spectra, which indicates that the emission intensity has a superlinear dependence on the excitation power, with the threshold at ~ 4 kw/cm². At the same time, the full width at half maximum (FWHM) of the spectra is strikingly decreased with increasing the excitation intensity (from ~8.5 to ~4.3 nm). The superlinear increase of peak intensity and the concurrent narrowing of the PL peak with the excitation power indicate a transition from spontaneous emission to stimulated emission [22]. Comparing the results of bulk CdS [23] and the present results for CdS nanowires at low temperature (<100 K) [19], the stimulated peak at ~492 nm (figure 2(a)) should originate from exciton-exciton scattering process. Figure 2(b) show the excitation power-dependent PL spectra of the CdS nanoribbons at room temperature, which obviously shows different emission characteristics with that at 77k. At low excitation intensities only one broad main-band appears at around 503 nm (2.47eV), which can be attributed to the radiative transition of free excitons at the CdS bandedge[24]. With increasing excitation power to about 20 kw/cm², a new sharp peak (FWHM, ~5 nm) clearly emerges at the low energy side (518.6 nm) of the broad main-band. The emission intensities of this sharp peak strongly increase with the rising pump power. The inset of figure 2(b) plots the excitation power dependence of the emission intensity for the emissions at 503 nm and 518.6 nm, respectively. It clearly shows that the PL intensity at 503 nm has an approximately linear increase with rising power, whereas the emission intensity at 518.6nm exhibits a superlinear dependence, with a threshold at ~22 kw/cm². The superlinear increase of the emission intensity for the sharp peak at 518.6 nm clearly indicates amplified stimulated emission or lasing [22]. The spectral position of the ~518.6 nm band is about 598 cm⁻¹ redshifted to the free exciton band at ~ 503 nm. The energy of this spacing is close to the energy of 2LO phonon (~600 cm⁻¹), and the linewidth of the 518.6nm band is very narrow comparable to that of the free exciton band. So this low energy emission band should originate from the 2LO-phonon-assisted exciton emissions.

**Figure 3** shows the room temperature micro-Raman modes of a single ribbon; the inset is the Raman spectrum of bulk CdS for contrast.
To further understand the phonon characteristics of the ribbons, we examined the room temperature micro-Raman modes of a single ribbon, which is shown in figure 3 (under 514.5nm excitation). The two strong peaks at ~300 cm\(^{-1}\) and 600 cm\(^{-1}\) are the 1LO and the 2LO mode, respectively. The peak at 521 cm\(^{-1}\) is from the silicon wafer substrate. The inset of figure 3 is the near resonant Raman spectrum of bulk CdS for contrast. Interestingly, the 2LO mode is much stronger than the 1LO mode for the ribbons. According to literature 25, one may assess the strength of the exciton-phonon coupling in semiconductors by using the intensity ratio of overtone of phonon to the fundamental in the resonant Raman spectrum. The intensity ratio \(I_{2LO}/I_{1LO}\) of the nanoribbons (~2.1) is extraordinary larger than that of the bulk CdS (~0.24), reflecting the significant exciton–LO phonon interaction in the CdS nanoribbons, which dominates their optical properties at room temperature. This is consistent with the conclusion of the broadening and redshift of the exciton emission band (see figure 2(b)) compared to that of low temperature (see figure 2(a)). Ref. 26 also shows that the exciton-LO phonon coupling strength in 1D semiconductor nanostructures is greatly larger than the corresponding bulk materials, due to the phonon confinement in the transverse directions.

From the above results, we can see that the phonon scattering plays an important role in the optical properties especially the stimulated emission of the CdS ribbons at room temperature. For defect-rich nanowires, this scattering may produce lasing from the electron-hole plasma formation at high intensity, but in this well-crystallized CdS nanoribbons, the situation looks different.

Compared with that at low temperature, the exciton at room-temperature would relax via thermal population or phonon assistance and lead to more population on the 2LO phonon coupled exciton. The latter show pronounced longer coherence and lifetime than free exciton and 1LO phonon coupled exciton, to lead to the lasing threshold reduction in the exciton-exciton process. Exciton coupled by LO phonons can contribute to more exciton stability to gain at room temperatures since the LO phonon energy (38 meV) is larger than the available thermal energy [27-29]. Moreover, the anomalously high intensity 2LO Raman mode indicates a dominant nonlinear exciton-phonon coupling in the CdS nanoribbons rather than that of linear process in powders. These 2LO phonon-coupled excitons could interact with attraction force lead to optical gain under high intensity excitation. This phenomenon somewhat behaves like the BCS superconductivity originated from Cooper pairs mediated by phonons.

In addition, as shown above, no supper-narrow lasing multi-modes were exhibited in the stimulated PL spectra, which may be due to the following reasons. Firstly, taking these CdS nanoribbons as Farby-Perot optical cavities, the longitudinal modes spacing can be determined by the equation below [15]: \(\Delta \lambda = \frac{\lambda^2}{2nL}\), where \(L\) the cavity length, and \(n\) the refractive index (\(n = 2.5\) for CdS). Since the length of the ribbons can reach several hundreds of microns, assuming a CdS nanoribbon with a length of 300 nm, the calculated mode spacing is 0.18 nm and 0.16 nm for resonant wavelength \(\lambda = 518.6\) nm and 492 nm, respectively. Both spacing are below the resolution of the spectrometer (0.2 nm), leading to the absence of the lasing modes. Secondly, the measured PL may represent the collective emission of several adjacent and simultaneously excited nanoribbons with different sizes (and thus different resonant modes) and orientations with respect to the measuring direction, then making the individual resonant modes not be well resolved [15]. Lastly, as shown in figure 1(C) and 2(D), the nanoribbons also have weak PL leaking in transverse directions, these non-axial wave would add to the stimulated emission band and render the broadening of the measured stimulated peaks as well as the co-existing of the spontaneous bands. In fact we would like to indicate that this stimulated emission may come from a new mechanism---BCS pair condensation, but not F-P effect.

4. Conclusions
The CdS nanoribbons were obtained by CVD technique, whose emission properties show clear temperature dependence. Their emission properties show clear power dependent waveguide behavior. They show lasing properties due to exciton interaction under ns laser excitation both at room
temperature and 77K, originated from the interaction between the 2LO phonon bound excitons and free excitons, respectively.

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5. References
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