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Multi-photon-pumped stimulated emission from ZnO nanowires: A time-resolved study

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ABSTRACT

In this work, we study temporal evolution of multi-photon-pumped stimulated emission from ZnO nanowires. In addition to second harmonic generation, ultraviolet stimulated emission is observed in ZnO nanowires under femtosecond pulse excitation at 800 nm. Sharp emission peaks appear when excitation flux reaches a threshold of 80 mJ/cm^2, which can be interpreted as lasing action in self-formed nanowire microcavities. Temporal evolution of the emission captured by Kerr shutter technique shows strong excitation-power dependence. The dynamic trace of stimulated emission exhibits a fast decay with a lifetime about 4.5 ps at intermediate excitation ($\sim$ 100 mJ/cm^2) and a lifetime about 2 ps at high excitation ($>$ 160 mJ/cm^2). The difference in the lifetime can be attributed to different gain mechanisms related to excitonic interaction and electron-hole plasma, respectively.

1. Introduction

One-dimensional nanostructures are currently under intensive research due to their potential applications in the area of optoelectronics. Miniature waveguides, nanolasers, and piezoelectric generators have been successfully demonstrated with nanowires in the past few years [1–4]. ZnO nanowires are regarded as good candidates for ultraviolet (UV) nanolasers at room temperature since they have wide band gap and high exciton binding energy [1]. Owing to the quantum confinement effect, excitons are more stable in nanowires than in bulk crystals [5–7], which leads to efficient optical gain in the process of radiative recombination via exciton-related inelastic collisions. Ultraviolet nanolasers can be demonstrated by coupling the optical gain to self-formed microcavities of nanowires [1]. In these lasers, wave-guiding nanowires act as cavities that support Fabry–Perot modes with optical feedback by reflections at the two end-facets [1,7,8]. To gain more insights into ZnO nanolasers, time-resolved (TR) spectroscopy (transient absorption spectra and TR photoluminescence (TRPL) spectra) has been employed to examine the temporal evolution of the light emission and dynamic behaviors of the carriers [9–14].

Recently, the nonlinear optical properties of nanostructures have attracted lots of interest [15–17]. For instance, nanoscaled frequency converters can be realized with second harmonic generation (SHG) in the nanowires, which can be further developed into a novel TR-technique to probe the carrier dynamics in single nanostructures [7]. Together with the TRPL technique, the TR-SHG in single nanostructure provides better understanding of the correlation between the lasing action and intrinsic carrier dynamics. In addition to SHG, multi-photon absorption (MPA) is frequently observed in semiconductor nanostructures. MPA process can be used to pump PL or even lasing from wide band gap semiconductors [18–20]. In ZnO nanostructures, MPA-pumped UV nanowire lasing and random lasing have been demonstrated recently [20,21]. Compared to the linear UV pumping, the MPA approach is more promising for biomedical applications such as bio-imaging and photomedical therapy, since infrared pumping light can penetrate into deeper tissue level with good spatial confinement [22]. However, temporal dynamic behaviors of MPA-induced stimulated emission or SHG have not been fully explored in ZnO nanowires.

In this Letter, we report our recent examination on the temporal evolution of the MPA-induced stimulated emission in ZnO nanowires with comparison of SHG. Stimulated emission from ZnO nanowires is generated with femtosecond (fs) pulse excitation at 800 nm. The pumping threshold is about 80 mJ/cm^2. Emission spectrum and PL image of MPA-pumped single nanowire lasers are recorded to illustrate the microcavity effect. Analysis of TRPL spectra and dynamic traces reveals carrier-density-dependent optical gain mechanisms. For the first time, the dynamic behaviors of coherent emission from ZnO nanowires under nonlinear optical pumping have been systematically studied.

2. Experimental details

ZnO nanowire samples used in this study are synthesized on silicon substrate by chemical vapor deposition process using silver film catalyst [23]. Characterized by scanning electron microscopy, most of the nanowires have the diameters of 100–200 nm and

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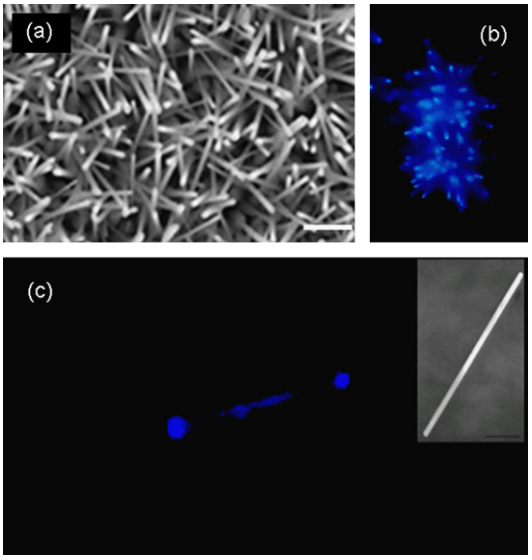

Fig. 1. (a) SEM image of the nanowire sample used in this studied (scale bar: 5 μm). (b) Image of MPA-pumped PL from the sample at the focal point with excitation of ∼ 120 mJ/cm^2. (c) PL image of a single nanowire pumped by MPA excitation of 120 mJ/cm^2 (inset shows the SEM image, scale bar: 1 μm).

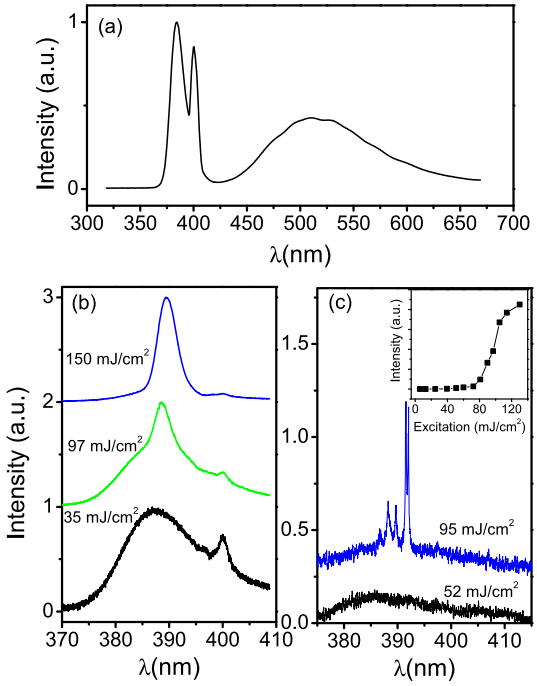

Fig. 2. (a) Up-converted emission from ZnO nanowire film sample under excitation at 800 nm with flux of 30 mJ/cm^2. (b) Near ultraviolet emission from the film sample under different excitation fluxes. (c) Emission spectra from single nanowire under different excitation fluxes. Inset shows the peak intensity as a function of the excitation flux.

lengths of 2–6 μm (Fig. 1(a)). Scanning electron microscopy and X-ray diffraction are used to characterize the morphology and crystalline structure of the sample. For MPA excitation, femtosecond pulses at 800 nm from a regenerative amplifier stage (Spitefire, Spectra-Physics) with a pulse duration of ∼ 120 fs are used. Excitation beam is focused onto the sample at an angle of 45° to the normal of the substrate. Emission spectra are recorded by a spectrometer with ∼ 0.05 nm spectral resolution (Spectropro 500i). For single nanowire experiment, nanowires are collected from the growth substrate, suspended in ethanol solution, and dispersed on new silicon substrates for optical measurement. Single nanowire is identified by a fluorescence microscope equipped with an objective lens (40X, NA 0.7) and a sensitive CCD camera. PL images are taken with optical filters to exclude the excitation residue, while PL spectra are recorded with an optical fiber coupled to a spectrograph. Time-resolved PL studies are realized with optical Kerr shutter technique using Kerr medium of 1 mm thick CS_2-filled cell with temporal resolution of ∼ 1.5 ps in our configuration.

3. Results and discussion

As shown in Fig. 2(a), under infrared pulse excitation with flux of 30 mJ/cm^2, emission spectrum (Fig. 2(a)) from an as-grown ZnO nanowire film sample exhibits three frequency up-converted peaks: the MPA-induced band edge emission at UV band (∼ 385 nm), SHG response at double frequency of incident beam (400 nm), and the MPA-induced deep level emission in the green band [24]. To generate MPA-induced lasing from ZnO nanowires, we perform power-dependent PL measurements. A transition from spontaneous emission to stimulated emission in ZnO nanowire film samples can be realized with excitation flux above a threshold about 80 mJ/cm^2 as shown in Fig. 2(b). At low excitation, spontaneous emission peak at 385 nm with a full width at half maximum (FWHM) bandwidth of ∼ 17 nm is detected. When the excitation exceeds the threshold, stimulated emission experiences a significant reduction of bandwidth (down to ∼ 5 nm). A slight red shift of the stimulated emission peak can be explained by the excitonic effect (exciton–exciton [1], exciton–carrier [25], exciton–phonon [25] scattering) for optical gain generation. The intensity of the stimulated emission increases more rapidly than that of the SHG signal.

With two-photon pumping, similar lasing action is observed from ZnO nanocrystalline film. This has been explained as random lasing since no well defined laser cavity is formed [21]. This lasing action is different from that in the nanowire samples which can form laser cavities. Previous studies have reported that ZnO nanowires with diameters larger than 100 nm can act as waveguides and confine the emission light effectively [7]. In a well facet nanowire, the waveguide, together with optical feedback of reflection at the two ends, can act as an excellent microcavity for the light amplification with well-supported Fabry–Perot modes. These modes exhibit discrete sharp emission peaks in the spectrum. Fig. 1(b) shows a PL image of the nanowire film sample, and the bright points at the nanowire ends are clearly identified, indicating the existence of the microcavity effect in the MPA-pumped nanowire lasers. For a Fabry–Perot nanowire cavity, the wavelength of the modes depends on the optical length of nanowire. Therefore, multiple nanowires with different lengths in the sample can lead to the absence of sharp emission peaks in the emission spectrum. To verify the assignment of the laser cavity, we perform experiments with single nanowire imaging. MPA-pumped lasing action can be realized in non-damaged single nanowires with thresholds in the range 70–150 mJ/cm^2 (inset of Fig. 2(c)). As shown in Fig. 1(c), the emission intensity at nanowire ends is dominant when excitation exceeds the threshold. Emission spectrum exhibits sharp lasing peaks (Fig. 2(c)). These emission peaks with linewidths of 0.2–0.5 nm should be assigned to the Fabry–Perot modes of nanowire microcavities.

In Fig. 3, we show results of the time-resolved PL study on the observed MPA-pumped stimulated emission from ZnO nanowires. Temporal evolution traces from the nanowires were recorded using optical Kerr shutter technique at different excitation fluxes. For clarity, the response curve of SHG at 400 nm is shown in Fig. 3(a). The temporal evolution of SHG reflects the response curve of Kerr medium since SHG responses to the incident pulse instantaneously. The slow decay component can be attributed to the broad-band spontaneous emission. With excitation flux below the threshold,