Resonance enhancement of optical second harmonic generation in a ZnO nanowire

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Two-photon absorption measurement has been carried out in a single 80 nm $\times$ 10 μm ZnO nanowire using femtosecond laser pulses in the wavelength range of 700–800 nm. In addition to the deep-level green emission around 530 nm due to surface defects and the near band-edge ultraviolet emission around 360 nm due to the exciton, a second harmonic peak has been observed. The strength of the frequency-doubled component is found to enhance while the two-photon absorption wavelength is tuned towards the exciton wavelength of the nanowire. This behavior can be ascribed to the resonant exciton absorption in ZnO nanowires. © *2006 American Institute of Physics*.
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Semiconductor nanocrystals have attracted much interest due to their fundamental importance in bridging the gap between bulk matter and molecular species. Zinc oxide is a remarkable II-VI semiconductor with potential applications owing to its diverse properties.[1] The combination of high excitonic and biexcitonic oscillator strength and good high temperature characteristics make ZnO a promising material for optical applications.[2] It has been used as a visible and ultraviolet photoconductor and as fluorescent material, apart from its usefulness in optical waveguides, acousto-optic devices, thin film transistors, etc.[3,4] Its wide band gap of 3.37 eV at room temperature makes ZnO suitable for short-wavelength optoelectronic devices, including light-emitting diodes (LEDs) and laser diodes (LDs). ZnO has a high exciton binding energy of 60 meV, which renders it more applicable for making room-temperature UV laser devices.[5] Small-diameter ZnO nanowires are expected to further lower the lasing threshold because quantum effects result in enhancement of density of states near the band edges and radiative recombination due to carrier confinement. The high exciton binding energy of ZnO at room temperature makes it a promising material for polariton lasers.[6–8] Among nanomaterials, a nanowire has the additional advantage of propagating these photon-exciton pairs due to better optical and carrier confinement.[9,10] However, the possibility of generating exciton-photon pairs by two-photon absorption process is not yet reported in ZnO nanowire. The goal of our research is to investigate the prospect to generate polariton modes that has huge importance for quantum optics and optical information transfer in photonic circuits. High optical nonlinearity due to the unequal atomic size of Zn and O is reported by Levine.[11] The acentrically located bond charge contributes a homopolar energy gap. Since nonlinear susceptibility is more sensitive to the crystal potentials, ZnO is found to be highly nonlinear. This high optical nonlinearity produces second harmonic photon, while the two-photon absorption creates excitons in ZnO nanowire. By tuning the second harmonic photon energy towards the exciton resonance, an enhancement in second harmonic generation (SHG) is revealed in the present investigation.

The II-VI semiconductors are efficient second harmonic generators since they possess strong second-order nonlinear susceptibility.[12] Very recently, it has been demonstrated that nanowires and ribbons of II-VI semiconductor compounds, such as CdS and ZnO, possess a remarkable ability to guide light in the near UV to visible region.[9,13] Wires with diameters in the 100 nm range and lengths of tens of micrometers transport optical modes with only moderate losses, even across bends and connections between two wires. This subwavelength waveguiding, sometimes called "active" waveguiding, is, however, poorly understood. It is also noted that the second-order susceptibility of ZnO depends on the quality and hence the growth technique of nanowire. Surface recombination is a serious dissipative effect in ZnO based devices. The surface recombination rate is high in small-diameter nanowires.[14] Transmission electron microscopy (TEM) measurements show that the nanowire in the present investigation has a radius of 80 nm. Further reduction in the radius will considerably increase the surface recombination.

ZnO nanowires are grown by the vapor-liquid-solid (VLS) technique using metal catalyst particles and carbothermal reduction of ZnO as the vapor source.[15,16] Synthesis is carried out inside a quartz tube with a wide (3 cm) and narrow (1 cm) ends, which was placed inside argon flushed tube oven. An aluminum oxide boat containing 0.5 g of an equimolar mixture of zinc oxide and carbon was placed at the wide end of the quartz tube. An epipolished sapphire (112) substrate was partially covered with a thin ($\sim$7 Å) gold film by means of plasma sputter deposition and placed at the narrow end of the quartz tube, 18 cm from the vapor source. At elevated temperatures, the gold film breaks up and forms nanoparticles which act as nucleation sites for the growth of nanowires. The oven is ramped to 930 °C in 40 min, dwelled at 930 °C for 30 min, and allowed to cool slowly. During the last 20 min at 930 °C, a flow of argon of 4 l/m ensures transport of the vapor to the substrates and thus the growth of nanowires on the substrate.

For single-wire luminescence and TEM measurements, the wires are transferred to a 20 nm thick SiN_4 membrane by rubbing the membrane over the wire covered substrate. The luminescence imaging setup is illustrated in Fig. 1. Femtosecond laser pulses from a Ti: sapphire laser (100 fs, 82 MHz repetition rate) served as the pump beam for two-

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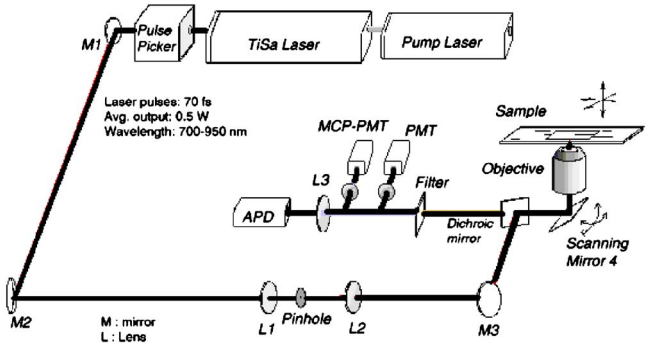

FIG. 1. Schematic representation of two-photon absorption luminescence measurement.

photon absorption in ZnO nanowires. The pump wavelength can be tuned from 600 to 900 nm. The pump beam is carefully focused onto the nanowire sample using a microscope objective. In order to avoid bleaching, the excitation density has been restricted to $<50\ \mathrm{mW/cm^2}$. The nanowires are spread on a TEM grid that helps to select isolated nanowire. The oil immersion objective of magnification of 40× and numerical aperture (NA) of 1.3 produces a laser spot size of $\sim 1\ \mu\mathrm{m}$ in the nanowire. A point by point scan helps to record the luminescence from a single isolated nanowire. A dichroic mirror is used to select the luminescence wavelength. The luminescence from ZnO nanowire is imaged using a charge-coupled device (CCD) and LIMO software.

For the two-photon absorption measurements at room temperature, we choose four pump wavelengths: (i) above band gap (700 nm), (ii) near band gap (720 nm), (iii) near exciton (753 nm), and (iv) below band gap (800 nm). Since the luminescence is recorded at room temperature, the fine structures due to the *A*-, *B*-, and *C*-type excitons are not visible. Instead, a thermally broadened peak due to the absorption of all these excitons is clearly observed in our measurements. While pumping above the band gap, we observed three major peaks as depicted in Fig. 2. The peaks are attributed to the SHG, the exciton emission, and the defect emission, respectively. If the two-photon excitation $2\hbar\omega$ is below the exciton transitions, only SHG single-wire emission is observed, with intensity that does not depend on the position of the excitation spot. For excitation with two-photon energy in resonance or above the exciton transitions, we found that the spatial excitation patterns depend sensitively on the intensity of the laser beam and its relative polarization with respect to the wires' long axis. It is clear from the figure that SHG intensity is enhanced while we tune the pump wavelength near the exciton wavelength (753 nm). This can be attributed to the resonance energy transfer between the exciton and the SHG. Detuning the pump wavelengths from the resonance peak to upper and lower wavelength sides decreases the strength of SHG.

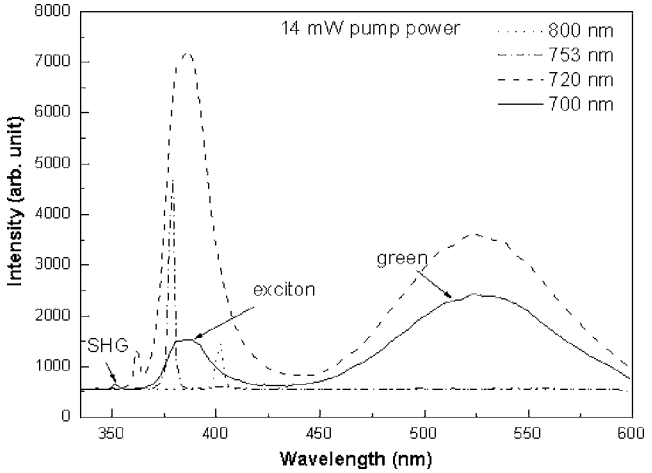

FIG. 2. Two-photon absorption luminescence spectrum of ZnO nanowire for different pump wavelengths. The solid line indicates 700 nm, the dashed line 720 nm, the dash dot line 753 nm, and the dotted line 800 nm pump wavelengths.

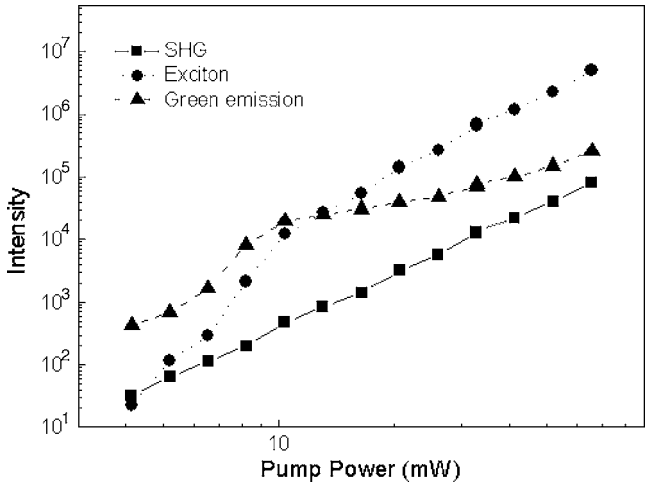

FIG. 3. Pump power dependence of luminescence at 720 nm pump wavelength. The solid line represents the pump power dependence of second harmonic, the dotted line represents that of exciton luminescence, and the dashed line represents defect emission.

Figure 3 shows the relative strength and pump power dependence of the SHG, exciton emission, and green emission for near band gap absorption. The strengths of the exciton emission and the green emission are weak at 753 nm pump compared to that at 720 nm. Linear fit to the variation of integrated intensity versus pump power in logarithmic scale shows that the SHG has slopes of 2.65 at 720 nm and 3.2 at 753 nm, whereas at 700 nm the SHG has the usual square dependence. This indicates that the slope of the power dependence has a direct relation with the resonance enhancement. The pump power dependence of SHG is studied for all

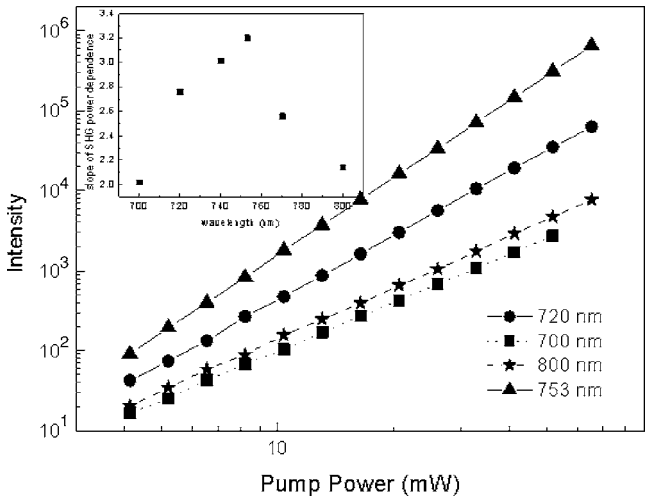

FIG. 4. Pump power dependence of second harmonic for different pump wavelengths. Wavelength dependence of the slope is depicted at the inset.

the four pump wavelengths and is illustrated in Fig. 4. In order to get a quantitative idea about the resonance enhancement, we substantially plotted the pump wavelength versus the slope of the pump power dependence of second harmonic intensity that is depicted at the inset of Fig. 4. This shows that at exciton resonance the slope of the pump power dependence registers a sharp increase.

In conclusion, excitons and second harmonic photons are simultaneously generated in a single isolated ZnO nanowire by two-photon absorption. Resonance enhancement of the second harmonic intensity has been observed, while tuning the two-photon absorption pump wavelength below band gap. We also observed a sharp increase in the pump power dependence of integrated second harmonic intensity when the two-photon absorption wavelength is tuned towards the exciton peak that further convinces the resonance energy transfer.

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