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Blue-shifted and picosecond amplified UV emission from aqueous chemical grown ZnO microrods

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ABSTRACT

Room-temperature amplified spontaneous emission (ASE) has been observed from aqueous chemical grown zinc oxide (ZnO) microrods. The well-faceted microrods have only a single narrow ultraviolet (UV) emission at 390 nm (3.2 eV) with average lifetimes as fast as 85–100 ps. The characteristic ASE also exhibits blue-shifted peaks and shortened lifetimes. At present, the peak shifting and the lifetime shortening are attributed to the band filling and photo-induced screening effects and to the nonradiative relaxation process, respectively. Results indicate that the ZnO microrods have good structural and optical quality which leads to their suitable use for optoelectronic applications.

1. Introduction

Zinc oxide (ZnO) has attracted much attention as a candidate material for various ultraviolet (UV) devices such as detectors, light emitting diodes (LEDs), laser diodes, among others [1]. Its wide and direct band gap (3.3 eV) and large exciton binding energy (60 meV) enable efficient excitonic UV emission at room and even higher temperatures [2]. With the increasing variety of ZnO growth methods being implemented, high quality single crystals and a massive assortment of micro/nanostructures have already been produced. Among the techniques used, the aqueous chemical growth (ACG) method (often referred to as hydrothermal method or solution route) is a low cost, simple, and effective way to fabricate hexagonal and crystalline ZnO micro/nanostructures. Using tabletop equipment and few chemical precursors, ZnO rods [3–9], flowers or multipods [10–12], stars [13], prisms [14], and nanoparticles [15] are produced with high yield at relatively low temperatures. ZnO microrods prepared by ACG, for example, can be isolated and can be used for device fabrication [16]. With the advancement of optical characterization techniques, stimulated emission and lasing action from different ZnO materials have also been observed [17–24]. Investigating the phenomena governing dynamic optical transitions is important for the fundamental understanding and full integration of these ZnO materials into their potential applications.

In this work, we report the amplified stimulated emission (ASE) of uniform and well-faceted ZnO microrods fabricated by the ACG method. The ASE is evidenced by the increase in the emission intensity and the decrease of the spectral linewidth with increasing optical excitation energy density. The microrods also exhibit blue-shifted peaks and shortened picosecond lifetimes attributed to the band filling and screening effects and to the nonradiative process, respectively. These observations give helpful insights on the use of the microstructures for their potential UV optoelectronic applications.

2. Experimental

Aqueous chemical growth method was implemented in fabricating ZnO microrods. Equimolar concentrations of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and hexamethylenetetramine ($(CH_2)_6N_4$) aqueous solutions were homogenously mixed in a beaker through ultrasonication. A (1 0 0) silicon (Si) substrate was then submerged into the solution and was set at the bottom of the beaker. The solution was eventually heated at 95 °C for 120 min in

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ambient atmosphere. After heating, the substrate was removed from the solution and was air-dried. The air-dried sample was subsequently annealed at 370 °C for 60 min in ambient air. A typical morphology of the as-prepared ZnO sample is shown in Fig. 1. Hexagonal structures are observed lying horizontally on the substrate exposing their prism sides to the surface. The well-faceted rods are homogenous with uniform lengths and widths ranging from 6–20 μm and 0.4–1.3 μm, respectively. A 10 μm × 10 μm area of the sample is occupied by approximately 11 microrods. X-ray diffraction (XRD) spectroscopy results also reveal that the as-prepared samples have reflections corresponding to hexagonal wurtzite ZnO.

Time-resolved photoluminescence (TRPL) spectroscopy was performed at room temperature to investigate the optical emission of the as-prepared ZnO microrods. The frequency tripled output (3ω, 290 nm) of a Ti:sapphire laser system with 1 kHz repetition rate and 100 fs pulse duration was used as the excitation source. The laser beam having a spot size ranging from 220–450 μm was made incident at an angle of 45° from the surface normal to the sample. Varying laser pump powers were used and were measured using a calibrated power meter. The sample emission was then collected also normal to the sample by a fiber optic bundle and was directed to an imaging spectrograph fitted with 600 grooves/mm grating. The spectrograph was coupled to a streak camera in conjunction with a UV–Vis high resolution charged-couple device (CCD) camera. The spectrograph-camera system has a spectral resolution of 1 nm and a temporal resolution of 10 ps.

3. Results and discussion

The initial room-temperature wide scan PL spectrum of the ZnO microrods prepared by the ACG method is shown in Fig. 2. Only one narrow emission peak is observed at 390 nm (3.2 eV) corresponding to the near-band-edge emission of ZnO [25]. Compared with the usual ZnO near-band-edge emission peaks at ~380 nm, the sample emission is slightly shifted to longer wavelengths (lower energies). The shift may be due to the relative contributions of the excitonic recombination and its longitudinal optical (LO) phonon replicas and/or to the thermal effects caused by laser heating [26–28]. In contrast with ZnO micro/nanostructures similarly fabricated by ACG method [4–11,14,15] and to those prepared by different techniques [29–31], the microrods do not exhibit any visible defect-related emissions. This result implies that the as-prepared ZnO microrod samples are of good optical quality.

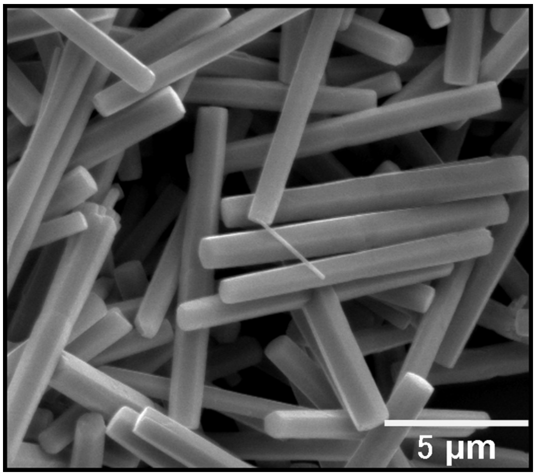

Fig. 1. Typical SEM image of ZnO microrods prepared by ACG method.

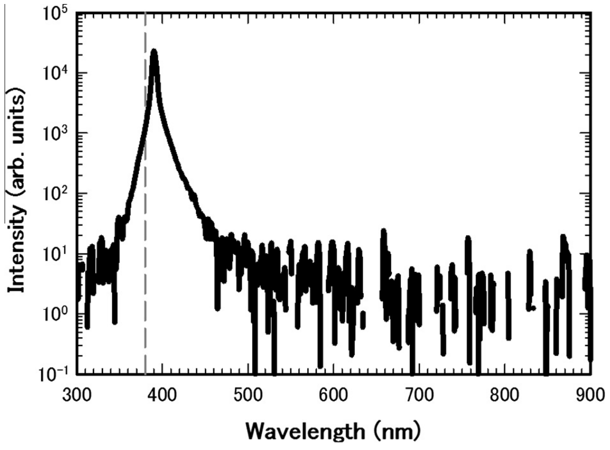

Fig. 2. Room-temperature wide scan PL spectrum of ZnO microrods prepared by ACG method.

Streak camera images of the room temperature UV emissions of the aqueous chemical grown ZnO microrods at different excitation energy densities are shown in Fig. 3. All streak camera images are normalized for easier comparison. The corresponding integrated spectral and temporal profiles are also presented in Fig. 4(a) and (b), respectively. At an excitation of 100 μJ/cm^2, the emission is faint and very weak. The emission becomes very intense and narrow at higher excitation up to 410 μJ/cm^2. Investigating the emission intensities and spectral linewidths (full-width at half maximum or FWHM), the light–light (L–L) curve of the ZnO microrods is shown in Fig. 5. With increasing optical excitation, the integrated emission intensity increases while the linewidth decreases. This energy dependence of the room temperature UV emission of the ZnO microrods, specifically the linear increase of intensity with incident pump energy, indicates an amplified spontaneous emission (ASE).

The room temperature UV emission peaks and average lifetimes of the ZnO microrods fabricated by the ACG method are also examined. The emission peak centers of the ZnO microrods at different excitation energy densities are plotted in Fig. 6(a). The peaks shift to shorter wavelengths by 1–3 nm (i.e. higher photon energies) with increasing energy density. Similar observation is also reported for various ZnO nanowire samples [22,32,33]. Meanwhile, the average lifetimes of the UV emissions of the ZnO microrods at different excitation energy densities are shown in Fig. 6(b). From the decaying part of the temporal profiles like those depicted in Fig. 4(b), the lifetimes are determined by fitting a biexponential function of the form:

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right), \qquad (1)$$

where I is the emission intensity, t is time, A_1 and A_2 are the numerical coefficients, and τ_1 and τ_2 are the computed decay constants. From the fitted biexponential functions, the average lifetimes, $\bar{\tau}$ are then calculated using the formula [34]:

$$\bar{\tau} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}. \qquad (2)$$

The ZnO microrods have fast average UV emission lifetimes around 85–100 ps. The UV emission lifetimes also shorten with increasing energy density.

The aqueous chemical grown ZnO microrods exhibit room-temperature amplified spontaneous UV emission without any fabricated mirrors, sample cleavage, or sample etching. This observation is also similar to other ZnO materials in the form of