Photoluminescence properties of a single ZnO microstructure for potential scintillator applications

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Abstract

Photoluminescence properties of ZnO microstructures are investigated for potential scintillator applications. Samples are successfully prepared by the carbothermal reduction method. A single free-standing ZnO microribbon exhibits UV and visible emissions which behave differently along the microstructure. Fast UV emission lifetimes of 40 and 150 ps have been observed for the microstructures compared to 440 ps and 2 ns for a bulk crystal. With waveguided emissions and fast lifetimes, the ZnO microstructures have promising applications as future XFEL scintillators.

Keywords: ZnO, oxides, microstructure, photoluminescence

1. Introduction

The development of efficient and fast scintillators is necessary for X-ray free electron laser (XFEL) research. Conventional Ce:YAG scintillators having 50 to 70 ns luminescence lifetimes [1, 2, 3, 4, 5] are still insufficient for the characterization and synchronization of femtosecond pulses. Fast scintillators are needed to accurately synchronize the XFEL with other laser sources enabling the characterization of ultrafast short wavelength optical pulses and the implementation

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of various pump-and-probe experiments [1].

Among the possible scintillator materials, zinc oxide (ZnO) is ideal because
10 of its high quantum efficiency in the short wavelength region [6]. ZnO has a wide
and direct band gap of 3.3 eV which leads to ultraviolet (UV) emission and a
large binding energy of 60 meV which enables room temperature excitonic emis-
sion [7]. A hydrothermal-grown ZnO single crystal has been reported to have ex-
cellent scintillation properties [8]. ZnO has a fast luminescence lifetime of about
15 1.0 ns with UV and extreme UV (EUV) excitations [8, 9, 10]. Since smaller-sized
samples maximize the oscillator strength [11], micro/nanostructure-based scin-
tillators in the UV and EUV wavelengths hold promise for future optoelectronic
applications.

In this report, we investigate the photoluminescence (PL) properties of ZnO
20 microstructures for potential scintillator applications. The ZnO microstructures
are prepared by the carbothermal reduction method. A single free-standing
ZnO microribbon exhibit both UV and visible emissions which channel along
the ribbon structure. The luminescence lifetimes of the ZnO microstructures are
also faster than that of bulk ZnO making the microstructures viable scintillator
25 materials.

2. Experimental

The ZnO samples were prepared by the carbothermal reduction method
similar to Ref. [12]. ZnO powder and activated charcoal with 1 : 5 mass ratio
were finely ground and were placed into a ceramic crucible. An ultrasonically
30 cleaned Si (100) substrate coated with a thin gold (Au) layer was used to cover
the crucible instead of the crucible lid. The crucible-substrate assembly was
then loaded inside a muffle furnace and was heated to 950 °C for 30 minutes in
ambient pressure. After the heat treatment, fibrous white crystals were observed
to grow on the Si substrate. The ribbon-like structures have typical lengths of
35 1.0 cm, widths of 50 to 500 μm , and thicknesses of 2.2 to 35 μm . Representative
SEM images showing the flat surfaces and the uniform thickness of the grown

microribbons are shown in Fig. 1 (a) and (b), respectively.

Room temperature PL spectroscopy and imaging were implemented using a Ti:sapphire laser system. The excitation source was derived from a commercial Ti:sapphire regenerative amplifier (Spectra Physics, Inc., Spitfire) seeded by a mode-locked Ti:sapphire laser oscillator (Spectra Physics, Inc., Tsunami 3941-M1S) with 870 nm fundamental wavelength. After passing through non-linear BBO crystals for frequency tripling, the output laser beam had a 290 nm wavelength, 100 fs pulse duration, 1 kHz repetition rate, and 10 μ J pulse energy. The schematic diagram of the experimental setups for the wide scan PL spectroscopy, PL emission imaging, and time-resolved PL (TRPL) spectroscopy are shown in Fig. 2 (a), (b), and (c), respectively. The wide scan PL spectra were taken by focusing the sample emission to a fiber optic bundle connected to a handheld spectrometer (StellarNet, Inc., BLUE-Wave UVNb-50). Moreover, the PL emission was imaged using a UV sensitive, electron-bombardment CCD camera (Hamamatsu Photonics K.K., EB-CCD Camera C7190). The sample emission was collected using a collimating lens ($f = 50$ mm) and a wide range (220 to 900 nm) transmitting camera lens (Nikon Corporation, UV Nikkor $f = 105$ mm). Color filter glasses were placed in between the lenses to image specific emissions. A UV transmitting, visible absorbing filter (Hoya Corporation, U360) was used to capture only the UV emission. On the other hand, a sharp cut filter (Hoya Corporation, Y46) was used to capture only the visible emission. Furthermore, TRPL spectroscopy was also done for an ensemble of ZnO microstructures prepared by the same method. The sample emission was focused unto the entrance slit of a 25 cm focal length spectrograph (CHROMEX, Inc., Imaging Spectrograph 250is) coupled to a streak camera (Hamamatsu Photonics K.K., C1587) and a UV-Vis high resolution CCD camera (Hamamatsu Photonics K.K., Digital Camera C4742-95-10 NR). This TRPL system had a spatial resolution of 1 nm and a temporal resolution of 10 ps in the fastest scanning range.

65 3. Results and Discussions

The room temperature X-ray diffraction (XRD) spectra of a single free-standing ZnO microribbon is shown in Fig. 3. The X-ray is incident at the flat wide surface of the microribbon. The peaks at around 32, 66, and 110 ° correspond to the (10 $\bar{1}$ 0), (20 $\bar{2}$ 0), and (30 $\bar{3}$ 0) reflections of hexagonal wurtzite ZnO [13]. All *a*-axis reflections are observed indicating that the *a*-plane is normal to the plane of incidence. The ZnO microribbon prepared by the carbothermal reduction method is highly oriented with its flat wide surface perpendicular to the *a*-plane.

The room temperature wide scan PL spectra of a single free-standing ZnO microribbon grown by the carbothermal reduction method is shown in Fig. 4. Two emission peaks are observed, and by exponentially modified gaussian (EMG) fitting, the peak centers are determined at 378 and 513 nm. The UV peak at 378 nm corresponds to the near-band-edge emission, while the visible peak at 513 nm corresponds to the defect-related emission [14, 15]. The visible emission of the single ZnO microribbon is more intense than the UV emission.

The room temperature PL emission images of a single free-standing microribbon grown by the carbothermal reduction method are shown in Fig. 5. The images are in grayscale and are normalized with respect to the highest intensity. Fig. 5 (a) depicts the PL image without the use of any filter. Fig. 5 (b) and (c) are the UV (300 to 400 nm) emission and the visible (460 to 750 nm) emission images, respectively. The UV and visible emissions have different behaviors along the microstructure. The UV emission is observed at the flat wide surface of the microribbon. While seen to radiate throughout the sample, the visible emission is more pronounced along the edges. This indicates that the visible light is being channeled by multiple reflections within the microribbon towards its edges.

A comparison of the streak camera images and temporal profiles of ZnO microstructures and of a bulk ZnO crystal is shown in Fig. 6. The temporal profiles were integrated over a 25 nm wide spectral region around 380 nm.

95 The decaying part of the TRPL data were well-fitted to double exponential decay functions. The fast and slow decay components are attributed to the free excitons and to the free and trapped carriers, respectively [11, 16, 17]. ZnO microstructures show faster decay times of 40 and 150 ps compared to 440 ps and 2 ns of the bulk crystal.

100 Decreasing the sample size likely affects the photoluminescence properties of a ZnO crystal. The near-band-edge luminescence lifetime of the ZnO microstructures is faster than that of the bulk crystal used here and those we have previously reported [6, 8, 10]. Many factors can affect the luminescence lifetime. Oscillator strengths are enhanced as the sample size is reduced [11, 18].
105 But since the sample dimensions ($\geq 2 \mu\text{m}$) are bigger than the exciton Bohr radius, the size effect does not contribute largely to the fast emission lifetime. On the other hand, even though the defect-related visible emission of the ZnO microstructure dominates the PL spectra, the visible emission lifetimes of ZnO are typically slow ranging from a few nanoseconds to milliseconds [14]. The UV
110 decay lifetime has also no obvious relationships with the point defect density, the defect luminescence position, and the UV to visible emission ratio [16, 19]. As compared to the bulk, the microstructure has a higher surface to volume ratio of about 3×10^4 . With a high surface to volume ratio, nonradiative recombination could have possibly shortened the lifetime with the activation of nonradiative
115 centers at room temperature [16, 20, 19]. The fast near-band-edge luminescence lifetime is largely attributed to the effective nonradiative recombination.

In addition, though the visible emission tends to overwhelm the UV emission, both emissions are observed to be channeled or guided through the microribbon structure. Numerical calculations are currently undertaken to further under-
120 stand why the UV emission is pronounced at the surface and why the visible emission is prominent at the sides. The ZnO microribbon can nevertheless act as an excellent PL waveguide similar to ZnO nanowires [15] and SnO_2 nanoribbons [21]. Having a uniform thickness and a flat surface, the microribbon can serve as an optical cavity given the differences in the refractive indices of ZnO
125 and air [22]. The UV emission can be enhanced by utilizing this flat wide sur-

face which is perpendicular to the a -plane. The presence of the visible emission as well as the low light yield associated with fast lifetimes [1, 23] can then be compensated. Satisfying the excitation and emission polarization conditions for ZnO microstructures leads to better UV emission. If these microstructures will
130 be used as scintillator materials, the microstructures will be wicked on plastic and will utilize refractive index matching. The spatial resolution of the scintillator, however, may not improve, contrary to the effect on the timing or temporal resolution. The actual spatial resolution measurement, similar to the method done on bulk ZnO [24], is currently being considered. With fast lifetimes and waveguiding properties, the ZnO microstructures nonetheless have
135 potential scintillator applications leading to temporal resolution improvement, optical density enhancement, and design flexibility.

4. Conclusions

We presented the photoluminescence properties of ZnO microstructures for
140 potential scintillator applications. The ZnO microstructures were successfully prepared by the carbothermal reduction method. A single, free-standing, and highly oriented ZnO microribbon exhibit both UV and visible emissions which channel along the microstructure. The luminescence lifetimes of the ZnO microstructures are very fast with 40 and 150 ps decay times. Further investigations on the manifestation of a waveguide effect and the enhancement of the UV
145 emission, as well as numerical calculations and spatial resolution measurements, are anticipated in the future. ZnO microstructures hold a promise as candidate scintillators utilizing microcavity and waveguiding effects not only for XFELs but also for EUV lithography and other related applications.

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Figure Captions

Fig. 1: SEM images showing (a) the flat wide surfaces and (b) the uniform thickness of ZnO microribbons prepared by the carbothermal reduction method

Fig. 2: Schematic diagram of the experimental setups: (a) wide scan PL spec-
265 troscopy; (b) PL emission imaging; and, (c) TRPL spectroscopy (Images are
not drawn into scale)

Fig. 3: Room temperature XRD spectra of a single free-standing ZnO microrib-
bon grown by the carbothermal reduction method

Fig. 4: Room temperature wide scan PL spectra of a single free-standing ZnO
270 microribbon grown by the carbothermal reduction method

Fig. 5: Room temperature PL emission images of a single free-standing ZnO
microribbon grown by the carbothermal reduction method: (a) both UV and
visible emissions; (b) UV (300 to 400 nm) emission only; and, (c) visible (460
to 750 nm) emission only

275 Fig. 6: Streak camera images and temporal profiles of the UV emissions of ZnO
microstructures grown by the carbothermal reduction method (a and c) and of
bulk ZnO crystal (b and d)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6