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Photoluminescence investigations of bulk and microstructured ZnO crystals for scintillator applications

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Photoluminescence properties of bulk and microstructured ZnO crystals are investigated for potential scintillator applications. A bulk crystal is prepared by hydrothermal method, while hexagonal micron-sized crystals are prepared by aqueous chemical growth and carbothermal reduction methods. The bulk sample exhibits UV emission only, while the microstructured samples exhibit both UV and visible emissions. The ZnO microstructures have faster near-band edge emission lifetimes of 100 to 800 ps compared to 440 ps and 2 ns of bulk ZnO. No direct correlation between the defect-related emissions and the near-band edge emission has been observed. ZnO microstructures with fast luminescence lifetimes have promising applications as EUV lithography and XFELs scintillators.

Key words: ZnO, Oxides, Microstructures, Photoluminescence, Scintillators.

Introduction

The research attention on zinc oxide (ZnO) may be attributed to the increasing demand of optoelectronic technologies for fast and efficient photoluminescent materials. ZnO is a II-VI semiconductor compound with a 3.37 eV wide and direct band gap and a 60 meV exciton binding energy. The direct band gap leads to ultraviolet (UV) emission, while the large binding energy enables room temperature excitonic emission [1]. Among other candidate scintillator materials, ZnO is ideal because of its high quantum efficiency in the short wavelength region [2].

A ZnO single crystal grown by hydrothermal method has been previously reported to have excellent scintillation properties [3]. It exhibits a luminescence lifetime of about 1.0 ns which is faster compared to 50 ns of a conventional Ce : YAG scintillator [3-5]. A fast lifetime is important to characterize ultrafast light sources for extreme ultraviolet (EUV) lithography and to perform pump-and-probe experiments for X-ray free electron lasers (XFEL). Since ZnO can be synthesized through different techniques, it can be grown into structures of varying shapes and sizes [6-8]. Deviating from large bulk crystals, smaller-sized ZnO-based scintillators may hold a promise for future optoelectronic devices. In this work, we report the photoluminescence investigations of bulk and microstructured ZnO crystals for potential scintillator applications. A bulk ZnO crystal was grown by hydrothermal method, while microstructured ZnO crystals were synthesized by aqueous chemical growth and carbothermal reduction methods. Microstructured ZnO crystals exhibit luminescence lifetimes of about 100 ps, faster than the bulk crystal, which could lead to the development of next generation scintillator materials.

Methodology

Bulk and microstructured ZnO crystals were prepared using hydrothermal [2, 3], aqueous chemical growth (ACG) [9, 10], and carbothermal reduction methods [11, 12]. The bulk ZnO crystal was grown using the hydrothermal method. Sintered polycrystalline ZnO precursors were set inside a platinum (Pt) container with lithium hydroxide (LiOH) and potassium hydroxide (KOH) aqueous solutions. The Pt container was then placed inside a pressure-resistant autoclave and was heated at 300 to 400 °C at pressures of 80 to 100 MPa. On the other hand, a set of ZnO microstructures was grown using the ACG method. Equimolar solutions of zinc acetate dihydrate (Zn(CH₃COO) · 2H₂O) and hexamethylenetetramine ((CH₂)₆N₄) were mixed together in a beaker containing ultrasonically cleaned Si (100) substrates. The solution was then heated at 95 °C for 120 minutes in ambient pressure. The substrates were removed from the solution and were then washed and

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Fig. 1. SEM images of microstructured ZnO crystals grown by the (a) ACG and (b) carbothermal reduction methods.

air-dried before annealing at 500 °C for 20 minutes in ambient pressure. Moreover, another set of ZnO microstructures was grown using the carbothermal reduction method. Finely ground ZnO powder and activated charcoal were placed in a crucible, which was then covered with an ultrasonically cleaned Si (100) substrate. The crucible-substrate assembly was placed inside a muffle furnace and was heated at 950 °C for 30 minutes in ambient pressure. All as-prepared samples were investigated by X-ray diffraction spectroscopy. The bulk and microstructured ZnO crystals have reflections that match that of hexagonal wurtzite ZnO.

The optical properties of the bulk and microstructured ZnO crystals were studied using photoluminescence (PL) spectroscopy. The excitation source was a Ti:sapphire laser system operating at its third harmonics (3w, 290 nm) having 200 fs pulse duration, 1 kHz repetition rate, and 10 µJ pulse energy. The PL spectra were measured using a handheld spectrometer, while the PL lifetimes were measured using a standard spectrographcamera setup. For the spectral measurements, the sample emission was fiber fed to the spectrometer device. For the TRPL spectroscopy, the sample emission was focused to the entrance slit of the spectrograph (25 mm focal length, 600 gr/mm groove density) coupled to a streak camera and CCD camera. The TRPL system has a temporal response of 10 ps in the fastest scanning range. All measurements were done at room temperature.

Results and Discussions

Figure 1 shows the representative scanning electron microscopy (SEM) images of the microstructured ZnO crystals. Both ACG and carbothermal reduction methods produce hexagonal-faceted structures. Hexagonal rods with lengths from 3.54 to 6.49 μ m and diameters from 0.56 to 1.26 μ m are formed from the ACG method. The apothem (*a*) and side (*s*) lengths of these facets are approximately 153 and 187 nm, respectively. On the other hand, the carbothermal reduction method forms larger hexagonal-like structures with apothem and side

lengths of about 13.0 and 18.8 μ m, respectively, and lengths extending up to 50 μ m.

Figure 2 shows the wide scan PL spectra of the bulk and microstructured ZnO crystals. The bulk sample exhibits only a UV emission, while the microstructured samples exhibit both UV and visible emissions. The emission peak characteristics of each sample are summarized in Table 1. The microstructured ZnO crystals have UV peaks shifted to higher wavelengths (lower energies). The UV peak corresponds to the nearband edge emission of ZnO, and the visible peak corresponds to the defect-related emission [13, 14]. The carbothermal-grown sample has the most intense defect-related emission and least intense near-band edge emission.

Figure 3 shows the streak camera images and temporal profiles of the near-band edge emissions of the bulk and microstructured ZnO crystals. The temporal profiles are taken from a 25 nm spectral region around each sample's peak center. The decaying part of the curves are well-fitted to double exponential decay functions. The fast decay components are attributed to free excitons, while the slow decay components are



Fig. 2. Wide scan PL spectra of bulk and microstructured ZnO crystals prepared by hydrothermal, ACG, and carbothermal reduction methods.

Table 1. Emission peak centers, line widths (FWHM), and lifetimes of bulk and microstructured ZnO crystals prepared by hydrothermal, ACG, and carbothermal reduction methods.

Sample	Preparation Method	UV Emission Peak		Visible Emission Peak		Intensity	UV Emission Lifetimes	
		Center (nm)	Width (nm)	Center (nm)	Width (nm)	(I_{UV}/I_{VIS})	Fast (ps)	Slow (ps)
Bulk	Hydrothermal	380	14	_	_	_	440	2100
Micro structure	Aqueous Chemical Growth	384	18	616	180	0.39	30	100
Micro structure	Carbothermal Reduction	393	13	520	91	0.0047	100	800



Fig. 3. Streak camera images and temporal profiles of the near-band edge emissions of bulk and microstructured ZnO crystals prepared by hydrothermal (a and d), ACG (b and e), and carbothermal reduction (c and f) methods.

attributed to free and trapped carriers [15-17]. The decay times are also summarized in Table 1. The microstructured ZnO crystals grown by the ACG and the carbothermal methods have faster decay times of 30 and 100 ps and 100 and 800 ps, respectively, compared to the 440 ps and 2 ns of the bulk crystal.

Photoluminescence properties are likely affected by the size and structure of ZnO crystals. The near-band edge emission lifetimes of the ZnO microstructures are faster than that of the bulk sample. The size effect has no large contribution to the fast emission lifetime because the sample dimensions, greater than 150 nm, are larger than the exciton Bohr radius of ZnO (1.4 to 2.9 nm) [12, 18-20]. Moreover, the defect-related emissions observed from the PL spectra of the samples have no direct relationship with the near-band edge emission lifetimes. The carbothermal sample has intense defect-related emission, but its lifetimes are faster than the bulk crystal and longer than the ACG sample. It has also been pointed out that the decay lifetime has no obvious relationships with defect luminescence position and the UV to visible emission ratio [16, 21]. Comparing to the bulk sample, the microstructured samples have higher surface-to-volume ratio (hexagonal prism geometry) of approximately 10^7 and 10^4 for the ACG and carbothermal samples, respectively. With a high surface-to-volume ratio, non-radiative recombination possibly shortened the emission lifetime with the activation of radiation centers at room temperature [16, 18, 22]. The fast near-band edge luminescence lifetime is highly attributed to the effective non-radiative recombination.

Conclusions

We presented and compared the photoluminescence properties of bulk and microstructured ZnO crystals for potential scintillator applications. The bulk and microstructured crystals were successfully fabricated using hydrothermal, ACG, and carbothermal reduction methods. Hexagonal-like structures formed from the carbothermal method had larger facets than the hexagonal microrods from the ACG method. The bulk ZnO exhibited UV emission only, while the microstructured samples exhibited both UV and visible emissions. The microstructured ZnO crystals have fast sub-picosecond near-band edge (UV) emission lifetimes compared to the 440 ps and 2 ns for a bulk crystal. A direct relationship between the defect-related emissions and the near-band edge emission lifetimes was not observed. The fast and improved luminescence lifetimes of microstructured ZnO crystals nevertheless lead to promising scintillator applications for EUV lithography and XFELs.

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