Intense and fast UV emitting ZnO microrods fabricated by low temperature aqueous chemical growth method

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Abstract

Intense and fast ultraviolet (UV) emitting zinc oxide (ZnO) microrods are successfully fabricated by low temperature aqueous chemical growth (ACG) method. Uniform and hexagonal microrods of varying dimensions are synthesized using different zinc acetate dihydrate (ZnAc) and hexamethylenetetramine (HMTA) molar concentration ratios. Although exhibiting broad orange emissions, the microrods have intense UV emissions with lifetimes as fast as 30 to 40 ps. Analyses show that there is no definite correlation between the microrod dimensions and the optical emissions. Nevertheless, with the ease on the microcrystal fabrication, these ZnO microrods with intense and fast UV emissions have potential use for future scintillator applications.

Keywords: ZnO, oxides, solution growth, photoluminescence, scintillator materials

1. Introduction

With its excellent optical properties, zinc oxide (ZnO) is one of the most advanced materials that can be utilized for short wavelength emitters, light emitting diodes (LEDs), piezoelectric devices, among others [1-3]. Its wide and direct band gap of 3.3 eV (~ 380 nm) corresponds to an ultraviolet (UV) emission, while its large exciton binding energy of 60 meV enables efficient excitonic emission at room and even higher temperatures [4-6]. With regards to scintillator applications, a bulk ZnO single crystal has been reported to exhibit fast emission lifetime of about 1.0 ns regardless of the incident excitation [7]. The lifetimes can be improved through intentional doping with the introduction of additional quenching channels [8-11] or through the use of nanostructures with enhanced oscillator strengths [12].

Different fabrication methods are now implemented to produce a wide variety of ZnO micro/nanostructures. One of the promising techniques is aqueous chemical growth (ACG), which is often referred to hydrothermal or solution growth method. Using few table top equipment, ZnO micro/nanocrystals can be easily prepared in a solution at temperatures less than 900 °C and at ambient atmosphere. With this synthesis technique, the need for sophisticated facilities such as those required for vacuum environments [13] and high temperature conditions [14, 15] can be transcended.

In this work, we report the successful fabrication of intense and fast UV emitting ZnO microrods by low temperature ACG method. The sizes of the grown microrods vary

with the precursor concentration ratios. The microrods also exhibit intense UV emission as fast as 30 to 40 ps. These optical emission properties, however, have no definite dependence on the microrod dimensions. Having a simple and controllable growth procedure, these uniform and hexagonal ZnO microrods with intense and fast UV emission will lead to the accelerated development of new scintillator devices.

2. Experimental

Different ZnO samples were prepared by the ACG method similar to Refs. 16, 17, and 18. Commercially available analytical grade zinc acetate dihydrate (99.5%, $\text{Zn}(\text{CH}_3\text{COO})\cdot 2\text{H}_2\text{O}$ or ZnAc) and hexamethylenetetramine (99.0%, $\text{C}_6\text{H}_{12}\text{N}_4$ or HMTA) were used without further purification. Aqueous molar solutions of both ZnAc and HMTA were prepared and were mixed together with different molar concentration ratios of 2:1, 1:1, and 1:2, respectively. The mixed ZnAc and HMTA solution was poured into a glass beaker containing ultrasonically cleaned (100) silicon (Si) substrates. The solution was subsequently heated at 95 °C for 120 min in ambient pressure. After heating, the substrates were removed from the solution and were washed with distilled water (H_2O) to remove unwanted residues. The samples were air-dried and then annealed at 500 °C for 20 min in ambient air to ensure complete ZnAc decomposition and to obtain samples with better crystallinity [19-21].

The ZnO samples fabricated by the ACG method were analyzed using a

high-resolution X-ray diffractometer (Bede, D3 XRD) and a field-emission scanning electron microscope (Phillips, XL30 SEM). The optical properties of the samples, on the other hand, were investigated using photoluminescence (PL) spectroscopy. A Ti:sapphire laser system (Spectra-Physics Lasers, Tsunami 3941-M1S and Spitfire) was used as the excitation source. After frequency tripling (3ω), the laser excitation had an output wavelength of 290 nm with 100 fs pulse duration and 1 kHz repetition rate. In measuring the PL spectra, the sample emission was collected and was fiber-fed to a handheld spectrometer (StellarNet, BLUE-Wave UVNb-50). Afterwards, the sample emission was focused on the entrance slit of a standard spectrograph-camera setup to measure the emission lifetimes. The time-resolved PL (TRPL) setup was comprised of a spectrograph (CHROMEX, Imaging Spectrograph 250is) coupled to a streak camera (Hamamatsu Photonics, C4742-95) and a charge-coupled device (CCD) camera (Hamamatsu Photonics, C1587). This TRPL system has a temporal response of 10 ps in its fastest scanning range. All of the measurements were done at room temperature and ambient conditions.

3. Results and discussions

The representative X-ray diffraction (XRD) spectra of the ZnO samples fabricated by the ACG method using different molar concentration ratios are shown in Fig. 1. All peaks can be indexed to hexagonal wurtzite ZnO [22]. The peaks correspond to the $(10\bar{1}0)$, $(10\bar{1}1)$,

(11 $\bar{2}$ 0), and (20 $\bar{2}$ 0) ZnO reflections. Moreover, the typical SEM images of the fabricated ZnO samples are shown in Fig. 2. Uniform rod-shaped structures with hexagonal facets are visible on the substrate surface. From different sample SEM images, the rod dimensions, surface-to-volume ratio, and density per 100 μm^2 substrate area are investigated and are summarized in Table 1. The sample prepared by 1:1 ZnAc and HMTA molar concentration ratio yields the smallest ZnO microrods with 3.40 μm length and 0.52 μm width, thus having the highest surface-to-volume ratio of 9.51 and density of 27 microrods per 100 μm^2 . In contrast, the sample prepared by 1:2 ZnAc and HMTA molar concentration ratio has the largest ZnO microrods with 7.14 μm length and 1.56 μm width, therefore having the lowest surface-to-volume ratio of 2.41 and density of 6 microrods per 100 μm^2 .

The wide-scan PL spectra of the ZnO microrods fabricated by the ACG method using different molar concentration ratios are shown in Fig. 3. All samples exhibit sharp and intense UV emission along with a broad visible emission. The peak positions, spectral linewidths, and total integrated intensities of each emission band are determined by least square fitting of two exponentially modified Gaussian curves on each PL spectra. Table 2 summarizes the PL emission properties of the ZnO microrods fabricated using different concentration ratios. The UV emission located at 387 nm (3.20 eV) corresponds to the near-band-edge emission of ZnO [4]. Taking into account the spectrometer's 1 nm spectral resolution and the fitting deviation, the peak position and spectral linewidths (~ 18 nm) are

almost the same regardless of the ZnAc and HMTA molar concentration ratio. This UV emission is also slightly shifted to longer wavelengths (lower energies) compared with the usual ZnO near-band-edge emission peak of ~ 380 nm at room temperature. Many factors can contribute to the observed emission peak shifting. The room temperature near-band-edge PL emission of ZnO is composed of the relative contributions from the free-exciton recombination and its longitudinal-optical (LO) phonon replica [23]. The PL spectrum may be dominated by the phonon replicas with a maximum at the first LO phonon replica whose position and intensity depend on the growth conditions and on the defect concentration [23, 24]. Aside from the LO phonon replica contributions, the slight red-shift can also be attributed to the thermal effects caused by laser heating [25, 26], to stress or strain caused by the lattice mismatch with the Si substrate [27, 28], or to self-absorption and inhomogeneous broadening caused by defects [29]. On the other hand, the visible emission with peak around 618 nm (2.01 eV) corresponds to the defect-related emission [4, 30]. Although the UV emission is more intense in terms of peak intensity, the visible emission of the fabricated ZnO microrods is broader thus having higher total integrated intensity (area under the curve). ZnO samples commonly exhibit visible emissions due to the presence of intrinsic defects [30]. Similar luminescence in the orange wavelengths is also observed from ZnO films and nanostructures and is associated to the excess amount of oxygen (i.e. oxygen-rich sample) or oxygen interstitials [30-32]. Among all samples, the ZnO microrods prepared using 1:1 ZnAc

and HMTA molar concentration ratio has the least intense orange emission thereby having the highest UV to visible emission intensity ratio ($I_{387\text{nm}}/I_{618\text{nm}}$).

The streak camera images and temporal profiles of the UV emissions of the ZnO microrods fabricated by the ACG method using different concentration ratios are shown in Fig. 4. The temporal profiles are taken from a 25 nm spectral region around the 387 nm emission peak wavelength. Instead of the usual double exponential fitting, the decaying parts of these profiles fit well to single exponential decay functions. Single exponential fitting of emission lifetimes has also been previously reported for ZnO thin films [21, 33]. With the 10 ps resolution limit of the TRPL system and the fitting deviation, all samples have similar emission lifetimes of 30 to 40 ps. The lifetimes do not differ with the microrod dimensions and even with the visible emission intensities. Compared with bulk and undoped ZnO crystals with 1 ns lifetimes [7, 11, 34], the ZnO microrods prepared by the ACG method exhibit faster picosecond UV emission lifetimes. Fast lifetimes can be largely attributed to the effective nonradiative recombination with the activation of nonradiative centers at room temperature [21, 33, 35]. Although this is the case, the intense UV emission and the characteristic single exponential decay resulting in an absence of a secondary component both suggest a fast radiative recombination process [21].

Varying the concentration ratio of the ACG precursors at a given temperature and time indeed plays a role on the formation of crystalline ZnO microrods. Aside from serving as

115 a weak base and a pH buffer, HMTA coordinates and bridges two Zn^{2+} ions, originally from
116 the ZnAc, favoring the ZnO formation [36, 37]. Different ZnAc and HMTA molar
117 concentration ratio results in different ZnO microrod dimensions; however, the microrod
118 dimensions do not seem to affect the optical properties of the microstructures. A direct
119 correlation between microrod dimensions and emissions, i.e. the surface-to-volume ratio and
120 the UV and orange emission intensity ratio, has not been observed. This may be due to the
121 fact that the emission detection was done over an ensemble of microrods instead of a single
122 and freestanding microstructure. Spectroscopy and microscopy of a single ZnO microrod
123 should be done to observe a definite correlation. Further investigations on the relationships
124 among the ZnAc and HMTA concentration ratio, microrod sizes, and emission properties
125 from this specific type of samples are then anticipated in the future. But regardless of the
126 ZnAc and HMTA concentration and resulting microstructure dimensions, the ZnO microrods
127 fabricated by ACG method exhibit similar characteristic UV emissions. These uniform and
128 well-faceted ZnO microrods with intense and fast UV emissions are suitable for
129 optoelectronic applications. The ZnO microrods can be easily harvested, isolated, and
130 manipulated using various techniques [38, 39]. If these microrods will be used as scintillator
131 materials, the microrods could be arranged and would be wicked in plastic similar to what we
132 proposed for freestanding ZnO microribbons [40]. Utilizing refractive index matching and
133 optical waveguide properties, the proposed ZnO microstructure-based scintillator will

possibly have a flexible design, improved temporal resolution, and enhanced optical density.

4. Conclusions

Uniform and hexagonal-faceted ZnO microrods were successfully fabricated using low temperature ACG method. The length and widths of the microrods ranged from 3 to 7 μm and from 0.5 to 1.6 μm , respectively. The microstructure dimensions were found to vary with ZnAc and HMTA molar concentration ratios at a given temperature and time. Intense UV emissions along with weak and broad orange emissions were also observed from all of the samples. A definite relationship among the ZnAc and HMTA molar concentration ratio, microrod sizes, and emission properties has yet to be identified. But regardless of the precursors' concentration ratio, the microrod size, and the visible emission position and intensity, the ZnO microrods have intense and fast UV emissions of about 30 ps. Given that these well-faceted structures can be easily prepared, harvested, and isolated, the ZnO microrods fabricated by ACG method can be of great use to the development of a new wave of scintillator devices.

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Figure Captions

Fig. 1. XRD spectra of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Fig. 2. Typical SEM images of ZnO microrods fabricated by ACG method using (a) 2:1, (b) 1:1, and (c) 1:2 ZnAc and HMTA molar concentration ratios

Fig. 3. Room-temperature wide-scan PL spectra of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Fig. 4. Streak camera images and temporal profiles of the UV emissions of ZnO microrods fabricated by ACG method using (a and d) 2:1, (b and e) 1:1, and (c and f) 1:2 ZnAc and HMTA molar concentration ratios

Table Captions

Table 1. Dimensions of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Table 2. Room-temperature PL emission spectral linewidths, total integrated intensities, and lifetimes of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Table 1. Dimensions of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Concentration ratio		Average dimensions(μm)		Surface-to-	Density(per 100
ZnAc	HMTA	Length	Width	volume ratio	μm^2)
2	1	5.18 ± 0.86	0.82 ± 0.15	5.74	17 ± 3
1	1	3.40 ± 0.35	0.52 ± 0.10	9.51	27 ± 4
1	2	7.14 ± 1.37	1.56 ± 0.19	2.41	6 ± 1

Table 2. Room-temperature PL emission spectral linewidths, total integrated intensities, and lifetimes of ZnO microrods fabricated by ACG method using different ZnAc and HMTA molar concentration ratios

Concentration ratio		Spectral linewidth (nm)		Total integrated intensity (arb. units)			UV emission lifetime (ps)
ZnAc	HMTA	UV	Orange	UV	Orange	Ratio	
		(387 nm) emission	(618 nm) emission	(387 nm) emission	(618 nm) emission	(I_{387nm}/I_{618nm})	
2	1	17.6 ± 1.00	191 ± 1.00	1.54×10^5	7.03×10^5	0.218	30 ± 10
1	1	16.5 ± 1.00	183 ± 1.00	1.74×10^5	4.39×10^5	0.396	30 ± 10
1	2	19.1 ± 1.00	170 ± 1.00	2.15×10^5	6.96×10^5	0.308	40 ± 10

Figure 1

Figure 2

Figure 3

Figure 4