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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 hexamethelynetetramine (HMTA) molar concentration ratios. Although exhibiting broad orange emissions, the microrods have intense UV emissions with lifetimes as fast as 30–40 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.

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 emissions as fast as 30–40 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 emissions will lead to the accelerated development of new scintillator devices.

2. Experimental

Different ZnO samples were prepared by the ACG method similar to Refs. [16–18]. Commercially available analytical grade zinc acetate dihydrate (99.5%, $Zn(CH_3COO)\cdot 2H_2O$ or ZnAc) and hexamethylenetetramine (99.0%, $C_6H_{12}N_4$ 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. The mixed ZnAc and HMTA solution was poured into a glass beaker containing ultrasonically cleaned (1 0 0) silicon (Si) substrates. The solution was subsequently heated at 95 °C for 120 min in ambient pressure. After heating, the substrates were

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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 $(10\bar{1}0)$, $(10\bar{1}1)$, $(1\bar{1}20)$, 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

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

Concentration ratio		Average dimensions (μm)		Surface-to-volume ratio	Density (per 100 μm^2)
ZnAc	HMTA	Length	Width		
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

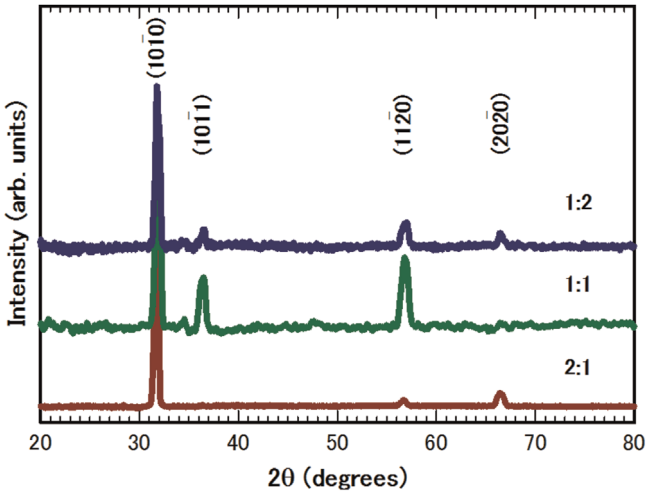

Fig. 1. XRD spectra of ZnO microrods fabricated by the ACG method using different ZnAc and HMTA molar concentration ratios.

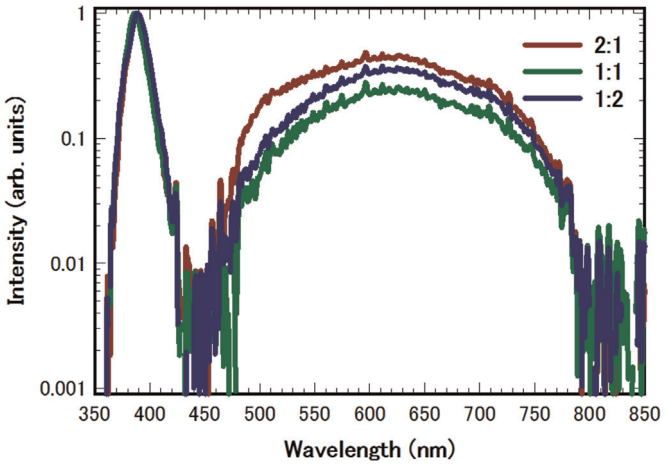

Fig. 3. Room-temperature wide-scan PL spectra of ZnO microrods fabricated by the ACG method using different ZnAc and HMTA molar concentration ratios.

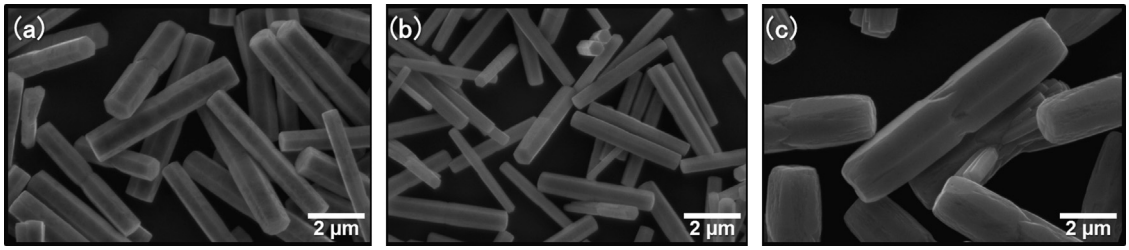

Fig. 2. Typical SEM images of ZnO microrods fabricated by the ACG method using (a) 2:1, (b) 1:1, and (c) 1:2 ZnAc and HMTA molar concentration ratios.