Synthesis and characterisation of zinc oxide tetrapod nanocrystals

Marcus C Newton, Steven Firth, Takashi Matsuura and Paul A Warburton

1 Department of Electronic and Electrical Engineering, University College London, Torrington Place, London WC1E 7JE, UK
2 Department of Chemistry, University College London, Gordon Street, London, WC1H 0AJ, UK

E-mail: M.Newton@ee.ucl.ac.uk

Abstract. Zinc oxide is an important group II-VI semiconductor material with optical properties that permit stable emission at room temperature. We report on the synthesis of highly uniform nanocrystalline ZnO tetrapod (ZnO-T) nanostructures through a modified chemical vapour transport process. These self assembled nanocrystals are characterised by four cylindrical arms with a hexagonal facet all of which are joined at a tetrahedral core. Studies are carried out on ZnO tetrapods using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), photoluminescence spectroscopy (PLS) and Raman measurements. We find a simple technique to quench visible emission found in ZnO tetrapods as grown. We also observe Raman active modes suggesting that nitrogen is incorporated within our samples.

1. Introduction
ZnO is a transparent electroconductive and piezoelectric material. Recently there has been much interest in the electronic and photonic properties of ZnO nanostructures as foreseeable applications include photo cells and laser diodes. A direct band gap of 3.37 eV and exciton binding energy of 60 meV allows for efficient UV stimulated emission at room temperature [1]. It may also be possible to observe coherent emission without population inversion induced by Bose condensation at the lower polariton band [2,3]. A substantial effort is therefore placed on utilising such properties within a new generation of short wavelength photonic devices. ZnO is nominally of n-type conductivity. A number of groups have attempted to create p-type ZnO through various doping techniques often with the hope of creating p-n junction devices [4-6]. The difficulty in creating high quality and reproducible p-type ZnO to date has strongly influenced any progress although successful attempts in doing so have been reported [7,8].

Here we focus on the characterization of ZnO tetrapod (ZnO-T) nanostructures grown via a chemical vapour transport (CVT) process. We use photoluminescence spectroscopy to study the various emission processes and further explore their origin using Raman spectroscopy.

2. Experiment
ZnO nanocrystals can be prepared through the evaporation of pure zinc powder in an oxygen atmosphere [9,10]. This method, however, provides little control over the size and morphology of the constituents. In an attempt to achieve such control, we carry out the synthesis of ZnO tetrapods in a
horizontal quartz tube furnace via a chemical vapour transport (CVT) process. The source material from which the tetrapods are synthesized consists of a 5:1 weight ratio mixture of zinc carbonate powder (ZnCO₃ • 2Zn(OH) • H₂O) to graphite powder (particle diameter ~20µm). The mixture is then placed in the central region of the furnace, within the quartz tube. A series of baffles were placed immediately downstream to assist the vapour mixing process. A bare Si <111> substrate is mounted vertically in the downstream region of the quartz tube, normal to the gas flow. Nitrogen carrier gas with an oxygen content of 0.5 – 5% is then introduced into the tube at a flow rate of 500 sccm while the temperature of the furnace is brought up to 900°C. During the reaction, a carbothermal reduction process is initiated causing supersaturated Zn vapour to be released for subsequent oxidation. After a 10 minute reaction period and gentle cooling of the system, a fluffy white layer of material appears on the surface of the substrate.

Growth produces were imaged as synthesized using a Carl Ziess 1540 XBeam field emission scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Photoluminescence spectroscopy (PLS) measurements were made using a 10 Watt HeCd laser (325 nm) as an excitation source, while conventional Raman spectroscopy was achieved using an Ar ion laser (515 nm). Moth techniques were made available using a Renishaw spectroscopy system.

3. Results

3.1. Structural Characterisation

A scanning electron microscope image of zinc oxide tetrapods (ZnO-T) is shown in figure 1. Under low oxygen partial pressures (<1%) the observed ZnO-T have thin arms less than 800nm in length where the diameter of each hexagonal facet is less than 200 nm. At an oxygen content of 5%, the diameter of each arm increases up to 400nm with arm lengths up to 5µm. All ZnO-T that were synthesised are hexagonally faceted with uniform arm lengths and diameter. This strongly suggests that each arm grows preferentially along the crystal c-axis in agreement with a number of previous studies and references therein [11,12].

![Figure 1. SEM image of typical ZnO tetrapod.](image1.png)

Energy dispersive spectroscopy (EDS) measurements on ZnO-T show closely matched Zn and O peaks indicating a 1:1 composition ratio. Additional peaks for N were not found. Figure 2 shows X-ray diffraction (XRD) patterns of ZnO-T shown in figure 1. In each case, the XRD data shows peaks that correspond to the ZnO wurtzite structure. There are no diffraction peaks indicating the presence of interstitial Zn or other structural impurities within our samples.

![Figure 2. X-ray diffraction from ZnO tetrapods.](image2.png)

3.2. Photoluminescence studies

Figures 3a and 3b show room temperature photoluminescence (PL) data from a ZnO tetrapod cluster and an isolated ZnO tetrapod respectively. Both graphs show a broad peak centred around 2.3 eV and a more narrow peak at 3.2 eV. Randomly orientated tetrapod clusters (fig. 3a) exhibit emission dominated by the broad peak at 2.3 eV. Although a number of authors have addressed the origin of
green and yellow emission within the literature, the processes involved had remained somewhat unclear [13,14].

Figure 3. Room temperature photoluminescence of ZnO-T cluster (a) and isolated ZnO-T (b).

Figure 4. Photoluminescence data of ZnO-T cluster deposited onto Si <111> substrate from methanol solution.

To further investigate the origin of green emission, ZnO-T were released from the substrate by sonication in methanol and subsequently dispersed onto a clean Si <111> substrate. It was found that ZnO-T remained dissolved within methanol but had a tendency to agglomerate after injection onto a surface. Figure 4 shows PLS data obtained from ZnO-T clusters injected onto a Si substrate. It is evident that the broad green emission peak measured on as grown ZnO-T is completely suppressed. Moreover, when these samples were placed in a vacuum and PLS measurements repeated the green emission peak did not return. This effect may be attributed to hydrogen electron passivation of radiative recombination states instigated by O-Zn defects [15]. It has been reported that coating ZnO-T with an n-hexyltrichlorosilane surfactant can have a similar effect [16]. Dissolving in methanol is, however, far less intrusive. We conclude that the observed green emission is directly related to the surface properties of these nanocrystals. The optical properties of ZnO tetrapods are therefore improved by sonication in methanol. Such a result is desirable for UV optical devices based on ZnO-T. Similar results were obtained for individual tetrapods. The broad peak centred at 2.3 eV found in figure 3 is therefore attributed to interstitial and complex oxygen defects residing at the surface of the structures, in agreement with previous work [17]. The large surface to volume ratio of ZnO-T clusters when compared to that of the bulk is likely to have caused a greater intensity of the peak at 2.3 over that at 3.2 eV.

When the excitation source is focused on an individual ZnO-T lying flat on the substrate surface (figure 3b), emission at 3.2 eV is greatly increased. This amplification is the result of resonant cavity effects coupled with waveguiding occurring along the vertical arm as each arm of a ZnO-T is well faceted with a natural cavity mirror. This also implies that some reflection occurs at the tetrapod core. Such effects result in emission at the ends of each arm which is more pronounced when pointed towards the detector. The incident light initiates standing waves within the medium thus amplifying the excitonic stimulated emission. This is particularly true when the resonant cavity is vertical to the substrate and normal to the excitation source also allowing the majority of the emission to point towards the detector.

From previously reported results on the PL spectrum of ZnO, narrow peaks caused by excitons bound to neutral donors (D0X) or acceptors (A0X), their excited two electron satellite (TES) states and longitudinal optical phonon replicas should be present within the range of 3.3 to 3.4 eV [18]. Although they are not visible in our measurements, it is likely that they have been overwhelmed by the peak at 3.2 eV previously attributed to donor acceptor pair transitions [19]. To gain further insight into these matters, we study the excitation power dependence of PLS data from a single ZnO-T.

Figure 5a shows PLS data for an isolated ZnO-T in which the power of the He-Cd (325 nm) laser excitation source is steadily increased from 0.05 to 10% of the total estimated as 10 W/cm². At lower excitation powers (0.05, 0.1, 0.5%), peaks centred on 3.3 eV are present and can be attributed to radiative recombination of electron-hole pairs near the band edge. As the power is further increased
excitons are no longer weakly coupled and a collective electron hole plasma (EHP) phase begins to form [20]. This effect is evident in the remaining emission peaks which have their maxima red shifted as far as 3.19 eV. Heating effects within the ZnO-T are also likely to cause a red shift of resonant modes within the structure due to an increased refractive index. At high exciton population, states within the k-space manifold become fully occupied and cannot be used to form excitons resulting in a reduction in intensity of peaks centred at 3.3 eV that were observed at low power excitation. This effect is more pronounced in low dimensional nanostructures where confinement effects further limit the number of available states near the band edge.

Figure 5a. Photoluminescence spectra of a single ZnO-T with varying excitation power.

Figure 5b. Red shift as a function of excitation power. Datapoints are taken from the maximum of each curve within figure 5a.

Figure 5b depicts the red shift as a function of the excitation power. As the excitation source power is increased above 1%, the band gap begins to reduce rapidly, possibly indicating a transition into the electron-hole plasma phase [20].

3.3. Raman Spectra
ZnO-T as grown on Si could not be used as it was found that the Raman spectra of Si and ZnO overlap significantly. ZnO tetrapods injected from methanol solution onto a SiO$_2$ substrate were therefore used for vibrational mode measurements. Samples were excited at 515 nm by an Ar ion laser.

Figure 6. Raman Spectra of isolated ZnO-T (a) and that of methanol (b).

Figure 7. Raman spectrum of isolated ZnO-T.

Figures 6a and 6b show the Raman spectra of an isolated ZnO-T and methanol respectively. Peaks characteristic of methanol and centred at 1029, 1450, 2836, 2944 cm$^{-1}$ are visible in the ZnO-T spectrum where the 1029 cm$^{-1}$ peak is most intense. Adsorption of methanol at the tetrapod surface adequately explains the presence of corresponding peaks between the two spectra.
Figure 7 shows an expanded view of the same Raman spectrum as in figure 6a at low wavenumber. When considering the Wurtzite structure of ZnO-T (space group P6_{3}mc), phonon modes E_{2} (low and high frequency), A_{1} (TO and LO) and E_{1} (TO and LO) are expected. The high frequency E_{2} mode is clearly visible at 437 cm\(^{-1}\) while the small peak at 330 cm\(^{-1}\) has been attributed to a second order E_{2} mode [21]. The asymmetric peak at 570 cm\(^{-1}\) can be decomposed into two Gaussian shaped curves at 570 and 643 cm\(^{-1}\), previously identified as nitrogen related vibrational modes [22,23,24]. The origin of the remaining peak centred at 791 cm\(^{-1}\) is unclear. The successful incorporation of nitrogen into ZnO is highly sought after as nitrogen is known to be a shallow acceptor and able to produce a material of p-type conductivity.

Summary
We have synthesised zinc oxide tetrapods in nitrogen using a chemical vapour transport (CVT) system and characterised them using a number of techniques. It is found that ZnO tetrapods dissolved in methanol solution no longer exhibit the green emission characteristic of as grown tetrapods. This finding has led us to clearly identify green emission as originating from Zn and O defects at the nanocrystal surface. It is also of technological importance to suppress unwanted emission within an optical device. We have also identified Raman active modes possibly indicating the absorption of nitrogen by our samples during synthesis. ZnO tetrapods remain promising and may become central to future UV optoelectronics device.

References
[1] Karpina V A et al. 2004 Cryst. Res. Technol. 39, 980
[2] Imamoglu A, Ram R J, Pau S and Yamamoto Y 1996 Phys. Rev. A 53, 4250
[3] Weisbuch C, Nishioka M, Ishikawa A and Arakawa Y 1992 Phys. Rev. Lett. 69, 3314
[4] Look D C and Claflin B 2004 Phys. Stat. Sol. (b) 241, 624
[5] Kim K, Kim H, Hwang D, Lim J and Park S 2003 Appl. Phys. Lett. 83, 63
[6] Park C H, S. B. Zhang S B and Wei S H 2002 Phys. Rev. B 66, 073202
[7] Tsukazaki A et al. 2005 Nature 4, 42
[8] Look D C, Claflin B, Alivov Y I and Park S J 2004 Phys. Stat. Sol. (a) 201, 2203
[9] Dai Y, Zhang Y, Li Q K Nan and C W 2002 Chem. Phys. Lett. 358, 83
[10] Yan H, He R, Pham J and Yang P D 2003 Adv. Mater. 15, 402
[11] Chen Z, Shan Z, Cao M, Lun L and Mao S 2004 Nanotechnology 15, 365
[12] Liu F, Cao P J, Zhang H R, Li J Q and Gao H J 2004 Nanotechnology 15, 949
[13] Reynolds D C, Look D C and Jogai B 2001 J. Appl. Phys. 89, 6189
[14] Reynolds D C, Look D C, Jogai B and Morkoç H 1997 solid state commun. 101, 643
[15] Ohashi N et al. 2003 J. Appl. Phys. 93, 6386
[16] Djurisicaronicacute A B et al. 2004 Adv. Func. Mater. 14, 856
[17] Lin B, Fu Z and Jia Y 2001 Appl. Phys. Lett. 79, 943
[18] Meyer B K et al. 2004 Phys. Stat. Sol. 241, 231
[19] Teke A et al. 2004 Phys. Rev. B 70, 195207
[20] Klingshirn C 2005 Semiconductor Optics (Berlin: Springer)
[21] Haboeck U, Hoffmann A, Thomsen C, Zeuner A and Meyer B K 2005 Phys. Stat. Sol. 242, R21
[22] Kaschner A et al. 2002 Appl. Phys. Lett. 80, 1909
[23] Wang Y G, Lau S P, Zhang X H, Lee H W, Hng H H and Tay B K 2003 J. Crystal Growth 252, 265