Supporting Information

Selective micro laser annealing for fluorescence tuning of carbon-incorporated zinc oxide nanowires arrays

Sing Teng Chua¹, Kim Yong Lim¹, Zheng Zhang, Chorng Haur Sow

Details of Experimental Methodology



Figure S1. Tube furnace set-up for CVD of C-doped ZnO NW arrays (not-to-scale).

1. Synthesis of C-ZnO nanowires

Prior to CVD, a silicon wafer was first coated with a 200 nm-thick ZnO seed layer using Denton Discovery-18 RF magnetron sputtering. As shown in Figure S1, a homogeneous mixture comprising ZnO (0.4 g) and carbon powder with equal molar ratio was placed at the closed end of the quartz tube (or the center of the sealed Carbolite 1200 series horizontal furnace), while a piece of ZnO-coated silicon substrate was positioned 15 cm away from the source. A combination of vacuum pumping and gas flow (99.5% Ar + 0.5% O_2) at 200 sccm maintained the system at 0.02 mbar. Temperature and carrier gas flow variation will giv rise to nanowires with different chemical composition. The tube was then heated at 930°C for 5 hours and left for cooling overnight. The substrate temperature was approximately 670°C during growth.

2. Focused laser beam modification

A laser beam (λ = 405nm) emitted from a diode laser with an adjustable power output (VD-IIA DPSS Laser Driver) was directed through a series of mirrors into an upright Olympus BX51 optical microscope and then towards an 50X objective lens via a beam splitter within the microscope. The focused beam spot size is estimated to be ~ 5 µm in diameter. A computer-controlled motorised sample stage (PI-micos) was used to move the sample with controllable speed. Various micropatterns could then be created in a programmable manner. A charge coupled device (CCD) captured the images of laser beam scanning process, which were then displayed through a television monitor. Most notably in the set-up is a housing chamber where laser treatment of the C-ZnO NWs can be carried out in a controlled environment. To control the environment of laser modification process, the sample was sealed within a small chamber with an elastomer O-ring and a glass lid on top. The chamber could be evacuated with a rotary pump to the order of 10⁻² Torr or purged with Helium gas and maintained at 10 torr. To minimise residual air within the chamber, the vacuum pumping took at least two hours until the pressure reading stabilised.

3. Material characterisation

3.1 Fluorescence Microscopy

An Olympus BX51 Fluorescence Upright Microscope couple with a mercury light source (U-HGLGPS) was used for optical (OM) and fluorescence microscopic (FM) imaging and spectral analysis. FM was also performed at different temperature, ranging from room temperature to -194°C (close to the boiling point of liquid nitrogen) at intervals of 50°C.

3.2 Photoluminescence and Raman Spectroscopy

Renishaw inVia micro-photoluminescence (PL) measurement was performed with an excitation source at 325 nm from a He-Cd laser. The reading was taken at temperatures ranging from -194°C to 50°C.

3.3 X-ray photoelectron spectroscopy (XPS)

XPS was conducted using Thermo Fisher Scientific Theta Probe XPS with an Al K α X-ray of 1486.7 eV on a 1 mm² square pattern which was created on each sample with laser rastering.

3.4 Scanning Electron Microscopy

JEOL JSM-6700F field-emission scanning electron microscope (SEM) was used to study the morphology and size of C-ZnO NWs before and after laser modification. Secondary electron imaging mode was applied throughout the work.

3.5 High-resolution Transmission Electron Microscopy

The samples were observed with JEOL JEM-2010F transmission electron microscope (TEM) under both bright field (BF) imaging and selected area electron diffraction (SAED) modes.

3.6 Plasma Etching

Plasma etching of C-ZnO NW arrays was performed with a SPI plasma etcher with 15sccm of argon gas flow at a power of 30 W for 30 seconds.



Figure S2. (a) Normalised; (b) Room temperature fluorescence spectra obtained from the C-ZnO NW arrays modified with laser power of 50 mW at a scanning speed of 450 μ m/s, with discontinuities between 560 and 580 nm due to instrumental errors.



Figure S3. Size distribution histogram of C-ZnO nanowires before and after exposure to focused CW laser in ambient air, Helium gas, and low pressure respectively, based on SEM.

Plasma etching of NWs

Region A demonstrated a surge in the PL exciton-to-defect ratio without peak position shift after laser modification in ambient air, concurring with the hypothesis that the inner core has fewer defects than the outer surface. While the pristine region also displayed a significant increase in the areal ratio of excitonic emission to defect-induced emission due to the removal of carbon defect complexes near the surface¹, the suppression of green emission without peak position shift in region A rules out the argument that the visible emission is a mere result of surface bound defects. Hence, the segregation of carbon from its defect complexes occurs more extensively throughout the NWs in region A. Otherwise, a red-shift of visible broad emission would also be observed in region A following a straightforward plasma etching of the NW surfaces. Similarly, plasma etching of regions H and L boosted the PL exciton-to-defect ratio, accompanied by a redshift of the broad defect emission to coincide with the normalised PL spectrum of pristine C-ZnO NWs after plasma etching. This demonstrates that the segregation phenomenon is less extensive in the NWs of regions H and L. The explanation is illustrated in Figure 8 in the main text, whereby plasma etching exposed the non-modified region. Assuming that the etched layer thicknesses are similar throughout the regions of the sample, the laser-modified layer was removed partially in region A and entirely removed in H or L.

Table S1. Ratio of area under the excitonic peak to defect emission peak in regions P, A, H and L before and after plasma etching in argon gas.

Region	Areal ratio (Exciton-defect)
Pristine (P)	0.29
Pristine after plasma etching	1.30
Ambient (A)	0.08
Ambient after plasma etching	0.37
Helium (H)	0.13
Helium after plasma etching	1.09
Low pressure (L)	0.20
Low pressure after plasma etching	1.20

Thermal effect on fluorescence properties



Figure S4. FM images of C-ZnO NW arrays modified in ambient air captured at different temperatures under UV illumination

The fluorescence properties of C-ZnO were studied at low temperatures before and after laser modification. These spectra were obtained via the fluorescence microscopy at temperatures ranging from 25 °C to -194°C. Thermal quenching of luminescence due to the loss of carrier trapping ability to thermal vibration of defect states is common in many materials². Notably, the extent of this change in the emission intensity was greater in the orange region (~600-700 nm) than that in the green region (~450-600 nm), visibly observed from Figure S4 that the UV-illuminated C-ZnO NWs became brighter and more yellowish as the temperature decreased. Similar results are also reflected through the PL spectroscopy, whereby the intensity is enhanced with decreasing temperature, more prominently in the orange region, as illustrated in Figure S5ai and S5bi.



Figure S5. Normalised PL spectra obtained at temperatures between 30°C and -194°C from the (a) C-ZnO NW pristine arrays and (b) after laser modification in the ambient air

As the temperature decreases, the near-band-edge (NBE) emission can be deconvoluted into more multiple peaks with narrower peak width as shown in Figure S6. At -194°C, the peaks could be resolved into the ground state free exciton (FX)³ at 3.37 eV, donor bound exciton (D ⁰X) between 3.35 eV and 3.36 eV, as well as the first (FX-1LO), second (FX-2LO) and third (FX-3LO) order longitudinal optical phonon replica of free exciton at about 3.31 eV, 3.23 eV and 3.16 eV respectively⁴. The FX emission peak is also emerging in the ambient-modified region, as indicated by a slight bump at 3.37 eV. Apart from the FX peak, all other emissions have similar peak position and relative intensity after normalisation with respect to the maximum peak intensity, throughout all three regions. The separation between FX and D⁰X is about 13.7 meV, in agreement with the reported value of 14 meV which is the binding energy of the donor-bound exciton⁵. The even separation of 75 meV between the adjacent LO peaks agrees with the longitudinal optical phonons which propagate along and perpendicular to the ZnO C-axis with energies of 71.46 and 72.95 meV respectively⁶. Other characteristic peaks such as the two-electron transitions, donor-acceptor pair and LO-phonon replica of D⁰X are generally observable below 80K⁷, which is the minimum temperature studied in this paper. The enhancement of FX-D ⁰X ratio with laser modification concurs with the hypothesis of lattice segregation. After laser cutting, the core of C-ZnO nanowire is rendered less defective with lower concentration of carbon complexes, thus giving rise to higher proportion of free excitons relative to the defect-bound excitons. On the other hand, the pristine C-ZnO nanowires contain a uniform distribution of carbon-induced lattice defects.



Figure S6. NBE emission PL spectra obtained at -194°C



Figure S7. PL spectra obtained at room temperature from C-ZnO NW arrays laser-modified in ambient air with varying laser power.



Figure S8. Variation of (a) exciton to defect emission ratio, (b) maximum defect intensity in the green region with laser power and rastering speed.



Figure S9. SEM images of C-ZnO NWs modified with different laser power at different laser speed in ambient air and helium gas.

1. K. Y. Lim, J. J. Linghu, X. Chi, K. D. Yuan, K. M. Hew, M. R. Zheng, M. Yang, E. S. Tok, A. Rusydi, X. J. Yu, W. Chen, Y. P. Feng and C. H. Sow, *Adv. Opt. Mater.*, 2017, **5**, 1700381.

- 2. G. Walker, O. E. Abumere and B. Kamaluddin, *Mineralogical Magazine*, 2018, **53**, 201-211.
- 3. S. Kentaro, N. Kohei, F. Atsuhiko, I. Tetsuo and O. Tatsuo, *Japanese Journal of Applied Physics*, 2009, **48**, 085001.
- 4. B. Wei, Y. Ji, X.-D. Han, Z. Zhang and J. Zou, *Opt. Express*, 2014, **22**, 4000-4005.
- 5. D. W. Hamby, D. A. Lucca, M. J. Klopfstein and G. Cantwell, *J. Appl. Phys.*, 2003, **93**, 3214-3217.
- 6. O. Madelung, *Semiconductors Basic Data*, 1996.
- 7. C. Klingshirn, *ChemPhysChem*, 2007, **8**, 782-803.