Electronic Supplementary Information

Temperature Dependent of Photoluminescence Studies in ZnO Microrods by FZ Method

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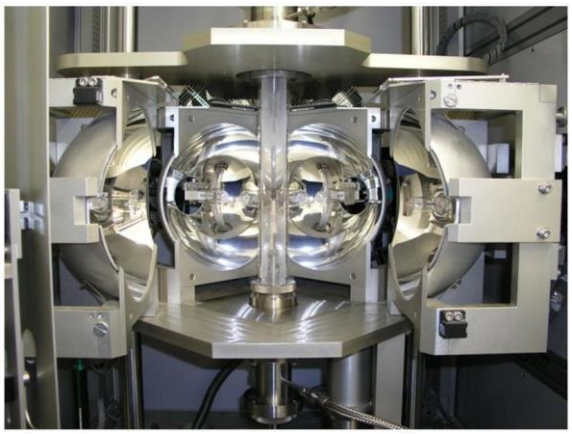

Figure S1: Photograph of a commercial optical floating zone furnace (image furnace): model FZ-T-10000-H-VI-VP, CSI Japan.

Figure S2: The growth morphology image of the ZnO microrods observed in the FZ furnace.

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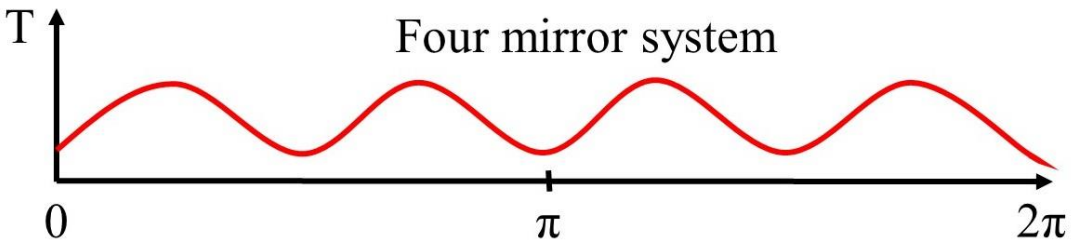


Figure S3: Temperature profile for four mirror used in the FZ furnace around the horizontal plane. The similar temperature profile can be found from the website: http://www.crystalsys.co.jp/english/product02_e.html or http://scidre.de/index.php?id=12.

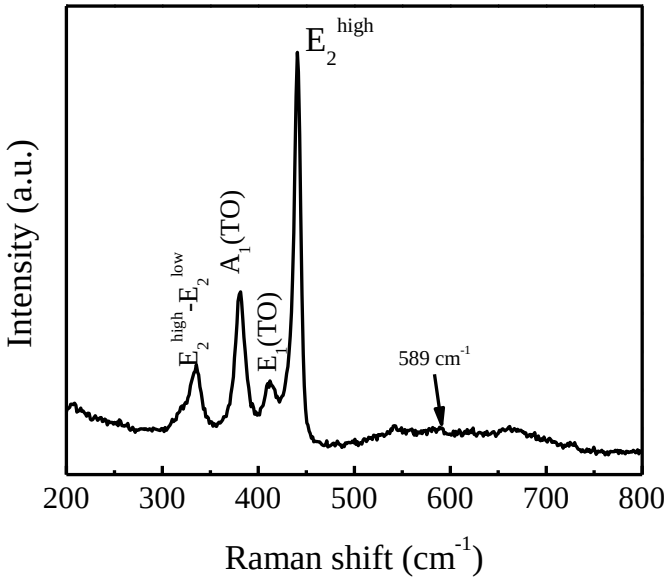


Figure S4: Raman spectrum of the ZnO microrods at room temperature

As shown in S4, four peaks at 331, 383, 412 and 436 cm^{-1} were observed. The peak at 436 cm^{-1} is attributed to ZnO non-polar optical phonons of the E_2^{high} mode, the peak at 412 cm^{-1}, 383 cm^{-1} and 331 cm^{-1} corresponds to E_1(TO) , A_1(TO) and E_2^{high}-E_2^{low} symmetry, respectively.[1-3] The peak at 589 cm^{-1} is related to local vibrational modes associated with intrinsic lattice defects.[3] This peak is weak in intensity which is consistent with the presence of low defect levels in the ZnO microrods.

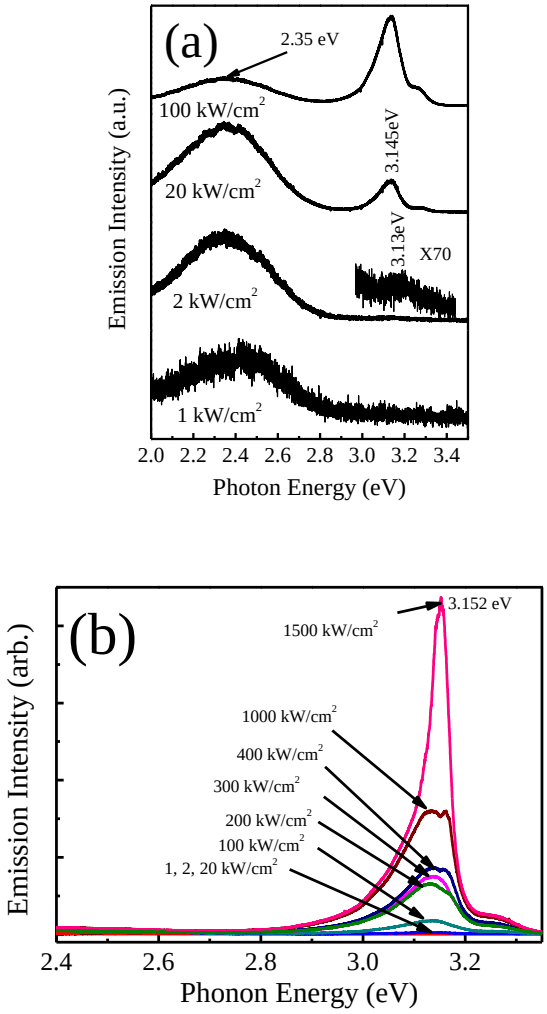
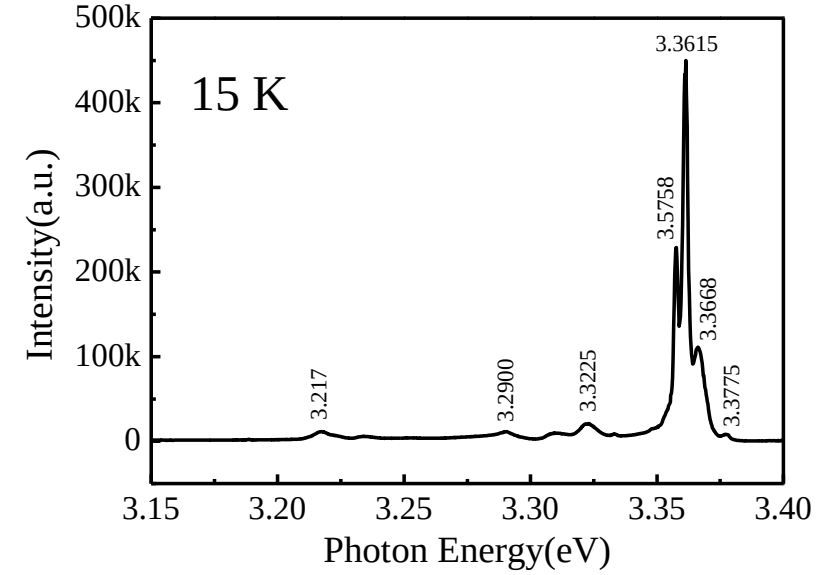
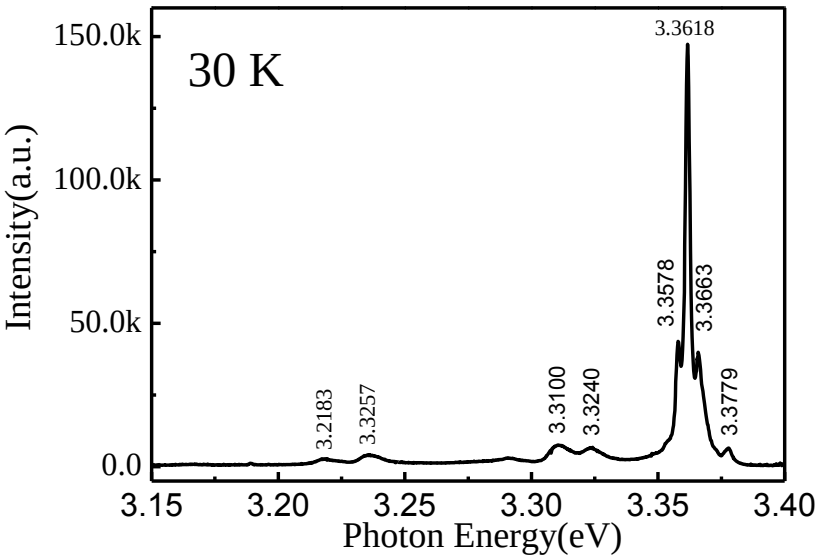
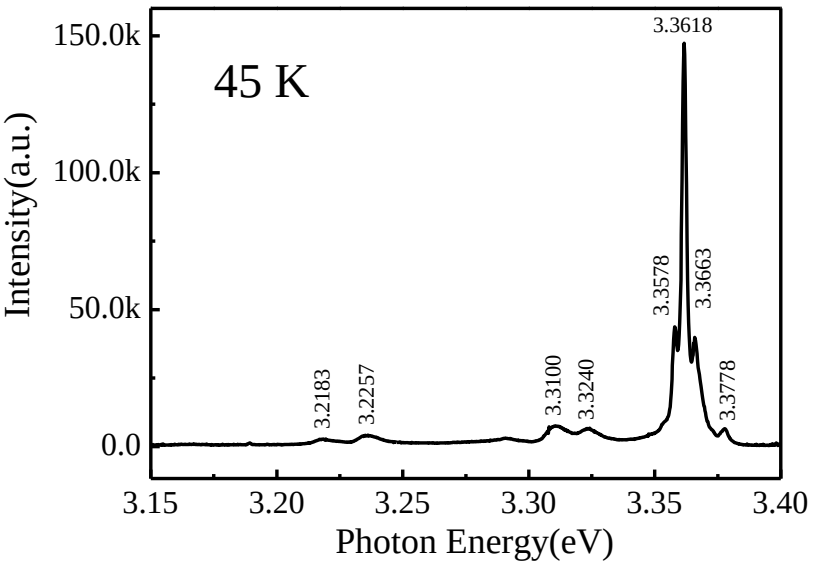


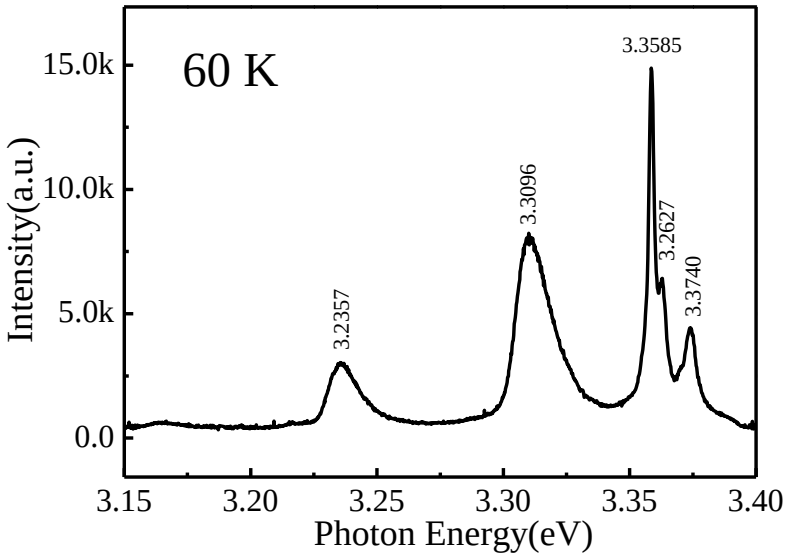
Figure S5: (a) Room temperature PL spectra of as prepared ZnO microrods recorded at different excitation intensities from 1 kW/cm^2 to 100 kW/cm^2. (b) Luminescence spectra as the as a function of excitation intensity is increased from power density.

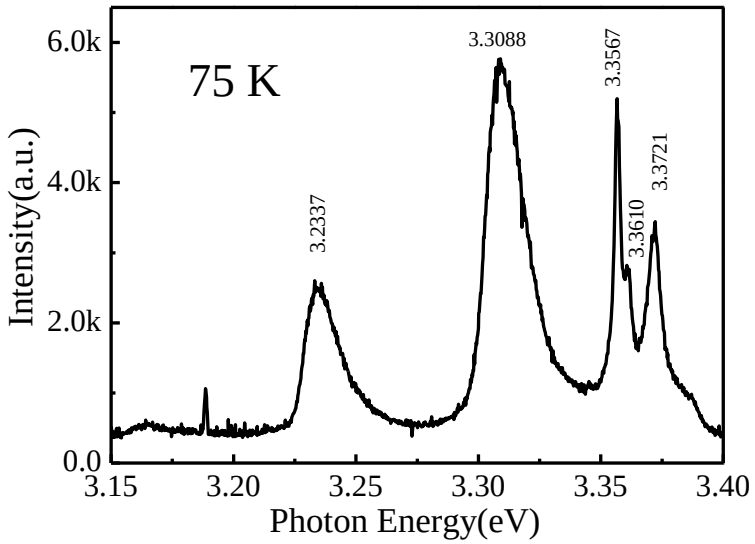
S5(a) shows the evolution of the band edge at room temperature as the excitation intensity is increased from 1 kW/cm^2 to 100 kW/cm^2. At low excitation intensities (1 kW/cm^2), a visible green fluorescence emission at 2.35 eV (527 nm) was observed due to the presence of ZnO defects.[4, 5] As the excitation intensity reaches 2 kW/cm^2, a second peak emerges at 3.145 eV (394 nm) which is due to the recombination of the free excitons of ZnO. At excitation intensities above 100 kW/cm^2, the free excitons peak dominates at PL spectra, as shown in S 5(b).

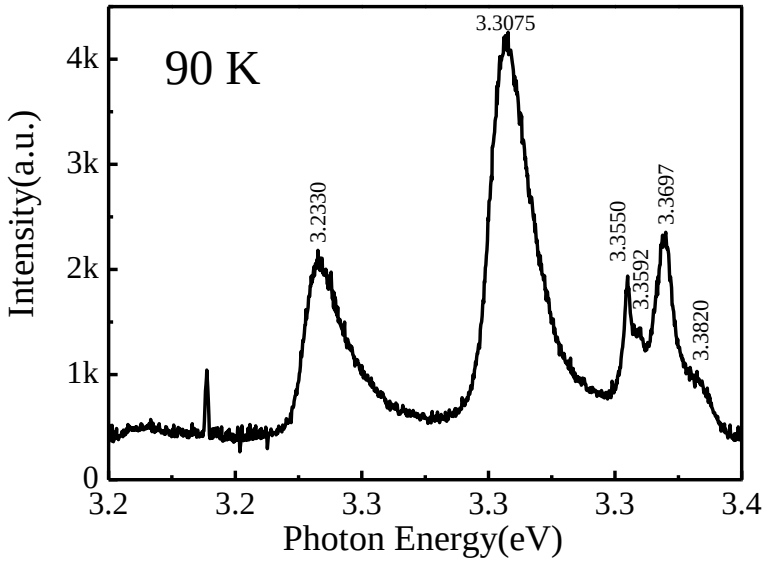

15 K
Intensity(a.u.)
Photon Energy(eV)
500k
400k
300k
200k
100k
0
3.15
3.20
3.25
3.30
3.35
3.40
3.217
3.2900
3.3225
3.5758
3.3615
3.3668
3.3775

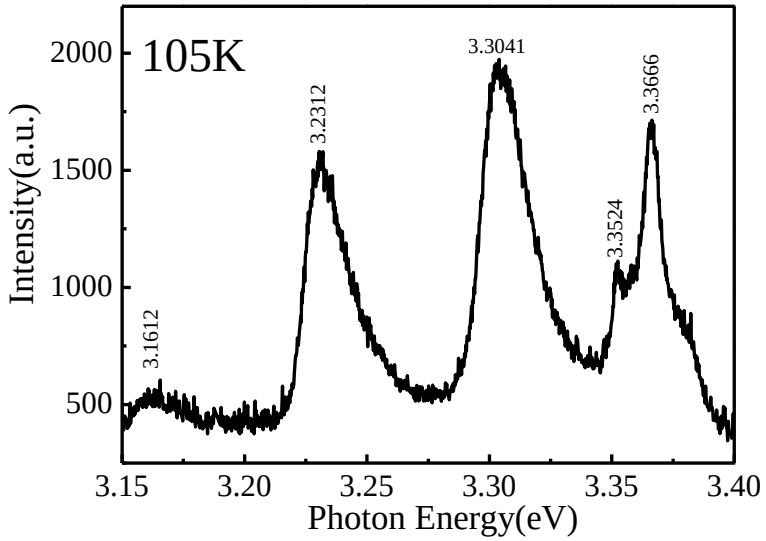

30 K
Intensity(a.u.)
Photon Energy(eV)
150.0k
100.0k
50.0k
0.0
3.15
3.20
3.25
3.30
3.35
3.40
3.2183
3.3257
3.3100
3.3240
3.3578
3.3618
3.3663
3.3779

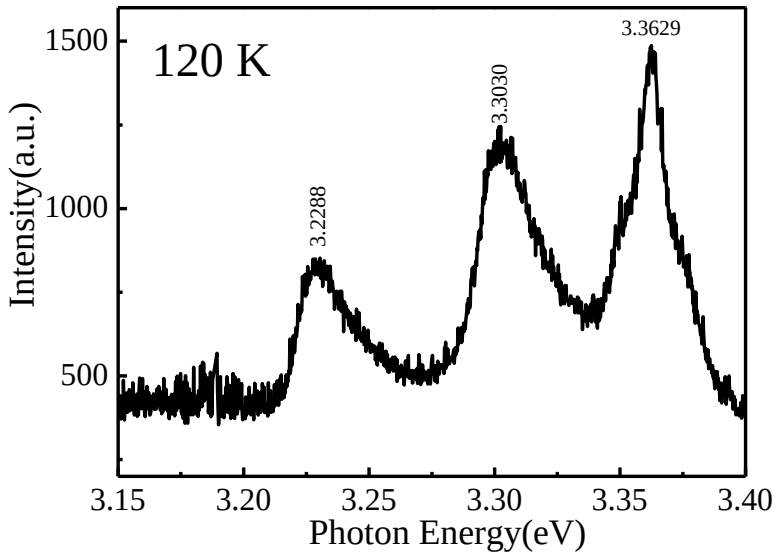

45 K
Intensity(a.u.)
Photon Energy(eV)
150.0k
100.0k
50.0k
0.0
3.15
3.20
3.25
3.30
3.35
3.40
3.2183
3.2257
3.3100
3.3240
3.3578
3.3618
3.3663
3.3778

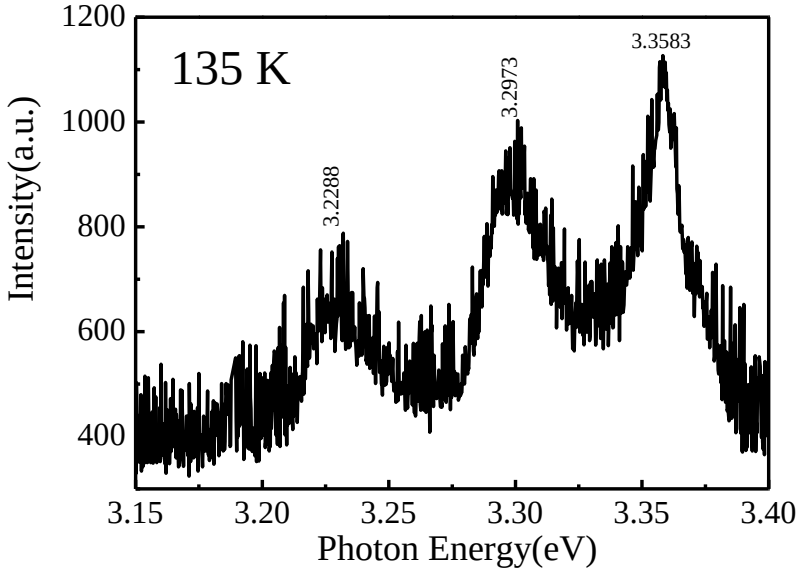

60 K
Intensity(a.u.)
Photon Energy(eV)
15.0k
10.0k
5.0k
0.0
3.15
3.20
3.25
3.30
3.35
3.40
3.2357
3.3096
3.3585
3.2627
3.3740

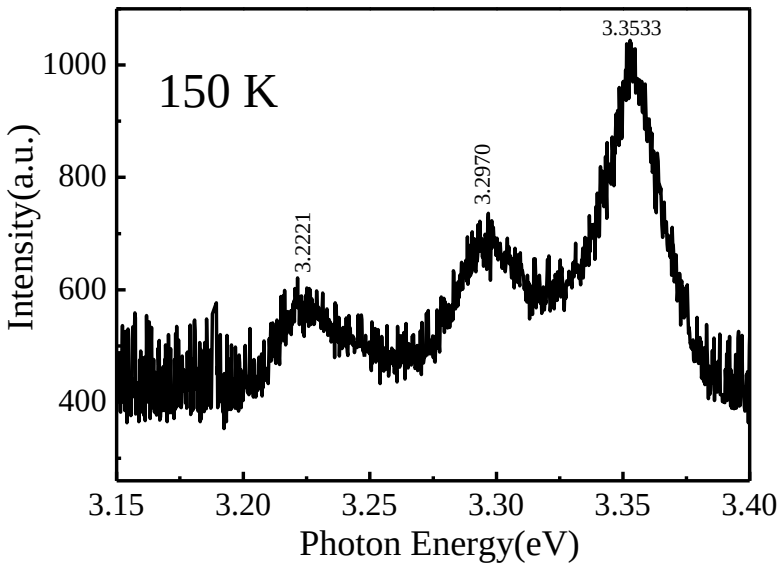

75 K
Intensity(a.u.)
Photon Energy(eV)
6.0k
4.0k
2.0k
0.0
3.15
3.20
3.25
3.30
3.35
3.40
3.2337
3.3088
3.3567
3.3610
3.3721


90 K
Intensity(a.u.)
Photon Energy(eV)
4k
3k
2k
1k
0
3.2
3.2
3.3
3.3
3.3
3.4
3.2330
3.3075
3.3550
3.3592
3.3697
3.3820


105K
3.1612
3.2312
3.3041
3.3524
3.3666
Intensity(a.u.)
Photon Energy(eV)


120 K
3.2288
3.3030
3.3629
Intensity(a.u.)
Photon Energy(eV)


135 K
3.2288
3.2973
3.3583
Intensity(a.u.)
Photon Energy(eV)



S6 PL spectra at different temperatures

Reference

1. Arguello, C.A., D.L. Rousseau, and S.P.S. Porto, *First-Order Raman Effect in Wurtzite-Type Crystals.* Physical Review, 1969. **181**(3): p. 1351.
2. Serrano, J., et al., *Pressure dependence of the lattice dynamics of ZnO: An ab initio approach.* Physical Review B, 2004. **69**(9): p. 094306.
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4. Xu, X., et al., *Evolutions of defects and blue-green emissions in ZnO microwhiskers fabricated by vapor-phase transport.* Journal of Physics and Chemistry of Solids, 2012. **73**(7): p. 858-862.
5. Djurisic, A.B., et al., *Defect emissions in ZnO nanostructures.* Nanotechnology, 2007. **18**(9).