

Effects of Lithium Doping and Post-processing on the Cathodoluminescence of Zinc Oxide Nanoparticles

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Zinc oxide (ZnO) is a wide band-gap (3.37 eV) semiconductor with a large exciton binding energy of 60 meV. Because of these properties, ZnO is a good candidate for a wide range of applications, including varistors, phosphors as well as a large range of optical devices. Although the optical properties of ZnO have been extensively studied, there is still intensive debate as to the origin of a number of the luminescence centers observed.

In this study, ZnO nanoparticles were synthesized by mixing equal volumes of 0.05 M zinc chloride (ZnCl_2) in ethanol and 0.20 M sodium hydroxide (either 97+% or semiconductor grade) in ethanol, for six hours at room temperature. To make lithium (Li) doped ZnO, 10 mol% of LiCl was added to the ZnCl_2 solution and the molar concentration of ZnCl_2 was reduced accordingly. The resulting cloudy supernatant was then decanted, centrifuged, washed with double-distilled water followed by ethanol and then dried under vacuum. The resulting ZnO powders were identified as ZnO (synthesized with 97+% NaOH), HP ZnO (synthesized with semiconductor grade NaOH) and ZnO:Li (Li doped ZnO). The affect of hydrogen on the cathodoluminescence (CL) properties of both ZnO and HP ZnO was observed by annealing a portion of both these samples at 700°C for 10 minutes in an atmosphere of 5% H_2 / 95% Ar and subsequently performing CL measurements of annealed and un-annealed samples. To observe the affects of Li doping on the CL of ZnO, both unannealed and a portion of ZnO:Li annealed at 700°C for 10 minutes in an inert atmosphere of argon, were observed.

Cathodoluminescence spectra and images were collected in a LEO Supra 55VP SEM using a Gatan MonoCL2 system equipped with a Hamamatsu R2228 PMT. A liquid helium circulation cold finger was used to cool the samples to approximately 6 K (see figures for exact temperatures). As seen in Fig. 1, un-annealed ZnO and HP ZnO display a near band-edge (NBE) emission at 3.27 eV, which is greatly intensified after annealing in H_2 (Fig. 2). Fig. 2 also shows the emergence of an additional peak, to the right of the NBE which is attributed to the affects of hydrogen. It can be seen from Fig. 3, that this luminescence centre, at 373 nm, has a different spatial distribution to the NBE emission (377 nm) and the longitudinal optical (LO) phonon replicas (385 nm, 394 nm), which demonstrates that the emission at 373 nm can be attributed to a different recombination centre

The affect of Li doping on the luminescence of ZnO is of interest due to its use as a charge compensating ion when doping ZnO with tri-valent metal ions. Fig. 4 shows that Li doping results in a visible emission centered at 2.3 eV in the un-annealed sample, but that annealing in Ar greatly enhances the NBE emission, and the visible emission is now observed at 2.5 eV. Ultimately, controlling the size of these particles (Fig. 5) will enable greater control of their luminescence and optimize their properties for a particular application.

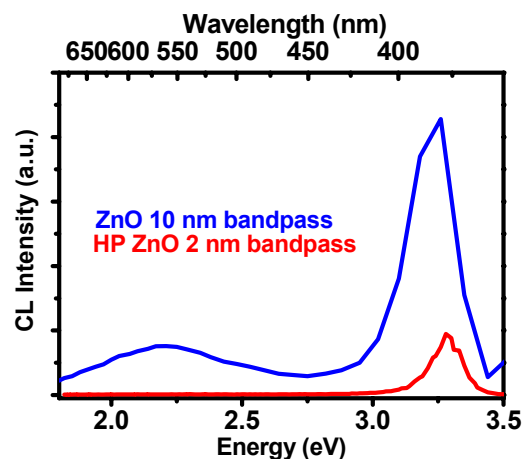


Fig. 1. CL spectra of un-annealed ZnO and HP ZnO (5 kV, 4.40 nA, 5 K)

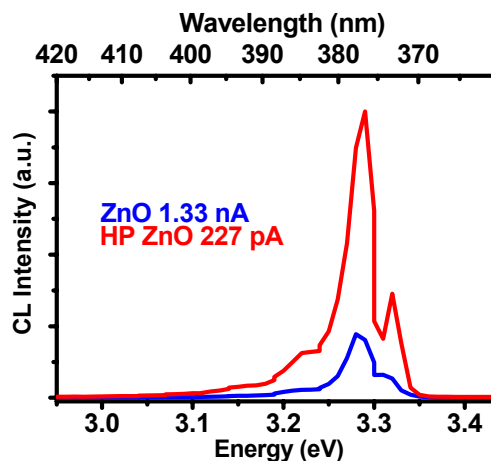


Fig. 2. CL spectra of H₂ annealed ZnO and HP ZnO (5 kV, 1 nm bandpass, 6 K)

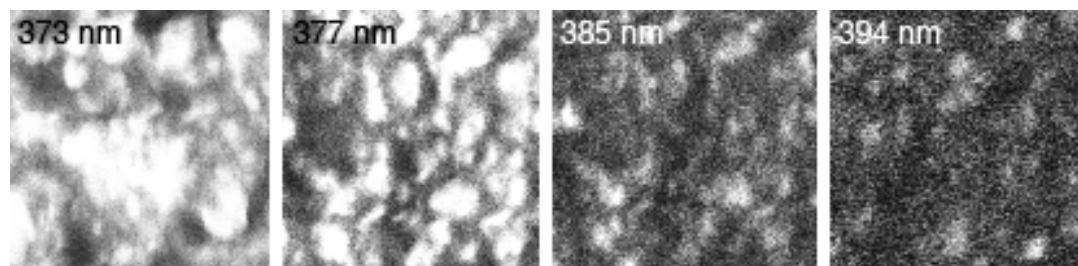


Fig. 3. Monochromatic CL images of HP ZnO, H₂ annealed (WOF = 2.3 μm, 5 kV, 227 pA, 1 nm bandpass, 5 K)

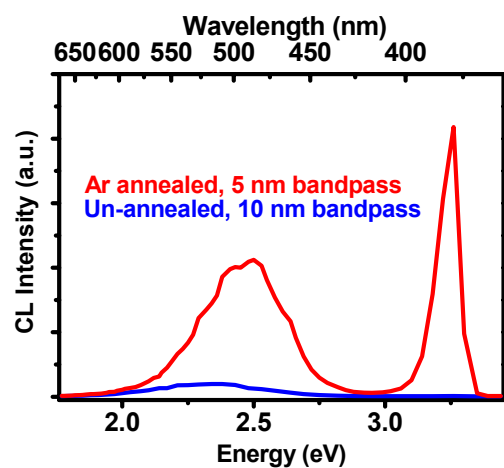


Fig. 4. CL spectra of un-annealed and Ar annealed ZnO:Li (5 kV, 4.40 nA, 4.6 K)

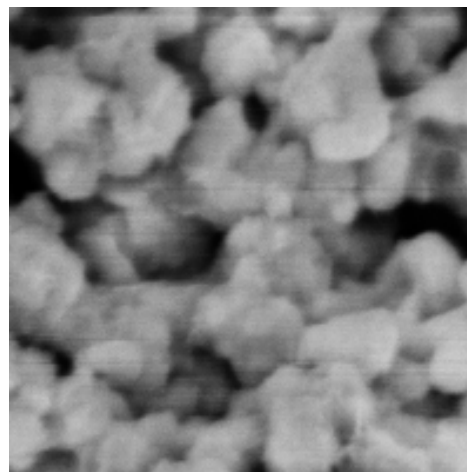


Fig. 5. Secondary electron image of un-annealed ZnO taken with in-lens detector (WOF = 2.2 μm, 5 kV)