

Electrochemical and hydrothermal synthesis of epitaxial arrays of doped ZnO nanowire emitters for light emitting diodes with tunable emission from near-UV to blue.

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Nanowires (NWs)-based light emitting diodes (LEDs) have drawn large interest due to many advantages compared to thin film based devices. Markedly improved performances are expected from nanostructured active layers for light emission due to efficient light extraction. Moreover, the use of wires avoids the presence of grain boundaries, it favors good interfaces and reduces non-radiative recombinations.

We have shown recently that high quality vertically aligned and arrayed ZnO nanowires/nanorods can be easily grown by solution-based techniques such as electrochemical and hydrothermal depositions.[1,2] Their principle consists in mixing a zinc salt with a hydroxide precursor which is released by an electrochemical reduction reaction or by thermal decomposition. In the case of electrodeposition, zinc ions and molecular oxygen are mixed in the deposition bath. O₂ is electrochemically reduced to produce OH⁻ and ZnO precipitates as NWs in a medium depleted in Zn(II). In the case of hydrothermal growth, zinc sulfate is mixed with ammonia and the solution mixture is rapidly heated at 90-95°C. The use of a single-crystal GaN substrate favors the heteronucleation of ZnO nanowires/nanorods. High quality ZnO structures have been obtained. These processes can be performed using p-type GaN single crystal substrates and give rise to n-ZnO NW/p-GaN heterostructures.[3-5] LEDs based on these structures emitted at room temperature a pure near-UV light centered at about 397 nm with no visible emission due to defects. The fabricated LEDs exhibited high brightness and low-threshold emission voltage. The emission arose from the ZnO structures and was directional, the strongest intensity being measured along the wire-axis direction because the wires acted as light waveguide.

We have also successfully prepared NWs doped at controlled level by adding the dopant salt in the deposition bath. Transition metals (TM) were then co-deposited with ZnO and dopings by Cd, Ag, Cu, Mg and Al have been achieved.[6-9] The structural, morphological and optical properties of doped-ZnO NW arrays have been fully characterized. We have shown that Cd, Ag and Cu produce a bandgap reduction.[6-9] Cd reduces the bandgap because its rather large size induces a lattice expansion.[9] In the case of Ag and Cu (both belonging to the 1B group), additional bands appear in the bandgap and give rise to the bandgap reduction.[7] Using electrochemical and hydrothermal deposition, high quality TM-doped n-ZnO NW/p-GaN heterostructures have been

prepared. The corresponding LEDs presented a main strong emission peak at low voltage, shifted compared to pure ZnO. The emission could be red- or blue-shifted at a controlled level by playing on the dopant element and its concentration in ZnO (and then in the deposition bath) (see Figure). The system is then highly flexible and these results confirm that the device emission arose mainly from the nanowires which act as the light emitters.

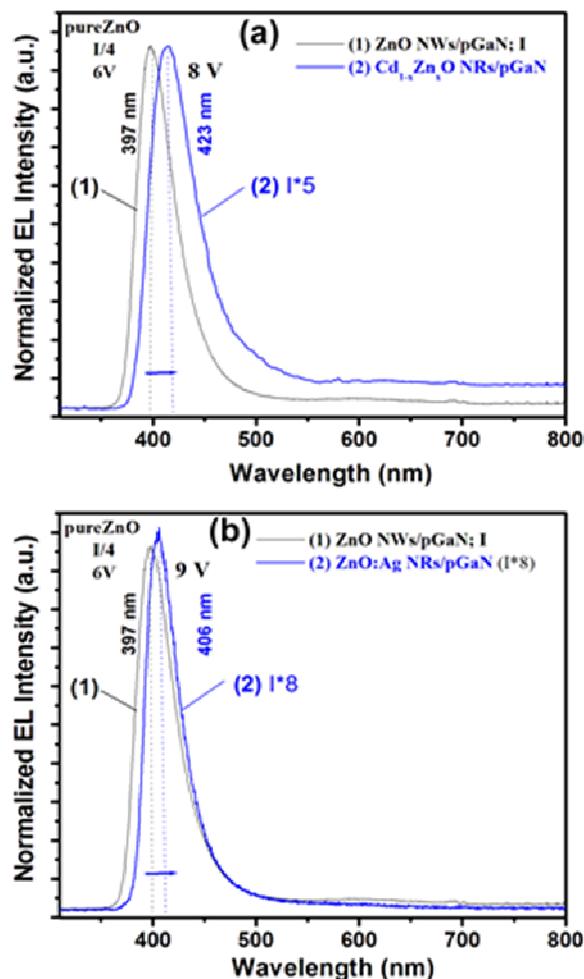


Figure : Emission wavelength shift of TM-doped ZnO NWs/p-GaN LEDs with (a) Cd and (b) Ag dopants.

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