FULL PAPER

Wavelength-Emission Tuning of ZnO Nanowire-Based Light-Emitting Diodes by Cu Doping: Experimental and Computational Insights

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The band-gap engineering of doped ZnO nanowires is of the utmost importance for tunable light-emitting-diode (LED) applications. A combined experimental and density-functional theory (DFT) study of ZnO doping by copper (Zn^{2+} substitution by Cu^{2+}) is presented. ZnO:Cu nanowires are epitaxially grown on magnesium-doped p-GaN by electrochemical deposition. The heterojunction is integrated into a LED structure. Efficient charge injection and radiative recombination in the Cu-doped ZnO nanowires are demonstrated. In the devices, the nanowires act as the light emitters. At room temperature, Cu-doped ZnO LEDs exhibit low-threshold emission voltage and electroluminescence emission shifted from the ultraviolet to violet–blue spectral region compared to pure ZnO LEDs. The emission wavelength can be tuned by changing the copper content in the ZnO nanoemitters. The shift is explained by DFT calculations with the appearance of copper d states in the ZnO band-gap and subsequent gap reduction upon doping. The presented data demonstrate the possibility to tune the band-gap of ZnO nanowire emitters by copper doping for nano-LEDs.

1. Introduction

The emerging fields of nanotechnology and nanoelectronics have attracted intense attention, notably with promising new low-dimensional optoelectronic devices with multifunctionality capabilities. Zinc oxide (ZnO) is a semiconductor with a wide and direct band-gap (3.37 eV at room temperature).[1] By doping zinc oxide with selected elements, it is possible to achieve versatile and desirable optical, electrical, or magnetic properties which are very important for device applications.[2] Recently, ZnO nanoarchitectures, such as nanowires (NWs) and nanorods (NRs) have been a focus of research interest for transparent conducting contacts, photodetectors, nanolasers, low-dimensional light emitters, light-emitting-diode (LED) screens, and solid-state lighting.[3–5] ZnO has a strong exciton binding energy (60 meV compared to 25 meV for GaN)[3,7] which should favor the development of ZnO-LEDs that are much brighter than the corresponding GaN light emitters.[8] However, ZnO is intrinsically n-type due to native defects and the fabrication of reproducible and stable p-type zinc oxide semiconductors is difficult, which makes the fabrication of nano-ZnO-based homojunction devices problematic. For such devices, a useful heterojunction is required that can be fabricated by using another p-type material with lattice constants well-matched to that of ZnO. This matching is important because lattice mismatch could introduce dislocations resulting in interface states between the two materials and reduced efficiency of the LEDs.

ZnO and GaN have the same wurtzite crystal structure with similar lattice parameters and a small in-plane lattice mismatch (ca. 1.9% for the *a* parameter).[6] ZnO NW/p-GaN films are promising heterostructures for nano-LEDs because nanowires can act as direct waveguides and favor light extraction without the use of lenses and reflectors.[3] Also, the emitted light from ZnO NWs/p-GaN film heterojunctions is confined within the nanowire and will be optically transmitted accordingly to the effective medium theory.

Reliable ultraviolet (UV) emission from ZnO-based device structures has been already demonstrated at both low and room temperatures.[3,4,10,11] However, for practical applications, it is important to develop an efficient technique for tuning the emission wavelength by engineering the band-gap of the nanomaterial. The literature is extensive about the band-gap tuning of ZnO films by addition of dopants.[9–15] Doping is also important to create quantum wells which facilitate radiative recombination by carrier confinement.[13] However, several issues have to be clarified, such as the possibility of doping NWs through a cost-effective and efficient electrochemical process, to tune their chemical and physical properties by incorporation of dopant into the lattice of ZnO. Copper is a prominent

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