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High Aspect Ratio Ternary $Zn_{1-x}Cd_xO$ Nanowires by Electrodeposition for Light-Emitting Diode Applications

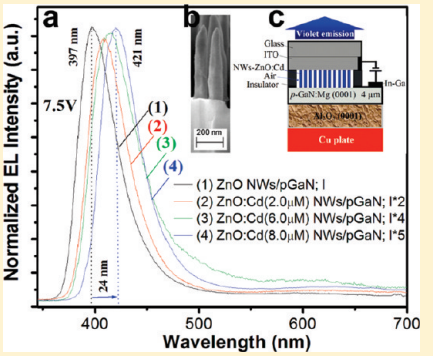
Oleg Lupan,[†,§] Thierry Pauporté,[*,†] Tangui Le Bahers,[†] Ilaria Ciofini,[†] and Bruno Viana[‡]

[†]Laboratoire d'Electrochimie, Chimie des Interfaces et Modélisation pour l'Energie (LECIME), UMR 7575 CNRS, Chimie ParisTech, 11 rue P. et M. Curie, 75231 Paris cedex 05, France.

[‡]Laboratoire de Chimie de la Matière Condensée de Paris, UMR 7574-CNRS-ENSCP-UPMC, 11 rue P. et M. Curie, 75005 Paris, France.

Supporting Information

ABSTRACT: We present a combined experimental and computational approach to study $Zn_{1-x}Cd_xO$ nanowires (NWs) and their integration in light-emitting diode (LED) structures. Self-standing $Zn_{1-x}Cd_xO$ NWs have been electrodeposited on fluorine-doped tin oxide and p-GaN substrates. The electrochemical behavior has been studied, and the reaction mechanism is discussed. Low-dimensional $Zn_{1-x}Cd_xO$ structures have been obtained for $CdCl_2$ concentrations in the deposition bath lower than 6 μM whereas at higher concentration it is admixed with crystallized CdO and the aspect ratio of the wires is decreased. According to scanning electron microscopy observations, the $Zn_{1-x}Cd_xO$ NWs have a higher aspect ratio (>30) than pure ZnO NWs (~20) grown in similar conditions. Analyses show that the ZnO is doped with cadmium incorporated within ZnO NWs and that Cd doping increases with increasing Cd(II) content in the deposition bath. X-ray diffraction studies show increased lattice parameters in Cd-alloyed ZnO NWs. Photoluminescence studies on pure ZnO and $Zn_{1-x}Cd_xO$ NWs show the near band-edge emission red shifted by 3−7 nm as a function of Cd(II) concentration (4 or 8 μM in the electrolyte). The structural and optical properties of the prepared $Zn_{1-x}Cd_xO$ materials have been interpreted using density functional theory (DFT) to computationally simulate the effect of Cd substitution for Zn in the ZnO lattice. DFT calculations show that the crystal lattice parameters increase with the partial replacement of Zn atoms by Cd and that the band gap enlargement is due to the increased lattice parameters. We demonstrate the possibility to tailor the electroluminescence emission wavelength by cadmium doping in ZnO nanowires integrated in $Zn_{1-x}Cd_xO$ NWs/p-GaN heterojunction based LED structures. Reported results are of great interest for the research on band gap engineering of low-dimensional zinc oxide by doping/alloying NWs and for wavelength-tunable LED applications.



1. INTRODUCTION

Zinc oxide (ZnO) has attracted great research interest due to its wide and direct band gap (3.37 eV), large exciton binding energy (60 meV), diverse groups of nanoarchitectures, and versatile physicochemical properties.[1] During the past decade, ZnO nanowires (NWs) and nanorods (NRs) with superior properties compared to bulk material have been reported extensively. It has generated great interest due to the importance of dimensionality, high crystalline quality, large aspect ratio, and quantum confinement effects. These effects are more evident in sub-100-nm structures[2] with high aspect ratio and favor the study of new quantum-mechanical phenomena and development of multifunctional nanodevices. Smaller-diameter ZnO NWs are expected to lower the lasing threshold,[3] to decrease the defect density at interfaces, and to increase the optical power extraction of the light-emitting diodes (LEDs).[4] Synthesis and characterization of ZnO nanostructures has been reported extensively. Recently, integration of ZnO NRs/NWs in nanosensors, dye-sensitized solar cells, light-emitting devices, photodetectors, and nanogenerators has confirmed their multifunctional character.[5−12] Control and tuning properties of nano-ZnO to achieve a specific functionality have become an important field of research. One important step is to control doping and alloying effects in zinc oxide at the nanoscale and controlled doping can tailor the properties of ZnO to specific applications. For ZnO, it is essential to understand the effects of anionic or cationic substitutions and their impact on the electronic and optical properties.[13] Modulation and engineering of the band gap in the growth direction are important for the fabrication of heterostructures. The ternary systems $Zn_{1-x}Cd_xO$ and $Zn_{1-y}Mg_yO$ permit a decrease or increase, respectively, in the band gap energy, in comparison with binary host material ZnO.[13,14] However, a technology tool with controlled regimes has to be developed for the synthesis of doped nano-ZnO, which will permit state-of-the-art, cost-effective,

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