ACS APPLIED MATERIALS & INTERFACES

Research Article

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Low-Temperature Preparation of Ag-Doped ZnO Nanowire Arrays, DFT Study, and Application to Light-Emitting Diode

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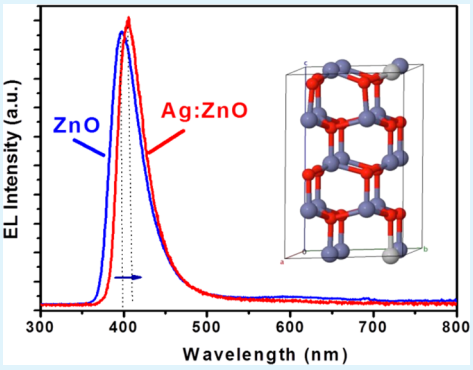
Supporting Information

ABSTRACT: Doping ZnO nanowires (NWs) by group IB elements is an important challenge for integrating nanostructures into functional devices with better and tuned performances. The growth of Ag-doped ZnO NWs by electrodeposition at 90 °C using a chloride bath and molecular oxygen precursor is reported. Ag acts as an electrocatalyst for the deposition and influences the nucleation and growth of the structures. The silver atomic concentration in the wires is controlled by the additive concentration in the deposition bath and a content up to 3.7 atomic % is reported. XRD analysis shows that the integration of silver enlarges the lattice parameters of ZnO. The optical measurements also show that the direct optical bandgap of ZnO is reduced by silver doping. The bandgap shift and lattice expansion are explained by first principle calculations using the density functional theory (DFT) on the silver impurity integration as an interstitial (Ag_i) and as a substitute of zinc atom (Ag_{Zn}) in the crystal lattice. They notably indicate that Ag_{Zn} doping forms an impurity band because of Ag 4d and O 2p orbital interactions, shifting the Fermi level toward the valence band. At least, Ag-doped ZnO vertically aligned nanowire arrays have been epitaxially grown on GaN(001) substrate. The heterostructure has been inserted in a light emitting device. UV-blue light emission has been achieved with a low emission threshold of 5 V and a tunable red-shifted emission spectrum related to the bandgap reduction induced by silver doping of the ZnO emitter material.



KEYWORDS: *ZnO, electrodeposition, light-emitting diode, Ag-doping, DFT modeling, UV–blue emission*

1. INTRODUCTION

Zinc oxide is a key material for advanced applications in the fields of nano- and microtechnologies.[1−4] This oxide is characterized by a wide direct bandgap of 3.37 eV at room temperature and a strong exciton binding energy of 60 meV.[1−4] It can be grown with various tunable nano/microstructures such as nanowires (NWs) and nanorods (NRs)[1,5,6] and can be doped by various elements.[7−12] A broad spectrum of tunable properties have been reported by doping ZnO at various levels.[7−24] They include high transparency, conductivity ranging from the metallic to the insulating ones, piezoelectricity,[2] selective sensitivity,[7] photocatalytic properties,[8] ferromagnetic properties,[9,10] and important magneto-optic effects.[11,12]

ZnO NW and NR array layers have attracted a tremendous attention due to various interesting properties related to their low-dimensionality, optical, and confinement effects and large surface to volume ratio.[1,5,6,25] They can be grown by various techniques using the vapor or the liquid phase.[1] Among the latter, many reports have focused on the sol–gel method, the hydrothermal growth, the chemical bath deposition and the electrodeposition. ZnO structures of high structural and optical quality have been prepared by electrochemical deposition at rather low temperatures.[1,2] Moreover, the heteroepitaxial growth has been successfully demonstrated on various conducting single crystals and the preparation of electrodeposited ZnO emitters for near-UV light emitting diodes (LED) application has been published by our group.[26,27] Moreover, we have shown that transition metal-doping of ZnO permits the adjustment of the light emission spectrum of the device.[28−31] Both red-shifted[28,29] and blue-shifted[31] LED emissions by electrochemical doping have been obtained depending on the cation additive dissolved in the electrodeposition bath.

Doping ZnO by the group-IB elements is of special interest since theoretical studies have shown that the defect formation energies of substitutional group-IB elements (Cu, Ag and Au) are low.[32−34] This is especially the case when Ag substitutes Zn

Received: February 15, 2015
Accepted: May 20, 2015
Published: May 20, 2015

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DOI: 10.1021/acsami.5b01496
ACS Appl. Mater. Interfaces 2015, 7, 11871−11880