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Europium doping-induced stability and quantum confinement effect in ZnO quantum well wires QWW: Electronic structure calculation and material structural investigation in terms of band-gap shift

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ABSTRACT

ZnO quantum well wires QWW have been grown on glass substrates by an inexpensive, simplified and enhanced spray pyrolysis technique, at 460 °C and using $Zn(CH_3COO)_2 \cdot 2H_2O$ as main precursor. Consecutively, the as-grown wires have been gradually doped by Europium within hexa-hydrated chlorinated Europium $EuCl_3 \cdot 6H_2O$ (ACROS, 99.0% purity) with different europium-doping levels (0, 0.5 and 1.0 at%). The effects of Eu-doping on the structural and optical properties of the QWW were investigated. Results reflect that accuracy of control can be achieved on functional performance by adjusting doping extent. Two-dimensional self-consistent calculations of the electronic structure within the Brillouin zone, along with Lattice Compatibility Theory analyses results show excellent agreement with the experimental results.

1. Introduction

Zinc oxide ZnO, with its direct wide band gap (3.37 eV) and large exciton binding energy (60 meV) is known as one of the most important functional semiconductor oxides [1–4]. ZnO-based quantum dots and wires have attracted increasing interest due to their unique electronic and opto-thermal properties. Recent studies outlined an obvious development in precise controllability of sizes and shapes of ZnO nano-materials, as a guide for enhancing optical and electrical performance.

Parallel to this development, appropriate doping protocols have demonstrated the possibility of controlling both electronic and the optical properties of ZnO-like nano-materials. Rare earth doping exhibited deep alteration of spin-dependent phenomena in ZnO nano-wires, which led to establishment of systems with new or enhanced functionality, such as sensitive biological sensors, high ferromagnetic-ordered narrow band-gap semiconductors and polarized solid state light sources [5–10].

In this study, we report a low-cost and effective method for obtaining mono-disperse radial-symmetric pure Eu-doped ZnO quantum well wires QWW on glass substrates. Stability and morphology-dependence of Europium ions incorporation and substitution kinetics within ZnO lattice host in the LCT scope have been analyzed and discussed.

2. QWW preparation

First, un-doped ZnO thin films (denoted Z_0) have been prepared at 460 °C on a glass substrate, using propanol and zinc Acetate $Zn(CH_3CO_2)_2$:10^{-2} M according to the chemical protocol summarized in precedent studies [11–14]. Consecutively, and under similar experimental conditions, Europium-doped ZnO:Eu wires have been fabricated by adding hydrated Ammonium meta-europeate (NH_4EuO_3, 99.9% purity) to the precursor solution while maintaining acidity level. Finally, three representative samples have been elaborated: (0, 0.5 and 1.0 at% ZnO:Eu).

3. Some characterization protocols

X-ray diffraction pattern of pure and Eu-doped Zinc oxide samples show defined peaks of (101), (100) and predominant

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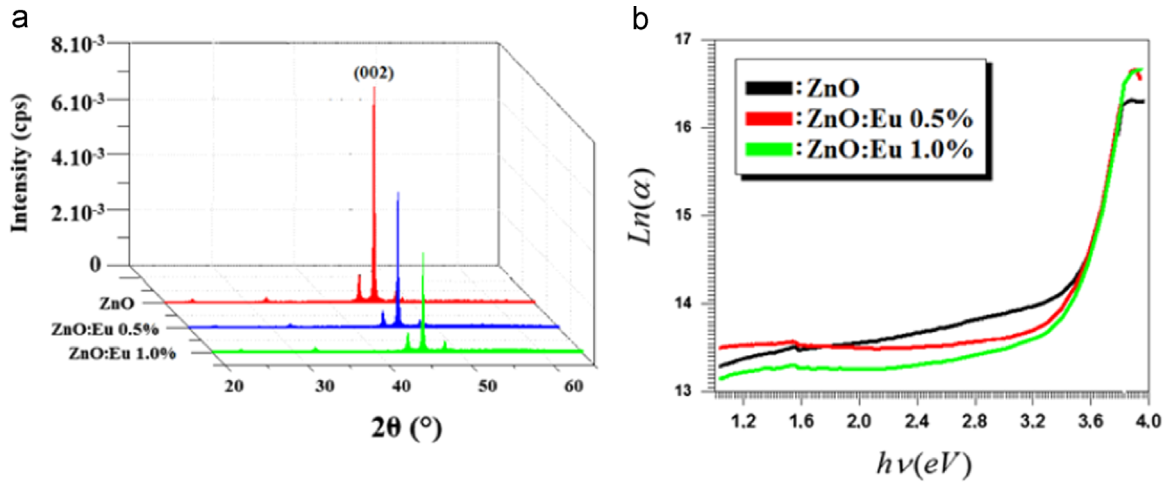

Fig. 1. Optical measurement results: (a) XRD diffraction spectra (b): plots of $Ln(\alpha)$ versus energy $h\nu$.

(002) principal orientation, corresponding to hexagonal würtzite phase, (Fig. 1(a)). The different films with un-doping and doping concentration have a preferential *c*-axis orientation. It is also worth noting that no peak related to the common europium oxide has been found in these spectra, which may be due to the low Eu content. This result implies that a little of Eu impurities do not change würtzite structure of ZnO.

Optical transmittance/reflectance measurements were fundamental guides for determining the values of the absorption coefficient α. It has been noticed that the incorporation of Europium does not alter significantly the values of the bandgap. The logarithm of the absorption coefficient $\alpha(\nu)$ is plotted as a function of the photon energy ($h\nu$) for different thickness and is shown in (Fig. 2(a)).

It is known that the incorporation of doping agents into the semiconductor often reveals the formation of band tailing in the band gap, the interactions with phonons, and the presence of tail absorption profile which follows the empirical Urbach law [15–17]:

Urbach energy E_u has been determined through the equations:

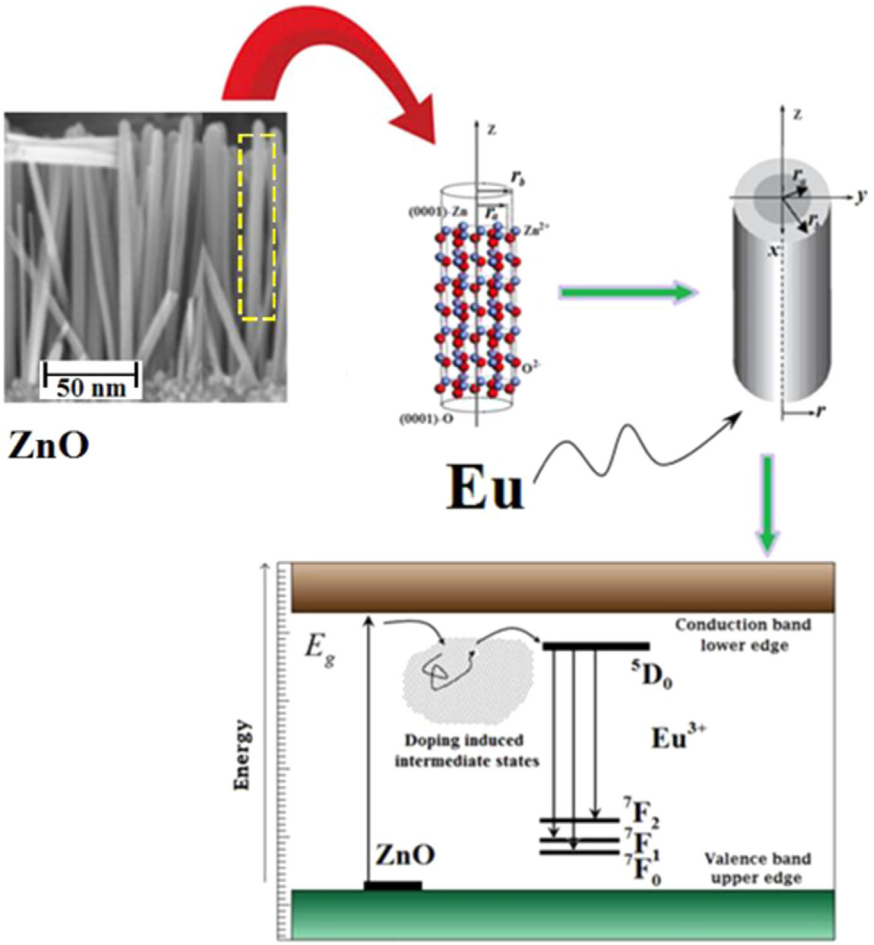

Fig. 2. Synoptic ZnO and Eu element energy diagrams coupling in the actual study, along with cylindrical nano-wire configuration of the as-grown ZnO QWW.