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Comparative study of hydrothermal treatment and thermal annealing effects on the properties of electrodeposited micro-columnar ZnO thin films

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ABSTRACT

We report a comparison of the role played by different sample treatments, namely, a low-temperature hydrothermal treatment by hot H_2O vapor in an autoclave versus thermal annealing in air on the properties of ZnO films grown by electrochemical deposition (ECD). Scanning electron microscopy studies reveal a homogeneous micro-columnar morphology and changes in the film surface for the two different treatments. It is found that post-growth hydrothermal treatments of ECD ZnO films at 150 °C under an aqueous environment enhance their structural and optical properties (photoluminescence, transmission, Raman spectra, etc.) similar to thermal annealing in air at higher temperatures (>200 °C). The modifications of the structural and optical properties of ZnO samples after thermal annealing in air in the temperature range of 150–600 °C are discussed. The removal of chlorine from the films by the hydrothermal treatment was evidenced which could be the main reason for the improvement of the film quality. The observation of the enhanced photoluminescence peak at 380 nm demonstrates the superior properties of the hydrothermally treated ZnO films as compared to the films annealed in air ambient at the same or higher temperature. This post-growth hydrothermal treatment would be useful for the realization of high performance optoelectronic devices on flexible supports which might not withstand at high temperature annealing treatments.

1. Introduction

Zinc oxide is an important wide-bandgap semiconducting material with numerous applications due to its unique physical and chemical properties [1–6]. In the past decades, it was demonstrated that post-growth treatments of ZnO in different atmospheres (e.g. air, O_2, H_2, N_2, etc.) at high temperature can lead to a substantial improvement of its structural, electrical and optical properties. The effect of thermal annealing treatments in conventional furnaces, rapid thermal annealing, and rapid photo-thermal processing on the properties of ZnO thin films [1–8] grown on different types of rigid substrates (e.g. Si, GaN, Al_2O_3, glass, indium-doped tin-oxide (ITO), fluorine-doped tin-oxide (FTO), etc.) have been investigated. However, recently, an increased interest in flexible plastic substrates (FPS) has arisen due to their cost-efficiency, light-weight, robustness, and the possibility of integration in flexible electronic and optoelectronic devices (e.g. smart cards & displays, etc.) and transparent electronics with higher functionality [8–11]. Therefore, a synthesis technique and gentle post-growth treatment, compatible with FPS (which is damaged at temperatures above 180–200 °C), has to be identified. In addition, such treatments should also lead to the same improved structural and light emission properties observed for high-temperature annealed microcrystalline ZnO thin films presently used in short-wavelength optoelectronic devices, solar cells, field-effect transistors, light emitting diodes and in sensing applications [11–20].

ZnO thin films and microstructures have been synthesized by a variety of processes [13,20–22] and subsequently treated to improve their optical properties and to fabricate higher performance devices. Among these, electrochemical deposition — ECD [23,24] is a low temperature process compatible with different types of substrates, including FPS [7], known to produce highly crystalline ZnO films of excellent electronic quality [23–26]. In this context, microstructured zinc oxide can be considered as a promising active material for various cost-effective optoelectronic applications on flexible or elastic substrates [27–33].

In this work, we report the growth of ZnO micro-columnar films by an electrochemical method compatible with FPS. The zinc oxide films are formed from vertically oriented micro-columns with the *c*-axis perpendicular to the substrate. It is demonstrated that their structural and optical properties can be enhanced by performing a post-

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