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Gallium-doped ZnO thin films deposited by chemical spray

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Abstract

Gallium-doped zinc oxide (ZnO:Ga) thin films were deposited on glass substrates by the spray pyrolysis technique. The effect of the variation of the [Ga]/[Zn] rate in the starting solution, the substrate temperature as well as the post-annealing treatments on the physical properties was examined. The electrical properties of the films show an improvement with the Ga incorporation and the annealing treatment. All the films were found to be polycrystalline and show a (0 0 2) preferential growth, irrespective of the deposition conditions. The films were of n-type conductivity with an electrical resistivity in the order of $8 \times 10^{-3}\,\Omega\,cm$ and optical transmittance higher than 80% in the visible region. These results makes chemically sprayed ZnO:Ga potentially applicable as transparent electrode in photovoltaic devices.

Keywords: ZnO; Annealing; Spray pyrolysis; Gallium; Electrical resistivity

1. Introduction

Zinc oxide in thin film form has generated a renewed interest in science and technology due to the wide applications in opto-electronic and electronic devices

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[1–3], namely transparent electrodes in thin film solar cells where a simultaneous high transparency and a low resistivity are present [4], in thin film gas sensors [5,6], varistors [7,8], surface acoustic-wave devices [9], etc. Many reports have been devoted to the manufacturing methods of ZnO films [10–12], e.g. sputtering [13,14], chemical vapour deposition [15,16], chemical spray [17,18], sol–gel [19] and molecular beam epitaxy [20], among others. The chemical spray technique has the advantages of low cost, easy-to-use, safe, and can be implemented in a standard laboratory. ZnO thin films adequate for some applications are obtained in a reproducible way. Although chemically sprayed ZnO thin films have been doped with In, Al, Li, Tb, in order to enhance transport properties, still some problems remain unsolved. The Ga doping is very promising; however, no successful results are obtained if compared with, for example, indium doping. In fact, there are some problems that limit mainly the transport properties, when the Ga is incorporated into the ZnO lattice.

In this work, the influence of the substrate temperature and annealing treatments on the resistivity, structural properties, surface morphology and optical properties of chemically deposited ZnO:Ga thin films is reported.

2. Experimental procedure

The starting solution consisted of zinc acetate (Merck) dissolved in a mixture of deionized water, methanol and acetic acid (250:650:100 in volume, respectively). Gallium nitrate anhydrous (Merck), diluted in deionized water at 0.1 M was added as dopant taking the atomic percent ratio [Ga]/[Zn] in the solution as a reference of the doping level in the films, and varied from 0.05 to 5 at%.

It is worth mentioning that with higher [Ga]/[Zn] rates (as in the case of 5 at%) the resulting films are highly resistive. The solution was sprayed at a flow rate of 12 ml/min onto cleaned soda-lime glass substrates ($2 \times 1 \times 0.1$ cm). Gas nitrogen with a flow rate of 10 l/min was used as carrier gas. The substrate temperature was varied from 425 to $525 \pm 5\,^{\circ}$C in 25 °C steps. A vacuum thermal annealing was performed at 400 °C during 1 h on as-deposited films. The electrical resistivity was measured at room temperature using the four-point probe technique by a Veeco equipment and with the appropriate correction factor. Carrier concentrations and Hall mobilities of all the films were measured using the van der Paw method with the corresponding corrections, at room temperature in air [21]. The deposition time was fixed in such a way that the thickness was approximately 0.6 μm in all cases. The thickness was corroborated with a profilmeter equipment, etching an edge to make a reference step. X-ray diffraction (XRD) and scanning electron microscopy (SEM) have been used to study the microstructure of films. We have used Cu K_α ($\lambda = 0.1542$ nm) radiation and the angle 2θ ranged between 20° and 80° with a Siemens Krystalloflex equipment. The lattice parameters, crystal size and lattice constant were obtained from these spectra. The optical properties were obtained using SHIMADZU UV-VIS equipment in the wavelength range 300–1000 nm.