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Nitrogen oxides and ammonia sensing characteristics of SILAR deposited ZnO thin film

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Abstract

Pure and Sn, Ni doped ZnO thin films were deposited on glass substrates using a novel successive ionic layer adsorption and reaction (SILAR) method at room temperature. Microstructures of the deposited films were optimized by adjusting growth parameters. The variation in resistivity of the ZnO film sensors was performed with rapid photothermal processing (RPP). The effect of rapid photothermal processing was found to have an important role in ZnO based sensor sensitivity to NO_2, NH_3. While the undoped ZnO film surface exhibited higher NH_3 sensitivity than that of NO_2, an enhanced NO_2 sensitivity was noticed for the ZnO films doped with Sn and higher NH_3 sensitivity was obtained by Ni doping.

Keywords: ZnO; SILAR; RPP

1. Introduction

ZnO is an interesting material because exhibits numerous characteristics suited for various technological applications such as antireflection coatings, transparent electrodes in solar cells [1], piezoelectric devices [2], gas sensors [3], and others. A few papers describe the sensing behaviour of ZnO films deposited by aqueous solution deposition techniques at low temperatures [4–6] and in particular by the novel successive ionic layer adsorption and reaction (SILAR) method. However, they did not describe the impact of impurities, growth and annealing on properties and

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sensitivity of ZnO thin film based gas sensors. SILAR is a relatively new and less investigated process first reported by Nicolau [7].

The present paper describes the effects of different dopants, and rapid photothermal processing (RPP) as post-deposition annealing on gas sensing characteristics of ZnO films prepared by SILAR. One of the advantages of the SILAR and RPP technique combination is that ZnO can be doped with different concentrations of Sn, Ni and RPP in different ambients for shorter durations (10–30 s) at lower temperatures (550–700 °C) than conventional furnace annealing (15-60 min at 700–1000 °C). Consequently, the sensitivity and selectivity of sensors could be investigated over a wide range of doping concentrations in aqueous solutions and RPP temperatures.

2. Experimental

Films of pure and Sn, Ni doped ZnO were deposited on glass substrates by successive ionic layer adsorption and reaction SILAR. The aqueous zinc complex solution comprises a mixture of $ZnSO_4$, NaOH and sodium stannate, or nickel sulfate. The concentration of complex solution was 0.8 and 0.12 M zinc concentration. Adding the sodium stannate in the aqueous solution 5 at.% (and 6 at.%) Sn concentration, or nickel sulfate 5 at.% (and 2 at.%) Ni concentration according to the doping level, the impurification was performed, respectively. The complex solution of cations was held at room temperature and the solution of anions at 98 °C during the deposition process. The details of tin doped ZnO film deposition following the SILAR method were reported previously [8].

In order to investigate the effect of post-deposition annealing, films have been RPP processed at various temperatures 300–750 °C for 20 s using an RPP system, the set-up presented in [8]. After RPP of ZnO thin films at 550 and 650 °C, 20 s, the electrodes were deposited by thermal evaporation of Al. The sensor studies were performed in a quartz chamber connected to a gas flow system described in [8,9].

3. Results and discussion

Scanning Electron Microscopy (SEM) and quantitative element composition analysis by energy dispersion X-ray spectrometry (EDX) demonstrate the formation of the ZnO and confirm the doping with Sn and Ni in ZnO microstructures. It was observed that the surface morphology strongly depended on the type of the dopant atoms (Sn or Ni) and the crystallites have the mean sizes around 400, 200 and 150 nm for ZnO, Sn–ZnO and Ni–ZnO films, respectively. The details of the dependence of the surface morphology on the type of the dopant atoms following the SILAR method were reported previously [10].

The impact of the rapid photothermal processing on the surface morphology of films obtained has been investigated. Increasing the RPP temperature up to 550 °C, for 20 s, for Ni doped zinc oxide and up to 650 °C, for 20 s, for pure, Sn doped zinc oxide decreases the voids in the film. The Sn/Zn and Ni/Zn ratios surveyed are 4/96 and 3.5/96.5 (at.%) in the films that were analyzed by EDX and was found to be less than those in the solution; nevertheless, there was determined a linear correlation between the two quantities.

There were observed irreversible changes in the electrical characteristics when the ZnO films were post-growth RPP processed at temperatures higher than 300 °C for 20 s. In the temperature range of 550–650 °C there was observed improvement of the quality and stability of the ZnO sensor samples; the measurements were carried out for one year and determined conductance