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Tuning of TCO properties of ZnO by silver addition

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ABSTRACT

In this work, we explore the influence of Ag dopant concentration (i.e. 0–2 wt.%) on the opto-electric properties of Ag doped ZnO thin solid films synthesized by chemical spray pyrolysis technique. Several analytical tools such as XRD, AFM, SEM and dc-two probe technique were used. Structural studies reveal that with increasing the doping level, more dopant atoms occupy the zinc lattice sites but after a certain level, they form neutral defects and become ineffective as dopant impurities. 1 wt.% of Ag doping was the optimum for enhancing electrical conduction and beyond that the distortion caused in the lattice inhibits further conduction. Distinct changes including a red shift and narrowing of band gap with increasing Ag content was observed. The low temperature conduction has been explained by variable range hoping (VRH) mechanism. The possible distribution of Ag in the Ag–ZnO thin films has been tentatively discussed.

1. Introduction

In the last couple of years the synthesis and applications of ZnO nanostructures have been intensively studied due to its enormous potential for a variety of applications. Owing to its wide band gap energy 3.37 eV and a large exciton binding energy of 60 meV, ZnO is expected useful for optoelectronics, transparent electronics, sensors and transducers [1–4].

Considerable work has been reported on the doping of ZnO with several dopants to tailor its electrical and optical properties. For instance, Chakraborty et al. [5] have investigated the effect of Al and

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In doping on ZnO thin films using spray pyrolysis technique. They concluded that the nature of the dopant influences the grain structure, surface morphology and nucleation process which ultimately govern the structural and optical properties of the sample.

Doping by introducing electron donor or acceptor elements into the host crystal is a successful approach in thin film devices. Usually, ZnO exhibits n-type conductivity because of native defects, such as oxygen vacancies and zinc interstitials. The strong n-type conductivity of ZnO restricts the application and it is complicated to fabricate p-type conductive ZnO [6]. Recently, research of ZnO has been focused on the synthesis of p-type ZnO using various dopants, such as N, P, As, Sb, and Ag [7,8–10]. Among these, Ag, as a group Ib element could also act as an acceptor in ZnO, if incorporated on substitutional Zn sites [11]. For instance, Fan and Freer suggested that Ag acted as an atmospheric dopant, existing both on substitutional Zn sites and in the interstitial sites [12]. So, the early research showed that Ag incorporation in ZnO reduces donor density, which means that Ag may be an effective acceptor in ZnO [13]. Infect, Ag is not only a good electric conductor with relatively low optical absorption coefficient in the visible region but also an important optical material in the visible region and the near infrared region. While the doping of the different metals was successful for tuning the electrical properties of ZnO in thin films [14–16] and in bulk forms which has been widely reported [17,18]. But the reports on the systematic studies of the optical and electrical properties of Ag–ZnO, either in bulk or in thin film forms are still very scarce.

Many techniques have been used to deposit ZnO films on different substrates, including chemical vapor deposition [19], sol–gel [20], evaporation [21], sputtering [22], pulsed laser deposition [23] and spray pyrolysis [24]. Among these methods spray pyrolysis, is an excellent, simple, versatile and economical method. Besides the high growth rates with uniformity, this is a simple method for large area coating applications such as window panels, automotive glass and solar cells.

In this contribution, we have prepared Ag–ZnO film by using spray pyrolysis method as Ag doping is expected to change the microstructure of the film heavily. Indeed, such changes are observed as one can see at a later stage. This prompted us to see the effect of such changes in other properties too. In this work, we describe the results for ZnO thin films prepared by spray pyrolysis technique, focusing on the crystalline quality, opto-electrical properties and impurity incorporation. Additionally, the possible distribution of Ag in the Ag–ZnO has been tentatively discussed.

2. Experimental procedure

2.1. Sample preparation

The ZnO and Ag–ZnO thin films were prepared using a spray pyrolysis experimental setup. The zinc oxide thin films are prepared by mixing (0.2M) zinc nitrate [$Zn(NO_3)_2$] and Ag doping was achieved by the addition of $AgNO_3$ dissolved in deionized water [25]. The following chemical reaction took place:

$$2Zn(NO_3)_2 \cdot 6H_2O + O_2 \rightarrow 2ZnO \downarrow + 4NO_2 \uparrow + 2O_2 \uparrow + 12H_2O \tag{1}$$

The films have been deposited on chemically and ultrasonically cleaned microscopy glass substrates. Several initial trials were made to adjust the deposition conditions before they could be set for this series of experiments. Before real sample preparation, several initial trials were made to optimize the deposition conditions.

Under the optimized conditions, during deposition, (i) the solution flow rate was maintained at 1 ml/min, (ii) the distance between the tip of the nozzle and the substrate was kept at 28 cm, (iii) the substrate temperature was maintained at 400 °C. The temperature was measured by using chromel–alumel thermocouple fixed on the hot plate. The atomization of the solution in the fine droplets was affected by spray nozzle with the help of compressed air, during the course of spray. The Ag–ZnO thin films with different concentrations viz 0, 0.25, 0.5, 1 and 2 wt.% have been prepared. Ag concentration was varied up to 2 wt.% because starting from this concentration, the segregation has been observed in the films in our study. The films were found no stickier for higher Ag concentration (i.e. 2 wt.%).