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Optical and electrical properties of zinc oxide thin films with low resistivity via Li–N dual-acceptor doping

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ABSTRACT

Zinc oxide thin films with low resistivity have been deposited on glass substrates by Li–N dual-acceptor doping method via a modified successive ionic layer adsorption and reaction process. The thin films were systematically characterized via scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction, ultraviolet-visible spectrophotometry and fluorescence spectrophotometry. The resistivity of zinc oxide film was found to be 1.04 Ω cm with a Hall mobility of 0.749 $cm^2 V^{-1} s^{-1}$ and carrier concentration of 8.02×10^{18} cm^{-3}. The Li–N dual-acceptor doped zinc oxide films showed good crystallinity with prior *c*-axis orientation, and high transmittance of about 80% in visible range. Moreover, the effects of Li doping level and other parameters on crystallinity, electrical and ultraviolet emission of zinc oxide films were investigated.

1. Introduction

As an *n*-type compound semiconductor with a hexagonal wurtzite structure, zinc oxide has attracted considerable attention for its wide band gap (3.37 eV), large exciton binding energy (60 meV) and high carrier mobility at room temperature [1]. It has exhibited enormous potential in many electronic device applications, such as light emitting diodes [2], ultraviolet (UV) lasers [3], transparent thin film transistors [4], gas sensors [5], and surface acoustic devices [6]. However, the bottleneck of preparing zinc oxide films with p-type conductivity should be overcome before zinc oxide could make inroads into the world of electronics devices [7]. Normally, undoped zinc oxide shows n-type conductivity due to the native donor defects such as zinc interstitial and oxygen vacancy, which makes it difficult to prepare p-type conductive zinc oxide [8]. Even so, considerable efforts have been made in this field, for example, p-type zinc oxide have been made employing N [9,10], P [11], As [12], Li and Ag [13] as dopants. Based on the theory of co-doping, In–P [11] and Al–N [14] co-doping methods were introduced into the fabrication of p-type zinc oxide.

Up to now, many existing thin film preparation techniques have been applied in the synthesis of zinc oxide films, including chemical vapor deposition [9], sputtering [12], pulsed laser deposition [15], molecular beam epitaxy [16], sol–gel techniques [17], chemical bath deposition [18], successive ionic layer adsorption and reaction (SILAR) [19–25], et al. However, it is well conceived that preparation of zinc oxide films via solution chemical routes provides a promising option for large-scale production of zinc oxide materials. SILAR method, first reported by Nicolau in 1985, involves the substrate alternate immersion in cationic and anionic precursor and the substrate rinsing procedures in between. It has attracted much interest because of low-cost and environment-friendly circumstance. Films prepared by this method have good adhesion and uniformity, and the thickness of the film can easily be controlled by changing cycle number, pH value, and other technical parameters. The SILAR method has been used to prepare zinc, lead and cadmium chalcogenide thin films.

In the previous work, we reported the synthesis and ultraviolet emission of un-doped zinc oxide polycrystalline films by a modi-

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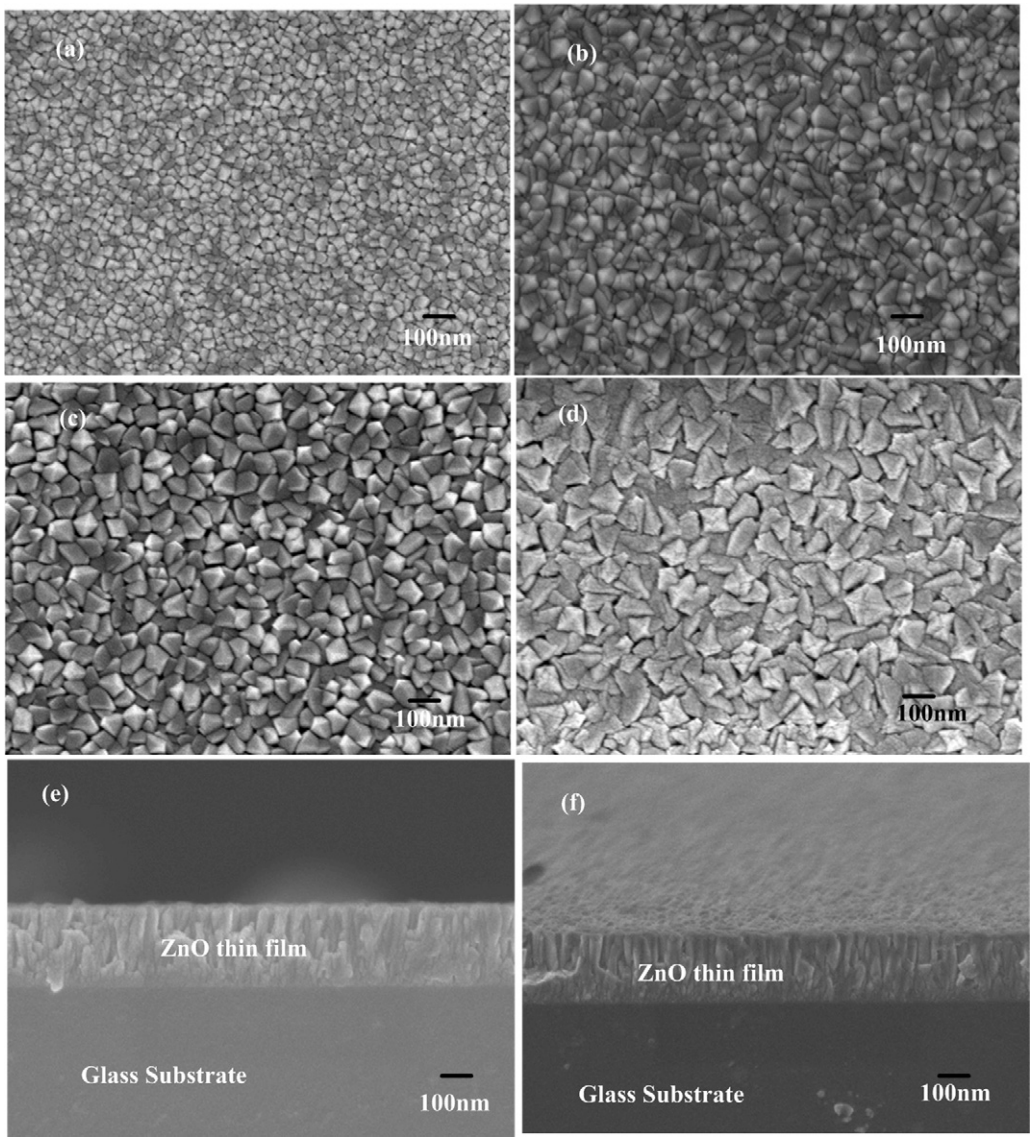

Fig. 1. SEM images of ZnO:Li_0 films without heat treatment process and with heat treatment at different temperatures in O_2 atmosphere for 2 h. (a) As-deposited ZnO film; (b) annealed at 350 °C; (c) annealed at 450 °C; (d) annealed at 530 °C; (e) as-deposited ZnO film; (f) annealed 530 °C.

fied SILAR method [21]. In this paper, stable zinc oxide thin films with low resistivity were fabricated by a Li–N dual-acceptor doping technique via the modified SILAR method. A heat treatment process was introduced in the present work, and the as-prepared zinc oxide films have good crystallinity, electrical and ultraviolet emission properties.

2. Experimental procedure

2.1. Treatment of glass substrates

The cleanness and hydrophilicity of substrates are very important to the deposition of high-quality zinc oxide films. Contaminated substrates will lead to formation of non-uniform films. In the present work, commercially obtained glass slides with dimensions of 25 mm × 75 mm × 1 mm were chosen as substrates. The substrates were cleaned by detergent and treated with hydrogen nitrate or chromic acid for 12 h, followed by ultrasonic cleaning in deionized water for 30 min and then drying.

2.2. Formation of zinc oxide thin films with low resistivity

A series of zinc oxide films with different Li contents were deposited on cleaned glass substrates. The cationic precursor of SILAR process was prepared as the following: 0.02 mol ethanolamine and 15 mL 6.65 mol L^{-1} ammonia solutions were added to 100 mL 0.2 mol L^{-1} zinc acetate solution, and then the solution was diluted to 200 mL with deionized water. Lithium nitrate, as lithium dopant, was also added to the solution. Lithium contents of 0, 0.1, 0.5, 1, 2, 5 and 10 at.% were employed in this study, and the zinc oxide films grown with these Li contents will be referred to as ZnO:Li_0, ZnO:$Li_{0.001}$, ZnO:$Li_{0.005}$, ZnO:$Li_{0.01}$, ZnO:$Li_{0.02}$, ZnO:$Li_{0.05}$ and ZnO:$Li_{0.1}$, respectively. Generally, the lithium doped levels in the films are not equal to the lithium contents in the solutions. The pH value of the cationic precursor was maintained at ~11.5. The ethanolamine was used to reduce the dosage of ammonia as a high ammonia concentration may result in dissolution of as-deposited zinc oxide films when being reintroduced into the cationic precursor [22]. Moreover, both ethanolamine and ammonia can be used as the N-doping source. Hot water of 90 °C was used as anionic precursor to provide hydroxyl anions during the fabrication of zinc oxide films.

A complete film deposition cycle involves four steps: (i) immersion of the substrate in cationic precursor at room temperature for 30 s, after which there will be a thin layer solution adhered to the substrate surface, (ii) immersion of the substrate in anionic precursor at 90 °C for 30 s, which leads to the chemical reaction on the substrate surface, (iii) water rinsing of the loosely bound particles, and (iv) heat treatment of the as-prepared films at 200 °C for 5 min to convert zinc hydroxide into zinc oxide. All samples in this paper were prepared with 15 deposition cycles. After the deposition, zinc oxide films were annealed in different ambient (O_2, N_2 and air) for comparison. Annealing process includes a preheating step at 300 °C for an hour to vaporize organic ingredients, and a post-heating step at different temperatures