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Hydrophobic and textured ZnO films deposited by chemical bath deposition: annealing effect

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Abstract

Highly textured ZnO cones have been grown onto glass substrates by chemical bath deposition (CBD) method. They were given heat treatment at 623 K for 2 h in air. The change in structural, optical and electrical properties were studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption, electrical resistivity and contact angle measurements. Structural analysis by X-ray diffraction pattern showed as-deposited ZnO film has high-orientation along *c*-direction (0 0 2), which remained the same with low-intensity after heat treatment. Well-defined cones almost perpendicular to substrate surface, which were slightly compressed in size after heat treatment, have been detected through SEM micrographs. Water wettability study revealed a contact angle of $72.28 \pm 1.5^\circ$ for as-deposited ZnO films, whereas hydrophobic surface with a contact angle of $152.84 \pm 1.5^\circ$ was obtained after heat treatment. This is attributed to the topographical change in structural morphology. Change in bandgap energy from 3.7 to 3.2 eV was observed after heat treatment. Electrical resistivity measurement showed semiconducting nature with room temperature resistivity $10^4\ \Omega$ cm for as-deposited ZnO, which was decreased to $10^3\ \Omega$ cm for annealed ZnO film.

Keywords: ZnO cones; CBD; Annealing effect; Contact angle; Optical absorption; Electrical resistivity

1. Introduction

Zinc oxide is one of the versatile and technologically important semiconducting material because of its typical properties such as resistivity control over the range 10^{-3} to $10^5\ \Omega$ cm [1], transparency in the visible range, high-electrochemical stability, direct bandgap (3.37 eV), absence of toxicity, abundance in nature, etc. It crystallizes in a wurtzite structure and exhibits n-type conductivity [2]. Stoichiometric ZnO films are highly resistive, but less resistive films can be made either by creating oxygen vacancies, which act as donors or by doping with Al, Ga or In [3]. ZnO is one of the semiconductor having good chemical stability against

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hydrogen plasma [4] and suitable for photovoltaic applications because of its high-electrical conductivity and optical transmittance in the visible region of the solar spectrum [5], which is prime important in solar cell fabrications. Thin films of ZnO can be used as a window layer as well as one of the electrodes in solar cells [4]. Along with these applications, ZnO thin films have been used in varistor [6], gas sensor [7], solar cell transparent contact fabrication [8], etc. In many industrial processes, such as cleaning, drying, painting, coating, adhesion, heat transfer and pesticide applications, wettability is an important parameter. For practical applications, both highly hydrophobic (water contact angle greater than 150°) and highly hydrophilic (water contact angle less than 10°) materials are particularly desired. Many Japanese groups [9,10] have reported the way to produce highly hydrophilic metal oxide surfaces.

Different chemical methods such as chemical bath deposition (CBD) [11,12], spray pyrolysis [13], successive ionic layer adsorption and deposition (SILAR) [14], electrodeposition [15,16], etc. have been used to obtain ZnO films. As compared to other deposition methods, CBD also referred to as solution deposition method, has its own advantages such as simplicity, reproducibility, non-hazardous, cost effectiveness, etc. The CBD method is well suited for producing large-area thin films. This method is low-temperature method and it does not require sophisticated instruments. It involves deposition of semiconductor thin films on substrates that are kept in the aqueous solutions. Lokhande [17] explain in detail the reaction mechanism for the formation of ZnO thin films from CBD. In case of chemical deposition of ZnO films, Ennaoui et al. [11] have argued that the as-deposited ZnO film consists of mixture of $Zn(OH)_2$ and ZnO. During chemical deposition of ZnSe film, the presence of $Zn(OH)_2$ in the deposition bath is unavoidable due to the aqueous alkaline nature of the bath [18]. The $Zn(OH)_2$ can be converted into ZnO by air annealing at temperature in excess of 473 K [19]. However, the presence of $Zn(OH)_2$ could not be detected by Chatterjee et al. [20] from X-ray diffraction (XRD) studies for ZnO films deposited by SILAR method. They obtained single-phase ZnO films after air annealing at 623 K. Considering the presence of $Zn(OH)_2$ in as-deposited films, we report on the property changes brought of ZnO films after air annealing at 623 K. In the present work, textured ZnO thin films have been deposited using CBD method from aqueous alkaline medium. The ZnO films are annealed in air at 623 K for 2 h to study annealing effect on structural, optical and electrical properties.

2. Experimental

Preparation of ZnO thin film by chemical bath is based on the heating of alkaline bath of zinc salt containing the substrates immersed in it. The source of zinc used was 0.1 M $Zn(NO_3)_2$, and to make it alkaline, aqueous ammonia was added. Initially, precipitate of $Zn(OH)_2$ occurs which gets dissolved after further addition of aqueous ammonia. The pH of the resultant solution was 12. The glass micro slides were used as substrates, which were cleaned with detergent and chromic acid, followed by rinsing with double-distilled water and finally treated with ultrasonic waves for 15 min. These cleaned substrates were immersed in the above bath and the bath was heated. When the bath attains the temperature of 323 K, the precipitation was started in the bath. During the precipitation, heterogeneous reaction occurs on the substrate and deposition of ZnO took place on the substrate. The ZnO films were air heat-treated at 623 K for 2 h. The thickness of the ZnO film was measured by weight difference method using sensitive microbalance. Structural identification of ZnO film was carried out using X-ray diffractometer [chromium target (λ = 202895 Å)]. Microstructure of film was studied using scanning electron microscopy (SEM) 2.2895 Å. For this, the film was coated with gold–palladium (Au–Pd) using polaron SEM sputter coating with E-2500. The SEM micrographs were obtained with Cambridge stereoscan 250 MK-3 assembly. The optical absorption studies were carried out within wavelength range 300–850 nm for ZnO film using Systronics spectrophotometer-119, with glass substrate as reference. To determine the electrical resistivity, d.c. two-point probe method was used. Contact angle measurements for as-deposited and heat-treated ZnO films were carried out by sessile-drop method, in which water drop was observed through a microscope coupled goniometer (Phoenix 150, Surface Electro Optics, Korea). The 2 mL drops