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Nanocolumnar zinc oxide as a transparent conductive oxide film for a blue InGaN-based light emitting diode

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Abstract

A comprehensive study of ZnO nanocolumnar structure has been conducted through x-ray diffraction spectroscopy, atomic force microscopy, field emission scanning electron microscopy and UV-visible spectroscopy measurements. This study involves the development of an efficient ZnO transparent conductive oxide film fabricated by RF magnetron sputtering for use in a blue indium gallium nitride based light emitting diode. FESEM measurements revealed that a maximum growth temperature of 500 °C induced the formation of a nanocolumnar structure. The XRD measurements revealed that the stress reduction in the film also contributed to a superior ZnO nanocolumnar structure. In addition, the reduction of the oxygen percentage during deposition resulted in significant improvement of the structure. The reduced atomic peening effect yielded lower stress in the film. Thus, a dense, uniform-thickness, fine nanocolumnar ZnO of lateral size measuring 30 to 60 nm was successfully fabricated at the lowest oxygen percentage of 7%. This film also exhibited good transparency at the blue region with 78% optical transmission.

Keywords: Zinc oxide; Nanocolumnar; Transparent conductive oxide; RF magnetron sputtering

1. Introduction

Transparent conductive oxide (TCO) film is predominantly used in optoelectronic devices, such as solar cells and light emitting diodes (LEDs). In both applications, TCO film is deposited on top of the device structure and functions as a window for light to pass; in LEDs, the light is from the active region. Also, the TCO film acts as an ohmic contact for carrier transport in the device. Therefore, the TCO should consist of material with a large bandgap, as well as high transparency and conductivity. Metal oxide materials, such as indium tin oxide (ITO) and zinc oxide (ZnO), are usually used as the TCO material. This paper describes the fabrication of nanostructured TCO film based on pure ZnO material. The work was designed to examine the deposition of pure ZnO as a TCO film on a blue indium gallium nitride (InGaN)-based LED. The TCO films were used to improve the light extraction efficiency (LEE) of the LED. Many researchers have attempted to obtain an InGaN-blue LED with optimal characteristics, including producing a high LEE via a surface roughening technique. The p-GaN layer can be textured by a maskless wet-etching process [1], while the use of either electron-beam [2] or nanoimprint [3] lithography can be used to promote a rougher LED surface. A rough surface will improve the amount of light that is scattered out from the LED, thus enhancing the LEE [4]. However, such methods exhibit low manufacturing yields and involve high cost, which are not suitable for the industrial. In our work, the nanostructured TCO film is deposited on top of the LED structure to produce a rough surface. We aimed for a film with nanocolumnar structure so that, in addition to a high surface to volume ratio, the columnar structure will also act as

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waveguides that function as an internal lens and a path for the light to be emitted. Furthermore, the denser and finer nanocolumnar structure possessed by the film may be used to produce a more efficient TCO.

Besides ITO, we worked on ZnO due its unique properties, including wide direct bandgap of 3.37 eV, strong binding energy of 60 meV, high transparency, efficient transmission in the blue spectral region and the same wurtzite hexagonal structure as GaN. The sputtering technique was chosen for the growth method due to high probability of producing a columnar structure, as reported by others [5,6]. In addition, sputtering is regarded as a relative simple and economical approach for scalable industrial production. The properties of ZnO are critically related to the growth parameters [7,8]. Hence, in this study, ZnO films were deposited under several conditions to observe their effects on its properties, and particularly on its nanocolumnar structure. The goal of this study is the improvement of ZnO as a TCO film for application in a blue InGaN LED because this application has been less studied by others. The ZnO film is grown on silicon (Si) (1 1 1) because of the lattice matching to the hexagonal wurtzite structure, which simulates growth on the wurtzite structure of GaN. The finest, most uniform nanocolumnar ZnO film was found to be successfully obtained by only changing the growth parameters. Also, the crystalline structure and surface morphology of the films grown in this work were well-studied. Furthermore, the optical properties of the film are reported.

2. Experimental

The ZnO films were deposited onto Si(111) substrates using radio-frequency (RF) magnetron sputtering. The substrates were sequentially cleaned using acetone, propanol and deionized water and were blown dry with nitrogen gas. A ceramic target of ZnO of 5 N purity was used for sputter deposition. Prior to each deposition, the target was pre-sputtered for 10 minutes to remove the contaminants on the surface. The target-substrate distance was kept at 14 cm. The films were grown for 1 hour using a fixed RF power of 200 W and a working pressure of 5 mTorr. During deposition, the substrate holder was rotated at 8 rpm to obtain a uniform ZnO layer. Argon and oxygen were used as discharge and reactive gases, respectively. Two conditions are considered for investigating the nanocolumnar structure of ZnO in this study: 1) maintaining the oxygen at 33% from total percentage of argon and oxygen of 100% while varying the growth temperature from RT, 100 °C, 200 °C, 300 °C, 400 °C and 500 °C, and 2) the growth temperature was maintained at 500 °C while varying the oxygen percentage at 7%, 47%, 67% and 93%. The effects on the ZnO structural and morphological properties were characterized by x-ray diffraction (XRD) (Siemens D5000), atomic force microscopy (AFM) (Park System XE-100), field emission scanning electron microscopy (FESEM) (JOEL JSM-7600F), and UV-Visible spectroscopy (UV-Vis) (Perkin Elmer Lambda 750 UV/Vis/NIR).

3. Results and discussion

Fig. 1(a) shows a phase analysis based on the XRD patterns of ZnO films deposited at 33% oxygen percentage and under varying growth temperatures, T_G (room temperature – 500 °C). All the deposited films exhibit a polycrystalline nature, with high and low intensity peaks at 34° and 65°, respectively. The peaks at 34° and 65° were identified as (0 0 2) and (1 0 3) reflections of wurtzite structure, respectively, and are highly *c*-axis oriented.

By changing T_G, a distinct (0 0 2) peak intensity variation was observed, demonstrating the dependence of the ZnO structural properties on the temperature during deposition [9]. However, the film orientation was not affected. The intensity of the ZnO (0 0 2) peak became more intense and sharper with increasing T_G up to 300 °C due to the improvement of the ZnO crystallinity. Meanwhile, when T_G is greater than 300 °C, the intensity decreases gradually, which indicates that the degree of crystallinity of ZnO (0 0 2) is deteriorating. The observed trend is in agreement with most of the earlier studies on ZnO deposited by RF sputtering [6,9,10]. The (0 0 2) peak intensity enhancement was observed at T_G up to

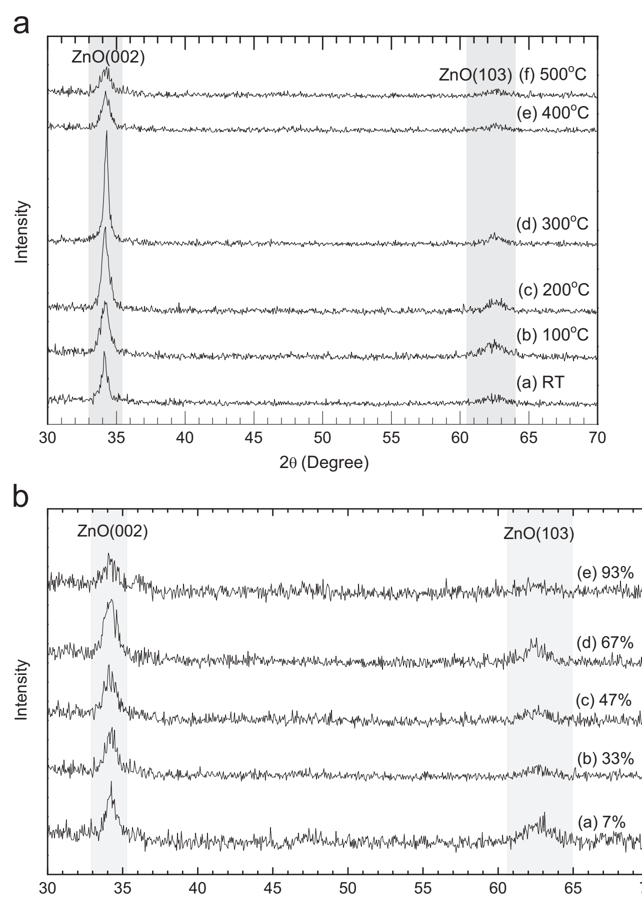

Fig. 1. (a)**.** Phase analysis based on the XRD patterns of ZnO films deposited at 33% oxygen percentage and under various growth temperatures (RT to 500 °C). Fig. 1(**b**)**.** Phase analysis based on the XRD patterns of ZnO films deposited at growth temperature of 500 °C and under varying oxygen percentages (7–93%).