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Effect of different solvents on the structural and optical properties of zinc oxide thin films for optoelectronic applications

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Abstract

Zinc oxide (ZnO) seed solutions were prepared using 4 different solvents, namely, methanol (MeOH), ethanol (EtOH), isopropyl alcohol (IPA) and 2-methoxyethanol (2-ME). The prepared seed solutions were used to synthesize ZnO thin films using a low-cost sol–gel spin-coating method. The effect of different solvents on the structural and optical properties of ZnO thin films was investigated by field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and an ultraviolet–visible–near infrared spectrophotometer (UV–vis–NIR). The images obtained in the FESEM and AFM showed that the thin film prepared using 2-ME has the smallest grain size. Moreover, the X-ray diffraction (XRD) results showed that the synthesized ZnO films are polycrystalline with preferred orientation along the (002) plane, whereas the IPA-derived films have a preferred orientation on (101) plane. The ZnO thin film synthesized with 2-ME has the highest transmittance (> 90%), lowest surface roughness of 3.131 nm and highest band gap energy of 3.28 eV. The experimental data are in agreement with the calculated results by specific models of refractive index.

Keywords: Zinc oxide; Solvents; Optical; Structural; Sol–gel

1. Introduction

Zinc Oxide (ZnO) is a well-known semiconductor that has wide direct band-gap (3.37 eV) at room temperature and large free excitation binding energy (60 meV). ZnO has high thermal stability, highly crystalline hexagonal structure, and high mechanical strength, which make it suitable for use as an electronic material in various fields such as bio-molecule sensor [1,2], ultraviolet (UV) detector [3], light-emitting diode [4], chemical and gas sensor [5,6], solar cell [7,8], and optoelectronic [9].

The nanoparticles in ZnO thin films act as a seeding layer in the formation of other nanostructures, such as nanowires [1,10], nanopores [11], nanorods [12], nanobelts [13], nanorings [14], nanocables [15], nanotubes [16,17], nanocolumns [18], nanocombs [19], and nanoneedles [20]. Therefore, ZnO has an important function in the growth of these nanostructures. Various methods are used in the deposition of ZnO thin films, such as spin-coating method [21,22], radio frequency sputtering [23], pulsed laser deposition, metal–organic chemical vapor deposition (MOCVD) [24], physical vapor deposition [25], spray pyrolysis [26], and ink-jet printing [27].

Previous research has shown that high-quality and uniform ZnO thin films are produced when deposited by sputtering methods and vapor phase techniques like MOCVD [21,28–30]. However, these techniques require complex and expensive experimental setups [28]. Therefore, a low-cost and simplified fabrication route for depositing ZnO thin films by sol–gel method is developed. This technique provides several advantages in terms of reliability, repeatability, low temperature, and ease of composition control. The optical, chemical, and structural properties of ZnO thin films are strongly dependent on precursors, solvents, temperature, and time. Thus, studying the effect of different solvents in the structural, morphological, and optical properties of ZnO thin films is important. Previous researchers have studied the

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effect of different solvents using isopropyl alcohol (IPA), methanol (MeOH), and 2-methoxyethanol (2-ME) [31]. However, few studies have published reports on ethanol (EtOH)-based ZnO thin films [32].

In this study, a low-cost spin-coating method was used in the synthesis of ZnO thin films on silicon oxide (SiO_2) substrate using different solvents. The aim of this current study is to investigate the effect of different solvents on the material properties. To the best of our knowledge, no published literature has analyzed the effect of different solvents on ZnO thin films and compared them with the specific models of refractive index.

2. Experimental

ZnO seed solution was prepared using zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (98%; Sigma-Aldrich), which was free from chlorine ions and used as a precursor. Different solvents were used without further purification, namely, MeOH (99.8%; Merck), EtOH (99.99%; J.T. Baker), IPA (99.5%; Sigma-Aldrich) and 2-ME (99.8%; Sigma-Aldrich). Monoethanolamine (MEA; 99%; Merck) was used as a stabilizer. To prepare ZnO seed solutions, 4.39 g of Zn $(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 100 ml of different solvents. The concentration of ZnO in all of the solutions was kept constant at 0.2 M. The mixed solution was then vigorously stirred with a magnetic stirrer at 60 °C for 30 min. MEA was added drop by drop to the milky ZnO solution with constant stirring at 60 °C for 2 h. Finally, homogenous and transparent ZnO solutions were obtained. The prepared solutions were stored at room temperature for 24 h. The process flow in the preparation of ZnO seed solution is shown in Fig. 1.

P-type silicon (100) wafer was used as a substrate to deposit the thin films. Three layers of ZnO thin films were deposited using the process shown in Fig. 1. Prior to the deposition process, the silicon substrates were ultrasonically cleaned with acetone and IPA. Buffer oxide etch solution was used to remove the native oxide layer from the substrates which were finally rinsed with deionized water. A SiO_2 oxide layer with ~180 nm thickness was grown on the cleaned substrate using wet oxidation process. In this process, the cleaned substrate was placed in the middle of the furnace at 1000 °C, with the water vapor continuously flowing into the tube furnace at a rate of 10 L/min for 1 h.

The stock solutions were spin coated on the pre-cleaned SiO_2/Si substrates at a spin rate of 3000 rpm for 20 s using a conventional photoresist spin coater. The coated layers were dried on a hot plate at 150 °C for 10 min. The coating-to-drying process of all the solvent-derived films was repeated 3 times. Using a conventional furnace, the coated films were annealed at 500 °C for 2 h in air.

The morphology of the ZnO thin films was examined using field emission scanning electron microscopy (FESEM; Carl Zeiss AG-ULTRA 55, Gemini). Crystallization and microstructures of the ZnO thin films were characterized using an atomic force microscope (AFM; SPA400-SPI3800, Seiko

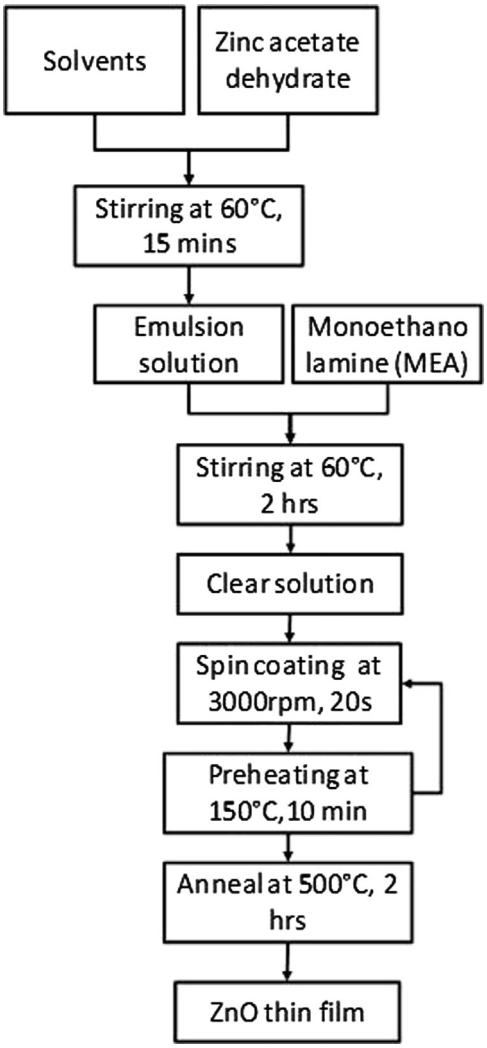

Fig. 1. ZnO thin films preparation process flow.

Instruments Inc., Japan) and X-ray diffraction (XRD; Bruker D8) with CuKα radiation from 30° to 70° 2θ operated at 40 kV and 40 mA. The elemental stretching vibration was analyzed using Fourier transform infrared (FTIR; Perkin-Elmer Spectrum 400 spectrometer) within the range of 400–2000 cm^{-1}. Optical transmittance measurements were carried out using an ultraviolet–visible–near infrared spectrophotometer (UV–vis–NIR; Perkin-Elmer Lambda 950) with a slit width of 2 nm at normal incidence. All measurements were carried out at room temperature.

3. Results and discussion

The surface morphology of the ZnO thin films coated by different solvents is shown in Fig. 2. The obtained FESEM images show that all the ZnO thin films consist of nanoparticles with diameters less than 50 nm. ZnO crystalline grains with hexagonal morphology consistently appear on the substrate surfaces. The different degrees of brightness of the grains indicate the presence of multiple layers of ZnO on the substrates. The brighter grains represent the upper layer of