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Metamorphosis of strain/stress on optical band gap energy of ZAO thin films via manipulation of thermal annealing process

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ABSTRACT

We report on the growth of Al-doped ZnO (ZAO) thin films prepared by the sol–gel technique associated with dip-coating onto Corning 7740 glass substrates. The influence of varying thermal annealing (T_a) temperature on crystallisation behaviour, optical and electrical properties of ZAO films has been systematically investigated. All films are polycrystalline with a hexagonal wurtzite structure with a preferential orientation according to the direction ⟨0 0 2⟩. The metamorphosis of strain/stress effects in ZAO thin films has been investigated using X-ray diffraction. The as growth films have a large compressive stress of 0.55 GPa, which relaxed to 0.25 GPa as the T_a was increased to 500 °C. Optical parameters such as optical transmittance, absorption coefficient, refractive index and optical band gap energy have been studied and discussed with respect to T_a. All films exhibit *a* transmittance above 80–90% along the visible–NIR range up to 1500 nm and a sharp absorption onset below 400 nm corresponding to the fundamental absorption edge of ZnO. Experimental results show that the tensile stress in the films reveals an incline pattern with the optical band gap energy, while the compressive stress shows opposite relation.

1. Introduction

As far as nanomaterials are concerned, ZnO is one of the versatile and technologically interesting semiconducting materials which has been attracting attention due to its numerous interesting properties such as direct band gap (E_g~3.37 eV) semiconductor with a large exciton binding energy of about 60 meV which makes excitons stable even above room temperature, high transparency in the visible wavelength, wide range of resistivity which can extend from 10^{-4} to 10^{12} Ω cm, the abundance of its components in nature, its non-toxicity and bio-compability [1–3]. Besides that, ZnO has a good thermal and chemical stability, specific electrical and optoelectronic properties for solar cell [4,5], light emitting diodes [6], energy efficient windows, electrochromic displays (ECDs), liquid crystal displays (LCDs), sensors [7], and immobilisation of biomolecules.

ZnO crystallises in a wurtzite structure and exhibits *n*-type conductivity which might be caused by intrinsic defects, zinc interstitials and oxygen vacancies [8]. Hexagonal wurtzite structure consists of oxygen atoms which are arranged in a hexagonal close packed type with zinc atoms occupying half the tetrahedral sites. In this structure, due to the sp3 hybridisation of the oxygen 2p orbital and the zinc 3d orbital, each atom of one kind is surrounded by 4 corresponding atoms of another kind in the tetrahedron located at the corners. Due to the tetrahedral coordination of the wurtzite structure, the bonding distance of the nearest neighboured 4 corresponding atoms is the same and the next nearest neighboured 12 same kinds of atoms are also identical.

The atomic arrangement of alternating planes of zinc and oxygen leads to spontaneous polarisation along the *c*-axis. The reason for this difference between the ideal and the real ratios may be the lattice stability and ionic character, which is dependent on the difference in electronegativity of the constituent atoms [9]. In addition, the lattice spacings are a=3.2498 Å and c=5.2066 Å where their ratio is c/a~1.6 which is close to the ideal value for hexagonal cell. Stoichiometric ZnO films are highly resistive, but the conductivity can be enhanced either by

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introducing oxygen vacancies which act as donors or by doping with group III elements as aluminium (Al), gallium (Ga) or indium (In) [10]. Al was preferable as a dopant source because the ionic radius of Al^{3+} ions (0.54 Å) is much smaller compared to Zn^{2+} (0.74 Å) which are more favourable to occupy the interstitial site in advance [11].

Variety of deposition techniques have been widely used to produce ZnO based thin films such as DC and RF magnetron sputtering [12–14], spray pyrolysis [11], pulsed laser deposition (PLD) [15,16] and metal organic chemical vapour deposition (MOCVD) [17]. Among all the deposition techniques, magnetron sputtering is generally agreed and accepted as an optimum deposition technique for preparing ZnO based film. However, the sputtering process demands a complicated, complex and a very expensive vacuum technique. Besides, this deposition process has to deal with various challenges for large area coating especially for the film deposition on substrates that require the characteristics of complex geometry. In this sense, the sol–gel method is a rather efficient, most reliable and economic deposition technique that can easily overcome these issues and has attracted much attention among the researchers in recent years [18–21].

The properties of ZAO films deposited by the sol–gel dip coating technique are determined by one of the essential parameters which is thermal annealing temperature, T_a. Although there are already many reports on the sol–gel deposition of ZAO films, relatively little is known about the structural, optical and electrical evolution during the T_a process of the film. The main goal of this research study is to examine the influence of T_a temperature on the structural and optical properties of ZAO films. A detailed study of strain/stress in the film would be worthwhile which can impart pragmatic information regarding the formation of defect, and to this end, the authors firmly believe that such knowledge is very important fora better understanding and improvement of high-quality film and for the fabrication of ZnO based devices.

2. Experimental procedure

ZAO thin films were prepared by the sol–gel method associated with dip-coating. Zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$; Merck] was used as a starting material. 2-Methoxyethanol [$C_3H_8O_2$; Merck] and aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$; Analar] were used as a solvent and dopant source, respectively. Aluminium nitrate nonahydrate was added into the ZnO solution at 1 at%. Finally, monoethanolamine, MEA [C_2H_7NO; R&M] was added dropwise into the solution as a sol stabiliser. The molar ratio of zinc acetate dihydrate to MEA was kept at 1:1 and the concentration of zinc acetate was 0.4 M. The resultant solution was stirred at 80 °C for 1 h to yield a clear and homogeneous solution. Afterwards, the solution was sonicated at 50 °C for 30 min using an ultrasonic water bath (Hwasin Technology Powersonic 405, 40 kHz) which served as the coating solution after cooling to room temperature.

The glass sheets were then dipped into the solution and withdrawn at a rate of 40 mm min^{-1}. To facilitate film thickness measurements, a section of the substrate was covered by adhesive tape which was subsequently peeled off after the deposition process. The coated substrate was heated at 300 °C for 10 min in a closed furnace after each dipping procedure to evaporate the solvent and remove organic residuals. If preheating temperature was below 300 °C, a random preferential growth will appear due to incomplete vaporisation and thermal decomposition of the precursor. All the samples in this study have undergone this procedure for five times altogether, therefore, leading to an initial

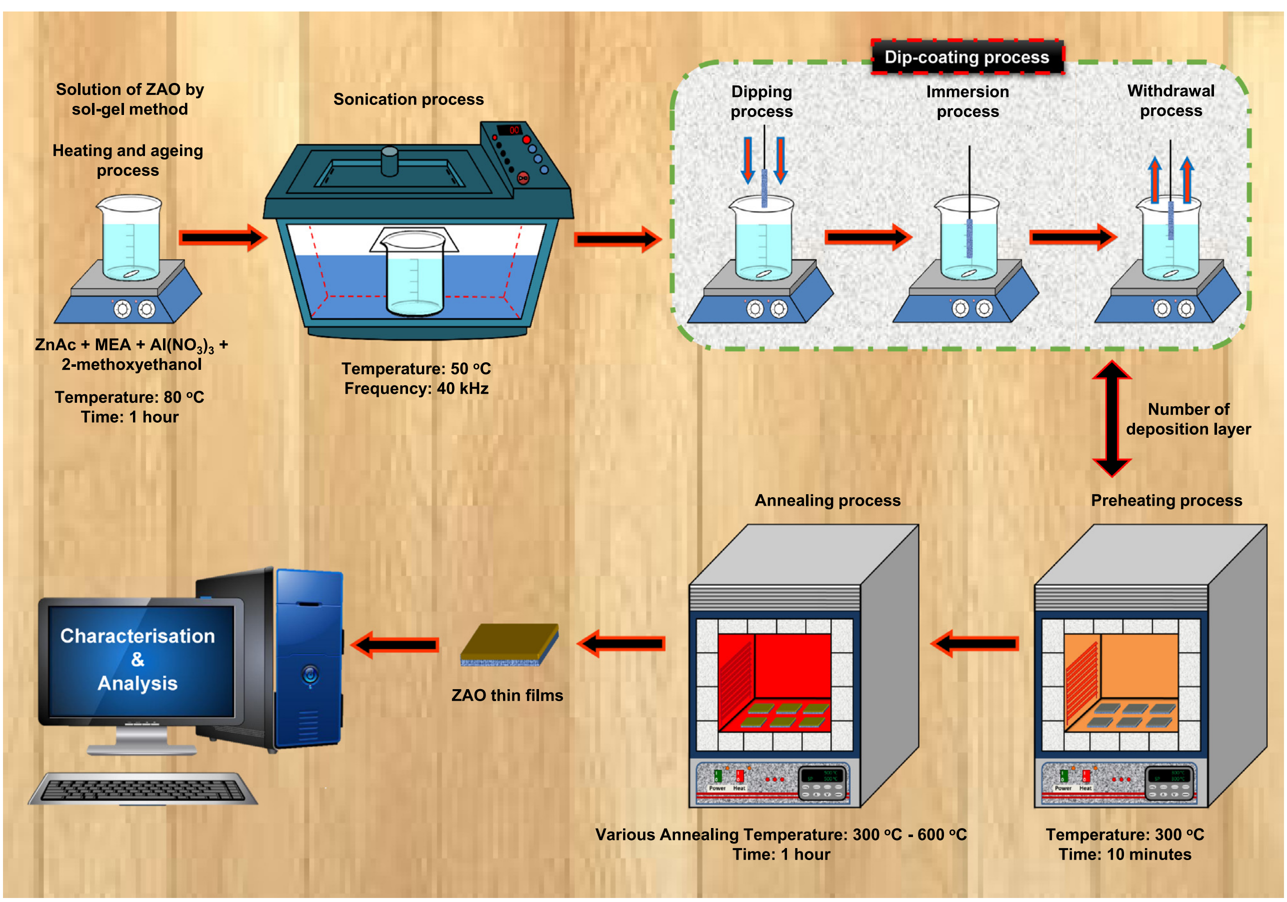

Fig. 1. Schematic diagram of ZAO thin film preparation procedure at various T_a temperatures.