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Growth and characterization of ZnO and $Mg_xZn_{1-x}O$ thin films by aerosol assisted chemical vapor deposition technique

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ABSTRACT

Poly crystalline thin films of ZnO and $Mg_xZn_{1-x}O$ have been deposited on glass substrates with varying Mg-content under constant growth parameters. Aerosol assisted chemical vapor deposition technique has been adopted for the deposition of thin films in which we use the solution of zinc acetyl acetonate and magnesium acetate in isopropyl alcohol and O_2 is used as the carrier gas. The depositions have been carried out at 480 °C. The films were found to exhibit high transmittance (>90%), low absorbance and low reflectance in the visible regions. Absorption coefficient and thickness of the films have been determined from transmittance spectra in the ultraviolet–visible-near infrared regions by applying widely used envelope method. The energy band gap of the deposited samples increases from 3.25 to 3.75 eV, with increasing Mg content in the films. The crystallographic structure of these films was analyzed by using x-ray diffraction method. The films were poly-crystalline in nature with preferred $(00\bar{1}1)$ orientation perpendicular to substrate surface. A systematic change in surface morphology is observed with increasing Mg content in the films.

1. Introduction

The growth and characterization of ZnO and ZnO based alloys e.g. $M_xZn_{1-x}O$ (M = Mg, Cd and Mn etc.) have become an active research field due to the wide ranging applications of the above materials in the fabrication of light emitting diodes, UV-photo detectors, UV-blue semiconductor lasers, flat panel displays, solar cells, gas sensors, photo-voltaic cells and transparent electrodes [1–3]. Since the oscillator strength of excitons is typically much larger than that of direct electron–hole transitions in direct band gap semiconductors, the large exciton binding energy of ZnO (60 meV) compared to GaN (25 meV) makes it a promising material for optical devices utilizing excitonic effects. Optically pumped lasing has been reported in ZnO platelets, thin films, clusters consisting of ZnO nano-crystals and ZnO nano wires [4–6]. Recently, several near ultraviolet diode sources have been reported that utilize the GaN material system [7]. As an alternative to the GaN material system, ZnO alloys are of great interest. Alloying ZnO films with MgO or CdO permits the band gap to be tailored between 2.8 and 4 eV, which facilitates band gap engineering [8]. This also suggests the possibility of hybrid optoelectronic devices comprising lattice-matched MgZnO/AlGaN heterojunctions. Although the crystal structure of ZnO is hexagonal, whereas that of MgO is cubic, the near equality of ionic radii of Mg^{++}(1.36 Å) and Zn^{++} (1.25 Å) allows some replacement in either structure [9]. According to the phase diagram, MgO allows a maximum of 56 wt.% ZnO at 1600 °C and maintains its NaCl structure with the lattice constant remaining close to that of pure MgO (4.208 Å) [10].

In the case of bulk ZnO, the bulk solid solubility of Mg is limited to only maximum 2%, and the unit cell retains its hexagonal structure [11]. However, the solubility of Mg in ZnO thin films has been reported to have different values, e.g. Ryoken et. al. [12] have reported the stable wurtzite formation up to $x = 0.18$ by pulsed laser deposition (PLD) technique. Kang et al. [13] have reported the solubility limit to be up to $x = 0.4$ by magnetron sputtering technique. Ohtomo et al. [14] have reported this limit to be up to $x = 0.36$ by PLD technique. Besides the above reports, $Mg_xZn_{1-x}O$ films have also been deposited by metalorganic chemical vapor deposition [15], molecular beam epitaxy [16], sputtering [13,17], spray pyrolysis [18], etc. In the present work, we have employed the aerosol assisted chemical vapor deposition (AACVD) technique for the growth of $Mg_xZn_{1-x}O$ films on soda lime glass substrates. AACVD is an attractive technique due to its low cost, simplicity, minimal waste production and the possibility of injecting liquid precursor or solid precursor dissolved in suitable solvents in the CVD reactor for growth of thin films. This technique becomes specifically beneficial for liquid/solid precursors with very low vapor pressure.

There are a few reports on the use of AACVD technique for the deposition of ZnO, ZrC, F:SnO_2, α-Fe_2O_3 thin film electrodes, yttria

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stabilized zirconia [19–23] etc. In this technique, a nozzle of extremely fine dimensions is used to inject the solution of the precursor directly onto the heated substrate. Using AACVD technique, we have been able to incorporate up to 20 wt.% Mg in ZnO while maintaining the wurtzite hexagonal structure. The crystalline structure and the surface morphology of ZnO films were investigated using X-ray diffraction (XRD) and atomic force microscopy (AFM) respectively. The optical properties of the films were studied via optical spectrophotometery. In this paper, we report the deposition of single phase wurtzite $M_xZn_{1-x}O$ thin films up to $x = 0.2$.

2. Experimental technique

In the present work, we have used an indigenously developed aerosol assisted chemical vapor deposition (AACVD) system for the growth of thin films of ZnO and $Mg_xZn_{1-x}O$. The schematic of the AACVD system is shown in Fig. 1. The system consists of a horizontal SS-304 cylindrical reactor, where the growth is carried out at atmospheric pressure. The precursor was dissolved in a suitable solvent and used as the source of the depositing material. This liquid precursor was injected into the reactor through a fine nozzle having an orifice of ≈500 μm diameter the schematic of which is also shown in the same figure. Oxygen gas was used as the carrier gas for the injection of the liquid precursor in the form of an aerosol inside the reactor. The flow rate of the precursor was controlled by varying the flow of carrier gas (O_2). The precursor, in the form of aerosol, flows close to the horizontally placed heated substrate and cracks homogeneously to form the required thin film. The temperature of the substrate is monitored by a thermocouple and the temperature was maintained within ±1 °C.

The substrate surface is placed at an angle ≈10° to the horizontal planes to ensure the deposition of uniform films. For the growth of $Mg_xZn_{1-x}O$, different mass proportions of Mg acetate ($Mg(CH_3COO)_2$) and zinc acetyl acetonate ($Zn(C_5H_7O_2)_2 \cdot H_2O$) were dissolved in isopropyl alcohol (IPA) and are used as precursors. For dissolving the solute, IPA was heated to its boiling point and the solution was stirred for about 15 min. The mass ratio of Mg to Zn in the precursor solution is henceforth referred to as x_{liquid}. This prepared precursor solution was transported through a fine nozzle with the help of oxygen gas at a constant flow rate of 0.5 lpm. The growth temperature was kept at 480 °C. Before growth, the deposition chamber was purged with oxygen gas for 10 min at a flow rate of 0.5 lpm. Soda lime glass substrates (1″×1″) were used for the deposition of the films.

The substrates were cleaned by boiling in trichlorothylene, acetone and methanol for 2 min each, prior to deposition. Transmission spectra of the films were obtained using a UV–Visible-NIR spectrophotometer (Shimadzu 1700UV) in the range of 250 nm to 900 nm.

The crystalline structures of the various films were determined from the θ–2θ patterns obtained using a Panalytical X-Pert PRO MRD system. The system uses a 2.2 kW X-ray generator and the measurement were carried out with copper K_α source. AFM measurements were carried out in a SOLVER-PRO setup (NT-MDT) using Si cantilever tips of radius of curvature ≈20 nm and resonant frequency ≈190 kHz in non-contact mode of measurement. Variation of Surface morphology and roughness of the films with respect to Mg content were determined.

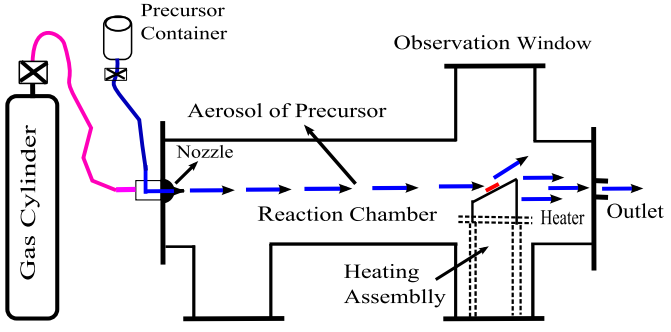

Fig. 1. Schematic of indigenously designed AACVD system.

3. Results and discussions

3.1. Optical characterization

The transmittance spectra of the deposited thin films of ZnO and $Mg_xZn_{1-x}O$ are shown in Fig. 2. Transmittance of the substrate is also shown in the same figure. The presence of interference fringes and a sharp absorption edge can be seen in all the films. Absorption edges have been highlighted in the inset shown in Fig. 2. Good optical qualities of $Mg_xZn_{1-x}O$ films are grown irrespective its Mg content. As expected, the sharp band edge absorption feature shifts to lower wavelengths (blue shift) with increasing Mg concentration [24]. The thickness of the deposited films was evaluated from the transmission data by using envelope method [25] and the respective values are given in Table 1. It appears worthy to note that the error bars for the measured thickness is only a few percent and depends upon the degree of accuracy of the measured refractive index. The absorption edge has been determined for all the films by the well established Tauc plot method, which are shown in Fig. 3 and used to calculate the band gap of films. The band gaps obtained for all the films have been compared with those available in literature [11] for the estimation of Mg/Zn ratio in the films (referred as x_{solid}). The observed values of x_{solid} for all the films are also mentioned in Table 1.

3.2. Structural characterization

The X-ray diffraction patterns of all the films obtained in the conventional Bragg-Brentano geometry. The obtained data indicates that all the $Mg_xZn_{1-x}O$ films are polycrystalline. Respective *(hkil)* values for all the peaks are indicated in Fig. 4. It is important to note that no extra peaks corresponding to the MgO phase is observed in the measured 2θ range that conform the deposition of single phase polycrystalline $Mg_xZn_{1-x}O$ ternary in the range of x_{solid} studied in this work. Although the growth of ZnO thin films mainly occurs along the c-axis $(00\bar{0}1)$.

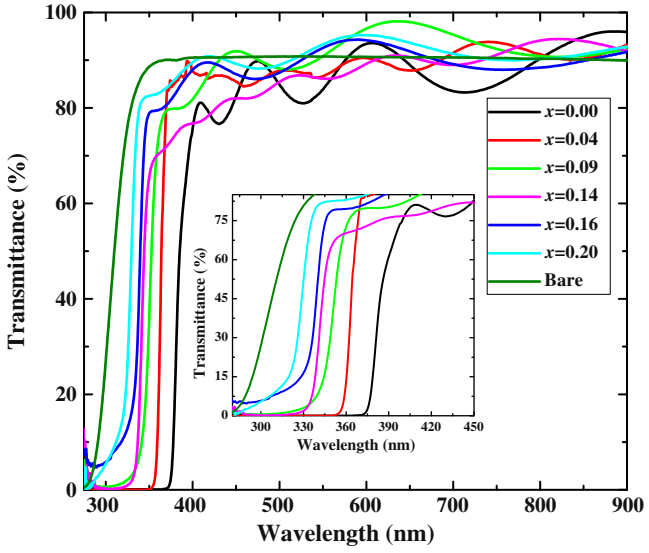

Fig. 2. Transmittance spectra of $Mg_xZn_{1-x}O$ thin films with varying Mg content (x_{solid}). Inset shows the range close to the band edge of the thin films.