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Pulsed laser deposition and optical band gap engineering in multinary transparent conducting oxide thinfilms

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ABSTRACT

Synthesis of ternary and multinary oxide-based films offers the possibility of tuning electrical and optical properties of the existing materials over wide range. Here we report about synthesis and characterization of $Zn_{1.9}Sn_{0.9}In_{0.1}Ga_{0.1}O_4$, $Zn_{1.9}Sn_{0.9}In_{0.2}O_4$, and $Zn_{1.9}Sn_{0.9}Ga_{0.2}O_4$ grown by a pulsed laser deposition method. These compounds have been synthesized on the base of Zn_2SnO_4 by substituting Zn^{2+} and Sn^{4+}cations with group-III elements such as In^{3+} and Ga^{3+}. The newly synthesized films are shown to possess a very smooth surface with lower RMS components and exhibit dense grown crystallites with homogenous distribution of small grains. Highly textured growth of inverse cubic spinel structured thinfilms along (111) direction is identified from X-ray diffraction studies. Raman analysis provided supplementary evidences for XRD results. Giant increases of the band gap from 3.60 eV to 3.90 eV have been reported by the development of multinary compounds. The electrical features obtained from Van der Pauw Hall measurements show enhanced charge carrier mobility, resistivity and moderate charge carrier concentrations.

1. Introduction

Transparent and conducting thinfilms are technologically important materials because of its numerous device applications as electrode materials in thinfilm transistors, organic light emitting diodes (OLEDs), LEDs, thin-film photovoltaic, flat-panel displays, polymer-based electronics and architectural windows [1–3]. They require energy efficient transparent conducting contacts for their proper functioning, since, most of these devices utilize the phenomena of light induced electricity or vice versa [3–6]. Materials derived from various metal oxides (TCOs), thin metal films, sulfides, selenides, nitrides, nanocomposites, graphenes and polymers are reviewed as efficient candidates for many practical purposes [2]. However, among these materials, TCOs exhibit more thermal stability, easy to deposit and possibility of synthesizing of new transparent conducting materials (TCM) with controllable properties [2]. Engineering of multicomponent oxides composed of binary and/or ternary compounds might offer possibility of tuning material properties in a suitable desired manner [7–8]. Zinc stannate (Zn_2SnO_4), a binary compound with Inverse cubic spinel structure is one of the suitable candidates for multication compound engineering since it exhibit very high optical transmittance and *n*-type electrical conductivity as a result of its intrinsic deviations

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from the actual stoichiometry [7]. As per the earlier investigations, the largest measured Hall mobility for a Zn_2SnO_4 thin-film was around 26 $cm^2 V^{-1} s^{-1}$, carrier concentration of 6–20 × 10^{-18} cm^{-3} and a sheet resistance of the order of 10^{-2} Ω cm [9]. Most of these results are observed for amorphous ZTO. However, crystalline Zn_2SnO_4 is a transparent high resistive semiconductor (~10^2 Ω cm) and non-stoichiometric with chemical formula $Zn_{2-x}Sn_{1-x}O_{4-\delta}$, in cation and anions sub lattices [7]. This opens up a way for modulating the electrical and optical properties of the material by partial coupled aliovalent substitution of elements. In ZTO, Zn^{2+} ions distributed equally at octahedral and tetrahedral sites of inverse cubic structure can be substituted with In^{3+}/Ga^{3+} ions or both. Such a doping might lead to the development of new types of TCOs. Herein this article, we report the synthesis of different compositions of $Zn_{2-x}Sn_{1-x}(In_{2x}/Ga_{2x})O_4$ and $Zn_{2-x}Sn_{1-x}In_xGa_xO_4$ thin-films by pulsed laser deposition technique. We also present the studies and analysis of the films by means of its crystal structure, surface morphology and chemical compositions as well as optical band gap engineering by substituting Zn and Sn by group-III impurities.

2. Experimental

The targets for thinfilm deposition were synthesized by high temperature solid state reaction route from the appropriate quantities of high purity (99.999%) powders of ZnO, SnO_2, In_2O_3 and Ga_2O_3 purchased from Sigma Aldrich USA. The heating was performed in cylindrical alumina crucibles in air, between 1000 °C and 1275 °C for several hours with different intermediate steps of heating, grinding and densification [7]. The powder X-ray diffraction technique (Rigaku Miniflex diffractometer) is used to verify the dilution of In^{3+} ions and Ga^{3+} ions is the host crystal matrix. Thinfilms are then grown from the phase-pure hot pressed ceramic targets by PLD method. PLD was accomplished with a 248 nm KrF Excimer Laser source (Lambda Physik-COMPEX-201) with a repetition rate of 10 Hz and pulse laser energy of 220 mJ, for 20 min and the target was rotated at 5-rotations per minutes about its axis to prevent localized heating. The target was mounted at an angle of 45° to the laser beam inside vacuum chamber, where a base pressure of 1 × 10^{-5} Torr was achieved through a turbo mechanical pump rotated at 10 rpm. All the films were grown under optimized conditions on single phased pre-cleaned amorphous quartz substrates; the target-substrate separation was fixed at 5 cm, in an O_2 ambient at a pressure of 15 mTorr. The substrates were attached to a resistively heated holder with silver adhesive paste and the deposition temperature was fixed at 750 °C. After the deposition, the thin films were allowed to cool naturally to the room temperature in the same oxygen environment as used for the deposition. Cu-Kα – X-ray diffraction (XRD) pattern of the compounds was recorded by Rigaku Miniflex diffractometer, with slow scanning rate in the Bragg angle range of 10–65°. PowderX, PDXL: Integrated X-ray powder diffraction software and ICDD data base were used for phase determination, peak reflection assignments and to analyse variations in peak positions and intensities [10]. Raman measurements were executed on the samples with a Raman spectrometer Model HR-800 Jobin Yvon employing a He–Ne laser (λ=488 nm) beam. The surface topography was examined in true Non-Contact Mode by Park AFM XE 70 system and energy dispersive spectra were employed for chemical composition analysis. Lambda-35 Perkin-Elmer UV–vis spectrophotometer in transmittance mode was used for optical characterization in the UV–visible region. Resistivity, charge carrier concentration and Hall mobility were obtained by means of Ecopia HMS-3000, Hall Effect measurements set up using the Van der Pauw configuration.

3. Results and discussion

3.1. Structural and surface morphological characterization

Fig. 1 displays Bragg's X-ray reflections of both bulk and the thinfilm samples of multication compounds; the reflection of peaks corresponding to each phase is also indicated in the figure. The peaks originated from the planes (111), (220), (311), (222), (331), (422), (511), (440) and (531) are the reflections of face centered cubic (fcc) Zn_2SnO_4(International Centre for Diffraction Data, ICDD: 00-024-1470) with structural formula 2ZnO.SnO_2, in the space group F*d3m* (227), by Sn^{4+} ions located in octahedral co-ordination, whereas 50% of the Zn^{2+} ions are in octahedral coordination and the rest are in tetrahedral coordination [7]. The compounds $Zn_{1.9}Sn_{0.9}In_{0.2}O_4$, $Zn_{1.9}Sn_{0.9}Ga_{0.2}O_4$ and $Zn_{1.9}Sn_{0.9}Ga_{0.1}In_{0.1}O_4$ exhibit structural properties similar to that of Zn_2SnO_4 with some distortions at the positions of the peaks. The XRD patterns do not indicate signatures of either In_2O_3or Ga_2O_3, due to the absolute dilution of them in the spinel zinc stannate lattice. Exceptional crystalline growths of thinfilms were identified from XRD spectra of thinfilms with characteristic inverse cubic spinel structure grown predominantly along (111) direction. For spinel thinfilm compounds, the growth of crystallites along (111) direction is the most favored. This offers highly textured films compared to the other crystallographic planes as it offers lower surface energy and greater oxygen packing density, which is a well-established result in spinel thin films [11–12]. Undoped films of Zn_2SnO_4 exhibit sharp well-defined peaks from (111) and (222) planes, however, other well defined characteristic spinel emissions are also observed from (220), (311), (440) and (511) planes. The thin films of $Zn_{1.9}Sn_{0.9}In_{0.2}O_4$, $Zn_{1.9}Sn_{0.9}Ga_{0.2}O_4$ and $Zn_{1.9}Sn_{0.9}In_{0.1}Ga_{0.1}O_4$ show similar structural features. Both (111) and (222) are parallel planes and growth along this direction is an ideal surface feature for two dimensional face centered cubic lattices. The absences of additional peaks are evidence for coupled aliovalent substitution in the films. Apparently, variations in terms of peak positions, peak intensities, FWHM and number of peaks were resulted because of this. By an effective substitution, a good amount of conduction electrons and oxygen vacancies are generated and this could contribute to the property enrichment in the multicomponent TCOs.

Undoped ZTO powders exhibit Raman active modes at 527.95 cm^{-1} and 669 cm^{-1}, which correspond to the spinel structure of Zn_2SnO_4. These two strong Raman active modes are well known ZTO peaks and were assigned previously to the highly inverse nature of