

Micro-strain, dislocation density and surface chemical state analysis of multication thin films

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Abstract

Multication complex metal oxide thin films are rapidly expanding the class of materials with many technologically important applications. Herein this work, the surface of the pulsed laser deposited thin films of Zn_2SnO_4 and multinary compounds based on Zn_2SnO_4 obtained by substitution/co-substitution with In^{3+} and Ga^{3+} are studied by X-ray photoelectron emission spectroscopy (X-PES) method. Peak asymmetries, complex multiplets splitting, shake-up and other surface states of elements of Zn, Sn, Ga, In and O on the film surface has been identified and contribution of the elements has been studied by the computer aided surface analysis (CASA) software. $Zn2p$, $Sn3d$ and $In3d$ electrons exhibit doublet peaks due to the interaction of the spins of the electrons with their orbital angular momentum. The emission of these metal species are found to possess symmetric peak shape owing valence stability, however, for $O1s$ and $Ga3d$ spectra the curve-fitting procedure was established to ascertain its ionic state in film surface. Binding energies, full-width at half maximum (FWHM), spin-orbit splitting energies, asymmetric peak-shape fitting parameters and quantification of elements in the films are discussed. Studies of structural properties of the films by x-ray diffraction (XRD) technique showed inverse spinel type lattice with preferential orientation. Micro-strain, dislocation density and crystallite sizes in the film surface have been estimated.

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1. Introduction

Because of the technologically important properties such as transparency to visible light and good electrical conductivity, transparent conducting materials (TCM) have found diverse optoelectronic device applications^[1-4]. Classic TCMs used in the semiconductor industry are based on oxides of elements with five closely grouped d^{10} cations (Zn, Sn, In, Ga and Cd)^[5]. Sn-doped In_2O_3 is most widely used transparent conducting oxide (TCO), Al-doped ZnO and Ga-doped ZnO have also been reviewed many times^[6-8]. Search of novel TCOs has led to the development of multication materials, which are based on combinations of divalent $2+$ (e.g., Zn^{2+} and Cd^{2+}), trivalent $3+$ (e.g., In^{3+} and Ga^{3+}) and tetravalent $4+$ (e.g., Sn^{4+}) cations^[9]. These combinations are known as ternary and multinary TCOs^[10]. In this paper, we discuss the structural properties and electronic structure of the thin films of the multication metal oxides. We deposited two compounds in (2-4-3) cation coordination and one in (2-4-3-3) coordination by pulsed laser deposition technique on quartz substrate^[11]. Cubic spinel structured Zn_2SnO_4 (ZTO) known also as zinc stannate, is selected as the parent material. The ZTO films possess wide band gap with high optical transmittance to visible light, are chemically stable and exhibit high electrical resistivity, so that they can be used as buffer layer in thin film solar cells^[12]. Meanwhile, ZTO exhibit pronounced non-stoichiometry with chemical formula $\text{Zn}_{2-x}\text{Sn}_{1-x}\text{O}_{4-\delta}$ and at high temperatures permits aliovalent substitutions and co-substitutions of by $\text{In}^{3+}/\text{Ga}^{3+}$ through solid state reactions^[10]. High temperature solid state reaction of ZnO, SnO_2 , In_2O_3 and Ga_2O_3 results in the development of $\text{In}^{3+}/\text{Ga}^{3+}$ substituted Zn_2SnO_4 (2-4-3) and $\text{In}^{3+}+\text{Ga}^{3+}$ substituted Zn_2SnO_4 (2-4-3-3) ceramics^[10]. As reported in our previous article the average optical transmittance of these films was $\sim 85\%$ with electrical resistivity of $264 \Omega \times \text{cm}$ in Zn_2SnO_4 , which was reduced to the order of $\sim 10^{-1} \Omega \times \text{cm}$ ^[11]. In all cases, regardless of the modest n -type carrier concentrations, the magnitude of mobility of electrons measured experimentally was much higher. The reported charge carrier mobilities are $20.06 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for Zn_2SnO_4 , $75.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for $\text{In}^{3+}/\text{Zn}_2\text{SnO}_4$, $21.25 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for $\text{Ga}^{3+}/\text{Zn}_2\text{SnO}_4$, and $70.02 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for $\text{In}^{3+}+\text{Ga}^{3+} \text{ Zn}_2\text{SnO}_4$ ^[11]. In this paper, we report about structural properties, electronic structure, and surface profile of thin films of complex metal oxides synthesized by pulsed laser deposition method.

2. Experimental Procedure

The thin films of the compounds are grown on quartz substrate by common optimized deposition conditions. Previously we have reported the structure, optical and electrical features of these materials ^[11]. The targets for thin film deposition were synthesized by high temperature solid state reaction route of the appropriate quantities of high purity powders of ZnO, SnO₂, In₂O₃ and Ga₂O₃ (Sigma Aldrich-99.999%). 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. Thin-films are then grown from the structurally phase pure hot pressed ceramic targets by PLD method. PLD was accomplished with a 248nm KrF Excimer Laser source-(Lambda Physik-COMPEX-201) with a repetition rate of 10 Hz and pulse laser energy of 220mJ, the target was rotated at 5-rpm about its axis to prevent localized heating. The target was mounted at an angle of 45° to laser beam inside vacuum chamber, where a base pressure of 1×10^{-5} Torr was achieved through a turbo mechanical pump and rotated at 10 rpm. All the films were grown under the optimized conditions on single phased pre-cleaned amorphous quartz substrates; the target-substrate separation was fixed at 5cm, in an O₂ ambient at a pressure of 15mTorr. 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-K α - XRD pattern were recorded on Rigaku Miniflex diffractometer, with slow scanning rate in the Bragg angle range 10-65°. The opto-electrical features of the films reported previously by us were also indicated in the article; however the core discussion is limited on film surface chemical state and how it signifies the results attained. The XPS was carried out by Thermo Scientific Multilab 2000 equipment with a standard Mg K α (1253.688eV) source excitation. Energy drift due to charging effects was calibrated, taking the C1s (284.05 \pm 0.1eV) core-level spectrum. Spectra were analyzed for percentage of elements using CASAXPS software ^[13]. Gaussian–Lorentzian (70%-30%), defined in CasaXPS as GL (30), profiles were used to fit the components. The composition Peak fitting, error estimation in XPS spectra and orbital energy level splitting observed in the spectrum were deconvoluted by using PEAKFIT41 software. A standard Shirley background is used as the baseline for fitting the narrow scan spectra. A reduced “chi-squared” parameter ranged from 0.5 to 1.5 is obtained for asymmetric

peak fitting, which establishes the goodness of XPS peak-fit. NIST database is also used to evaluate the binding energy and binding energy shifts^[14].

3. Results and discussions

3.1. Structural, micro-strain and dislocation density analysis

Figure 1 displays the Bragg's x-ray reflections of ZTO and its derivatives. Analysis shows that the results correspond to inverse cubic spinel crystal symmetry of face-centered cubic (fcc) type lattice and are consistent with the standard XRD data for Zn_2SnO_4 in the International Centre for Diffraction Data, ICDD: 00-024-1470. The lattices possess the space group $Fd3m$ (227). According to the database, Sn^{4+} ions are located in octahedral co-ordination, 50% of the Zn^{2+} ions are in octahedral coordination and the rest Zn^{2+} are in tetrahedral coordination^[10]. The multication In^{3+} and Ga^{3+} containing films exhibit structural properties that are similar to that of Zn_2SnO_4 . The XRD patterns of the films do not indicate signatures of either In_2O_3 or Ga_2O_3 which might indicate substitution of Sn^{4+} with In^{3+}/Ga^{3+} in the spinel ZTO lattice. The analysis of XRD spectra shows that the films were grown along (111) plane, this feature of spinel thin films are evidences of fine texture, low surface energy and large oxygen packing density, which is a well-established result in spinel thin films^[11]. Lattice properties of thin films of ternary and multinary compositions are consistent with those of the inverse spinel ZTO with ascendancy of (222) plane along (111) plane. These two planes are parallel to each other. The absence of additional peaks in the XRD spectra is one of the evidences for coupled aliovalent substitution in ZTO.

The average crystallite size of the films was calculated by using the Scherrer's formula^[15]. The micro-strain was obtained from the uniform deformation model (UDM) using the Williamson-Hall (W-H) method^[16]. According to UDM, the strain was assumed to be uniform along all crystallographic directions and hence the materials properties are expected to be independent on the direction. The W-H equation is given by

$$\beta \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta, \quad (1)$$

where, ε is lattice micro-strain, D is the crystallite size and β is FWHM. The intercept value of the W-H plot represents the average crystallite size and the slope represents micro-strain in the lattices [Table I]. Dislocation density is determined from the Williamson and Smallman's formula, $\delta = 1/D^2$ [Table I]^[17]. Referring the Table I, the hierarchy of micro-strain values among

the films can be assorted as Ga-substituted Zn_2SnO_4 , In-and Ga-co-substituted Zn_2SnO_4 , and In-substituted Zn_2SnO_4 . These results can be justified by accounting for the ionic radii of the impurities. Compared to other cations mentioned above, In^{3+} has the largest ionic radius (0.092nm), so they are expected to expand the lattice^[18]. The net micro strain on the lattice must be higher in this context and the results are consistent with our calculations. The value of ϵ for other samples is found to be higher, which might be influenced by the inclusion of dissimilar materials in the crystal symmetry. We also mention that the crystallite size for the materials we have studied is calculated by using the Scherrer formula and Williamson-Hall method and they are approximately the same. Furthermore, the films are composed of nano-grains.

3.2. Electronic structure from XPS measurements

The XPS spectra for the films are quantified in Tables II, III, IV, and V. The following elements were detected from the wide scan: Zn, Sn, In, Ga, and O. No other elements are detected. The survey was based on the results obtained by computations by CASA software. It provides the information about the amount of elements that present in the compounds and percentages of impurities. The peaks corresponding to Zn, Sn and O are seen in the survey spectrum. The peaks are less sensitive to low concentrations impurities. Analysis of the Tables II-V showed presence of large amount of Zn and Sn ions. Since the films were not sputtered, strong influence of oxygen is expected, which includes surface oxides as well. Best possible amount of ion environment of In and Ga is identified from the scan with promising reduction in Zn/Sn contents indicating the best possible ion substitution.

To further analyze the materials chemically, we have performed compositional analysis. The elements are analyzed individually for different films. The effect of ion substitution is more discernible when it is compared with the same elements, binding energy shifts, FWHM, peak fitting parameters, ionic states and the shape of the peaks. The asymmetric peak shapes were fitted using a Gaussian/Lorentzian mixed function. In narrow scan, $Zn2p$, $Sn3d$, $O1s$, $In3d$ and $Ga3d$ peaks have been detected and the OKL23L23 Auger peaks were also observed in the films. $Zn2p$ and $Sn3d$ peaks were symmetric and hence don't require any fitting procedure. However, $O1s$ and $Ga3d$ peaks clearly show asymmetry and needed to be fitted for its multiple bonding at the surface area.

Figure 2 shows two strong elemental photo-electron emissions from both Zn2*p* and Sn3*d* regions. The core level peaks corresponding to Zn2*p*, Sn3*d*, Ga3*d*, In3*d* orbitals give rise to two possible energy states with different energy states known as spin-orbit splitting (*j-j* coupling). The *j-j* coupling constant, difference between Zn2*p*_{1/2} and Zn2*p*_{3/2} binding energies are of the same magnitude ~23.1eV and the Zn2*p*_{3/2} peak is dominant than the Zn2*p*_{1/2}. The peaks corresponding to Zn2*p*_{1/2} and Zn2*p*_{3/2} in Zn₂SnO₂ spectra are situated at 1022.21±0.1eV and 1046.23±0.1eV, respectively, which are very close to the *j-j* coupling constant of Zn2*p*. The results observed from other samples also continuously reproduced *j-j* coupling constant with an estimated error of 0.1eV. The binding energies of Zn2*p* in In/Zn₂SnO₄ are centered at 1023.4±0.1eV (Zn2*p*_{3/2}) and 1046.5±0.1eV (Zn2*p*_{1/2}), in Ga/Zn₂SnO₄ at 1046.65 ±0.1eV, (Zn2*p*_{1/2}) and 1023.56±0.1eV (Zn2*p*_{3/2}) as well as in co-substituted Zn₂SnO₄ at 1046.02 ±0.1eV (Zn2*p*_{1/2}) and 1022.98±0.1eV (Zn2*p*_{3/2}). Analysis shows that in all samples the Zn2*p* core level spectra match well with the Zn²⁺ state. The symmetric peak shape emphasizes this result. The binding energies of Zn2*p*_{1/2} are in agreement with previous reports (see, e.g., Refs. ^[19-20]). It can also conclude that status of the BE positions was slightly affected by the presence of substituted lattice ions.

Sn3*d* core level spectra typically have two components due to the *j-j* coupling. The peaks are displayed in Fig.2 in the vicinity of 494.45 eV and 486.40 eV corresponding to Sn3*d*_{3/2} and Sn3*d*_{5/2}, respectively, of ZTO. The doublet separation (DS), 8.1 eV is consistent with other reports and NIST data base ^[21-22]. The binding energy 486.40eV is close to that of Sn3*d*_{5/2} corresponding to Sn⁴⁺ state in ZTO. We have also examined the chemical bonding between Sn and O [Fig. 5]. The higher BE positions in XPS spectra might correspond to Sn⁴⁺ state. In the remaining samples, the Sn3*d*_{3/2} peak is appeared with a broad shoulder and possibly can fit with a second component at 498.34 eV. However, the Sn3*d*_{5/2} the pair peak was missing and the curve appeared smooth. The main Sn emission is Sn3*d*_{5/2} and we were unable to fit the peak with a second component and hence this establishes the spectral symmetry. Hence the peak with Sn3*d*_{3/2} emission cannot be indexed as Sn²⁺ phase in the compound. Besides this, Sn²⁺ state appear at the close vicinity of Sn⁴⁺ state (peak separation~0.7eV) and here the separation was ~ 3eV. We found that the emission located at 498.34eV is possibly from O KL23L23, which varies its position in between ~ 494eV and ~ 512eV^[23-24]. Thus the absence of multiple oxidation state of

Sn is proved. Meanwhile, the values of BE positions are slightly altered due to presence of dissimilar cation on the surface.

$Ga3d$ signals were weak in the survey scan. However, the narrow scan between regions 15-30eV give rise to two strong signals. For the ternary compound the first peak was centered at $18.1\pm 0.1\text{eV}$, while the second peak was at $25.96\pm 0.1\text{eV}$. The $Ga3d$ line is composed of two lines centered at the following BE $\sim 19\text{eV}$ line and 20eV . The emission $\sim 19\text{eV}$ corresponds to Ga^{3+} in the Ga-O bonding and the energy line at 20eV could be from the Ga sub oxide at the surface. In Ga_2O_3 films, the typical XPS spectra of $Ga3d$ will come along with $O2s$ photoelectron peaks. The results related to the binding energy positions of $Ga3d$ and $O2s$ are consistent with many reported literature data [25-26]. The corresponding BE shifts in quaternary sample do not show any noticeable peak shifts and kept a similar binding energy level. As shown in Fig.4, the $In3d$ spectra of the films split into two components from the energy levels of $In3d_{5/2}$ and $In3d_{3/2}$ lines. The deconvolution was not required for $In3d_{5/2}$ and $In3d_{3/2}$ lines, since we were able to fit it with single components. The BE lines at 445.01eV and 452.6 of the indium substituted samples correspond to $In3d_{5/2}$ and $In3d_{3/2}$ states of In^{3+} state at the surface. These lines are slightly occupied to the lower binding energy position at 443.97eV and 452.2eV , respectively, due to the formation of complex combination [27]. However, these variations are not significant enough to state a new elemental feature in the material and this suggests valence stability of indium ions with its most stable In^{3+} state.

$O1s$ spectra have natural wide line width comparable to spectrum of other elements. Moreover, in case of the mixed oxide system containing several cations, the spectra will be much broader. Hence, broad and intense lines of $O1s$ species are obtained from the scanning of samples in the region of 528-536eV [Fig.5.]. The broad curves of $O1s$ spectra are fitted with a maximum of three components in all samples. In Zn_2SnO_4 films, the peaks centered at $530.95\pm 0.1\text{eV}$, $531.78\pm 0.1\text{eV}$, and $532.94\pm 0.1\text{eV}$, respectively, can be attributed to Zn^{2+} -O, to excess hydroxides (O-H), and to Sn^{4+} -O bonding. In $O1s$ spectra of thin films containing Zn ions, the lowest binding energy components are attributed to O^{2-} ions. The other two assignments for the peaks located at higher binding energy positions are roughly matching with the earlier reports [28]. Second curve located $531.78\pm 0.1\text{eV}$ is probably attributed to the excess loosely bound oxygen present at the surface oxides (O-H) [29]. The chemical bonding of Sn^{4+} -O is more complex while considering co-existence of Sn^{2+} -O bonding on the surface, however, this

was not indicative in Sn3d spectra. As per many observations the binding energy difference between the Sn 3d_{5/2} and O1s peaks for the stoichiometric SnO₂ is ~43.9eV^[30], which is considerably lower than~ 46eV in this work. This would be indicative of excess amount of oxygen at the surface. In other films, Fig.5, the O1s spectra have been fitted with a maximum number of three peaks located at binding energies of 530.96±0.1eV, 531.89±0.1eV and 532.92±0.1eV for Ga-doped Zn₂SnO₄, of 530.96±0.1eV, 521.75±0.1eV and 532.99±0.1eV for In-doped Zn₂SnO₄ and of 530.98±0.1eV, 531.78±0.1eV and 532.98±0.1eV for the co-substituted samples. The lower binding energy curves are assigned to 3+ state of In or Ga or both. The intensity and area of these peaks are broader than expected because of the overlapped hydroxide curves in the same region. The other binding energy assignments in the Figure are consistent with literatures.

4. Conclusion

In summary, we have studied Zn₂SnO₄-based thin films of multication oxides synthesized by pulsed laser deposition technique. The effect of ionic substitution on inverse cubic spinel structured Zn₂SnO₄ is studied by X-ray diffraction technique, which confirms the structural phase purity and the inverse cubic spinel structure of Zn₂SnO₄ with distortions in the peak positions and intensity. The average crystallite size of the materials is obtained from Scherrer's formula and Williamson-Hall plot. The micro-strains and dislocation density are obtained from Williamson-Hall method and Williamson-Smallman's formula. X-ray photoelectron studies (XPS) confirm the presence several cations without distorting the structure of the original material and this has led to forming of *n*-type electrical properties of the films. The chemical compositions of the films are obtained from the computer assisted surface analysis and excess amount of surface oxides is identified on the surface. XPS elementals suggest valence stability of the elements. Due to peak asymmetries, the various chemical states of Sn, Ga, and O are analyzed and reported.

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