



Magnesium indium oxide (MgIn_2O_4) spinel thin films: Chemical spray pyrolysis (CSP) growth and materials characterizations

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ABSTRACT

MgIn_2O_4 , which has an inverse spinel structure, has been adopted as the transparent material in optoelectronic device fabrication due to its high optical transparency and electrical conductivity. Such a technologically important material was prepared by the spray pyrolysis technique. Precursors prepared for the cationic ratio $\text{Mg/In} = 0.5$ were thermally sprayed onto glass substrates at 400 and 450 °C. We report herein the preparation and characterization of the films by X-ray diffraction (XRD), energy-dispersive absorption X-ray spectroscopy (EDAX), and atomic force microscopy (AFM). The XRD results showed the single phase formation of the material that revealed the presence of Mg^{2+} and In^{3+} in the inverse spinel-related structure. The FTIR and EDAX results further confirmed that the nanocrystalline films were mainly composed of magnesium, indium, and oxygen, in agreement with XRD analysis. We surmised from the AFM micrographs that the atoms have enough diffusion activation energy to occupy the correct site in the crystal lattice. For the 423-nm-thick magnesium indium oxide films grown at 400 °C, the electrical conductivity was $5.63 \times 10^{-6} \text{ Scm}^{-1}$ and the average optical transmittance was 63% in the visible range (400–700 nm). Similar MgIn_2O_4 films deposited at 450 °C have a conductivity value of $1.5 \times 10^{-5} \text{ Scm}^{-1}$ and an average transmittance of 75%. Hall coefficient observations showed n-type electrical conductivity and high electron carrier concentration of $2.7 \times 10^{19} \text{ cm}^{-3}$.

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1. Introduction

New transparent conducting oxide (TCO) films that have spinel structures, where metallic particles are dispersed in an oxide matrix, have received great attention because of their improved mechanical, optical, electrical, thermal, and magnetic properties. Despite their larger band gaps greater than 3 eV, they can sustain a high carrier concentration of electrons with high carrier mobility. The most commonly used post-transition-metal oxides ZnO , SnO_2 , and In_2O_3 are serving as TCO electrodes in optoelectronic devices [1,2]. However, the recent growing demands for high-performance and low-cost TCO materials have led to an intensive search for new TCO materials with higher transparency and conductivity [3–6]. New materials with improved electrical and optical properties would be of interest to the rapidly developing flat panel display technologies.

From this viewpoint, the properties of several spinel structured compounds such as MgIn_2O_4 [7], CdGa_2O_4 [8], ZnGa_2O_4 [9], and

Zn_2SnO_4 [10] have been studied for their enhanced properties. Among these ternary oxides, magnesium indium oxide (MIO) thin films have found important applications as new transparent conducting as well as active electrodes in photo-electrochemical solar cells [11]. It is an n-type wide-band gap semiconductor, which has a separate conducting path in the crystal lattice. It has a general structure resembling the mineral spinel MgAl_2O_4 with the formula AB_2O_4 . At elevated temperatures, the binary oxides AO and B_2O_3 can form the ternary oxide AB_2O_4 with a spinel structure (A^{2+} is a general divalent and B^{3+} is a general trivalent cation). It falls under the normal and inverse spinel oxide category, according to the lattice substitution of A and B cations in the tetrahedral and octahedral voids in the fcc-cp oxygen sublattice.

2. Materials and methods

The AB_2O_4 spinel unit cell contains 56 atoms and belongs to the space group $\text{Fd}\bar{3}\text{m}$. The oxygen ions are located at (u, u, u) , forming a distorted face-centered-cubic structure. The 'A' cations are at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ positions, occupying 8 of the 64 tetrahedral interstices in the direct spinel, and the 'B' cations are at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

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positions, occupying 16 of the octahedral interstices in the direct spinel. However, MgIn_2O_4 falls under an inverse spinel category, according to the lattice substitution of Mg and In cations in the tetrahedral and octahedral voids in the anion sublattice.

According to the definition of unit cell, the following general equations for spinel-type structures are easily obtained [12],

$$V = \frac{a^3}{8}, \quad V_{\text{tetra}} = \frac{64}{3} V \left[u - \frac{1}{8} \right]^3, \quad V_{\text{octa}} = \frac{128}{3} V \left[u - \frac{3}{8} \right]^3 u, \\ d_{\text{A-O}} = \sqrt{3} a \left[u - \frac{1}{8} \right] \quad \text{and} \quad d_{\text{B-O}} = a \sqrt{\left(u - \frac{1}{2} \right)^2 + 2 \left(u - \frac{1}{4} \right)^2}, \quad (1)$$

where V , V_{tetra} , and V_{octa} stand respectively for the molecular, tetrahedral, and octahedral volumes, a is the lattice parameter of the cubic unit cell, and $d_{\text{A-O}}$ and $d_{\text{B-O}}$ are the cation–anion bond lengths at the tetrahedral and octahedral interstices, respectively. Note that the occupied tetrahedra are regular regardless of the value of u , the anion displacement parameter, and therefore V_{tet} can be expressed using only the $d_{\text{A-O}}$ variable. However, the occupied octahedra are distorted (only at $u = 0.25$ are regular) and the V_{oct} expression in terms of $d_{\text{B-O}}$ includes the variable u . Thus when u increases, the tetrahedral bond length increases while the octahedral bond length decreases and the tetrahedral bond length increases faster than the decrease of octahedral bond.

In an inverse spinel, the tetrahedral sites are occupied by B atoms while the octahedral sites are occupied by an equal number of A and B atoms. The cation inversion energy ΔE is slightly negative, which is a strong indication of its stable configuration. Intermediate phases with the formula $(\text{A}_{1-x}\text{B}_x)(\text{A}_x\text{B}_{2-x})\text{O}_4$ also exist [13]. Here the cations in the square brackets occupy the octahedral sites and cations in the parentheses occupy the tetrahedral sites. The cation inversion parameter x ranges from zero for a normal spinel to one for an inverse spinel. Recently, by calculations it was observed that spinels with smaller u values would be more stable in an inverse distribution. Essentially, u describes the deviation of the anion sublattice from regular close packing and obviously well varies according to the relative sizes of the cation in the structure. The parameters x and u have relative dependence in their electrical and optical properties.

Wide-gap conductors have favorable electrical characteristics, only if they satisfy two necessary conditions. The first is to restore high mobility of electrons in the conduction band. Most of the electrical insulators are truly insulators because of their low mobility in addition to their wide band gap. The second requirement is related to the possibility of doping. In the case of n-type oxides, electron carriers are in principle introduced by substitution of M^{i+} ions with $\text{M}'^{(i+1)+}$ ions [14,15] and of O^{2-} ions with halogen ions [16] for the generation of oxygen vacancies or interstitial positively chargeable atoms [17]. However, there is no established science that enables one to predict which technique is applicable to a specified material; therefore, the predictions are based only on the condition of high mobility.

For having high mobility in n-type wide-gap semiconductors, one of the cations must belong to p-block with ns^0 electronic configuration (e.g., Zn^{2+} , Hg^{2+} , Ga^{3+} , In^{3+} , Ti^{3+} , Ge^{4+} , Sn^{4+} , Pb^{4+} , Sb^{5+} , and Te^{6+}). In this case, the bottom edge of the conduction band is composed mainly of ns atomic orbitals of the M-cation. In addition, a linear chain of edge-sharing octahedra (rutile chain) is preferred, in which the p-block cations occupy the central position. This is the case of the oxides having high mobility. There is no intervening oxygen between the two neighboring M cations in the rutile chain running along (110) and its equivalents. These chains are connected to each other by the cations existing in the tetrahedral sites.

Consequently, the M–M distance becomes short compared with that in the M–O–M linear structure frequently seen in a vertex-sharing structure. Direct overlap between ns atomic orbitals of the neighboring M cations is possible for the heavy p-block cations. This feature as well as covalency in M–O bonds gives rise to large dispersion of the conduction band, which is appropriate for high mobility of the electron carriers. The large dispersion is an indication of less effective mass of electrons. All the above said conditions are favorable for MgIn_2O_4 and therefore it exhibits the properties of an n-type semiconductor. Normally in multication oxides, mobility decreases with increase of the second cation proportion. Mobility variation has been explained in terms of the scattering of carrier electrons by the substituted ions in the lattice [18,19]. The drop in mobility due to doping may be avoidable or reducible if the doping site and conduction path of carrier electrons are separated spatially by selecting the crystal structure having two different cation sites.

As nonequilibrium conditions often exist during thin film deposition, physical properties of stable phases can be helpful in interpreting and directing thin film work. Various techniques have been reported for preparing MgIn_2O_4 films, viz. pulsed laser deposition [14], combustion synthesis [15], and magnetron sputtering [16–18]. Preparation of MgIn_2O_4 films from solution is very rare and the reported results are not quite adequate. In this paper, spray pyrolysis deposition of MIO spinel thin films and their structural, electrical, surface morphological, and optical properties are reported.

Spray pyrolysis is a simple, low-cost, and elegant technique for large area preparation of TCO thin films. This technique has advantages in preparing quality films with proper control on the film composition, high deposition rates, and the possibility of high-temperature depositions. It has uniform deposition and good control over the physical properties of the deposited films. The physical properties of the films prepared by spray pyrolysis depend on the spray parameters, such as the substrate temperature, precursor concentration, carrier gas pressure, and precursor flow rate apart from the substrate to nozzle distance. The spray pyrolysis experimental setup and the detailed procedure engaged for the deposition of thin films have been described elsewhere [19].

MgIn_2O_4 thin films were prepared by spraying an alcoholic precursor containing magnesium acetate $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and indium chloride $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ in a 1:2 proportion onto heated quartz substrates. The precursor solution was always buffered by adding a small quantity of hydrochloric acid to increase the solubility of the solution. The required deposition parameters to obtain high-quality films were optimized by controlling the spray parameters. The parameters such as the substrate–nozzle distance (SND) and the flow rate of the solution were kept constant at 30 cm and 5 ml/min, respectively. The carrier gas pressure was kept constant at 0.4 kg/cm². In all depositions, the amount of solution sprayed was 25 ml and the films were deposited in the temperature range 400–450 °C.

Purity and reproducibility of the films were confirmed by comparing the experimental data on several MIO films prepared under identical and optimized conditions. The thicknesses of films were about 0.36 μm as estimated by the Stylus profilometer (Mitutoyo). The structural properties were investigated by X-ray diffraction (PANalytical-3040 X'pert Pro) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The surface chemistry of the sprayed films was obtained by recording FTIR transmittance spectra between 400 and 4000 cm^{-1} using Thermo Nicolet Nexus. Optical transmittance spectra were recorded with a Hitachi-330 UV–Vis–NIR spectrophotometer in the wavelength range $\lambda = 280\text{--}1500 \text{ nm}$. The sheet resistance and conductivity were measured using the four-probe method at temperatures from 30 to 150 °C. For electrical measurements, a rectangularly shaped sample was taken and ohmic contacts were provided by sputtered Ag metal and they were contacted by Cu wires. The

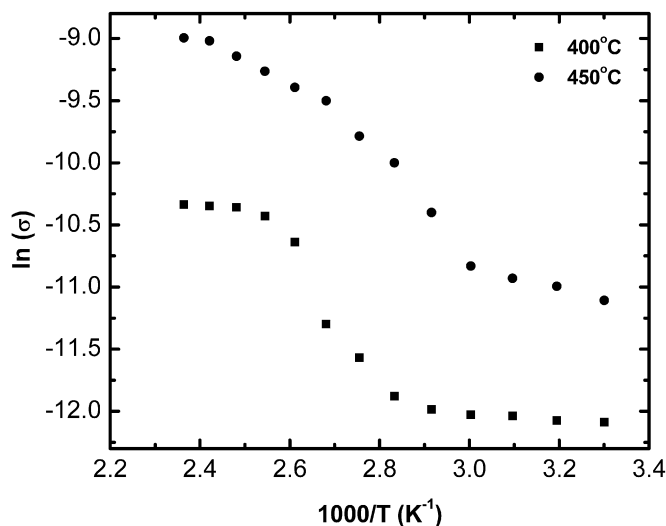


Fig. 4. Electrical conductivity variation of MIO films with temperature.

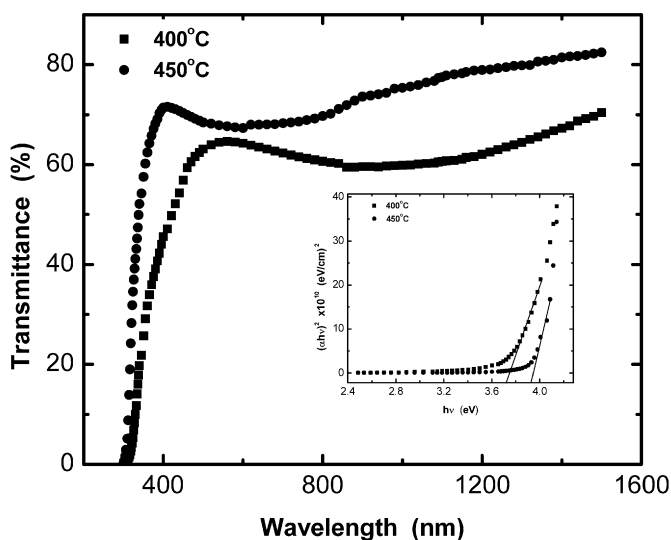


Fig. 5. Optical transmittance spectra of the MgIn_2O_4 films deposited at 400 and 450 °C. Inset shows the $h\nu$ vs $(\alpha h\nu)^2$ curve extrapolated to obtain the optical band gap.

The dc electrical conductivity of the MIO films was measured in the temperature range between 30 and 150 °C by the four-probe technique. The variation of conductivity of the MIO films deposited at 400 and 450 °C as a function of temperature is shown in Fig. 4. Temperature-dependent conductivity is revealed from the observations. Hall effect studies revealed n-type conductivity which is generated either from the interstitial or from substituted cations and oxygen vacancies. The measured carrier concentration is found to be about $2.7 \times 10^{19} \text{ cm}^{-3}$ for the MIO films prepared at 450 °C, whereas $1.9 \times 10^{19} \text{ cm}^{-3}$ for the films prepared at 400 °C. The optical behavior of magnesium indium oxide films has been studied from the recorded transmittance spectra (Fig. 5). The MIO films deposited at 450 °C have an average optical transmission value of ~80% in the visible wavelength range of 400–900 nm, which shows very low absorption in the visible and IR region. The optical band gap energy of MgIn_2O_4 was also estimated from the transmittance data. The absorption coefficient of the film was found to be of the order of 10^4 cm^{-1} which exponentially decreases as photon energy decreases. The optical band gap energy of MgIn_2O_4 thin film is found to be 3.82 eV, which is greater than that of MgIn_2O_4

Table 2

Electrical and optical data of the prepared MgIn_2O_4 films.

Observed parameters	MgIn_2O_4 films deposited at 400 °C	MgIn_2O_4 films deposited at 450 °C
Conductivity (S m^{-1})	5.6×10^{-6} – 3.2×10^{-5}	1.5×10^{-5} – 1.24×10^{-4}
Activation energy (eV)	0.75	0.57
Carrier concentration (cm^{-3})	1.9×10^{19}	2.7×10^{19}
Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	0.3×10^{-3}	9.5×10^{-3}
Transmittance (%)	67	80
Optical band gap (eV)	3.75	3.82

powder (3.45 eV) synthesized by the ceramic route [7]. The observed electrical and optical constants are tabulated in Table 2.

In order to investigate the film growth process, surface morphologies of the film were observed by using the AFM after deposition. Recorded images have been used for surface quality analysis and for quantitative measurement of the surface parameters like surface roughness and grain size. Fig. 6 shows the 2D and 3D AFM images of the magnesium indium oxide spinel films deposited by keeping the quartz substrate at temperatures 400 and 450 °C. A quantitative analysis of the surface roughness on the images was performed by using the root-mean-square (RMS) function of the Nanoscope III, DI software [23]. RMS is defined as the standard deviation of the surface heights, calculated from all points obtained during a given scan [24], and were used to analyze the surface roughness quantitatively.

4. Discussion

The XRD patterns of the spray-deposited MgIn_2O_4 films at 400 and 450 °C were completely indexed for the single phase MgIn_2O_4 spinel structure. Further, it reveals that the film deposited at 450 °C has better crystallinity. No other characteristic peaks pertaining to impurity or extraneous phases have been observed. These results confirmed the single phase formation of the material. Films are polycrystalline in nature and (311) is the preferred orientation. The lattice constant was calculated from the high intensity peak, i.e., using the (311) peak which is invariably present in both films. The unit cell dimension of the MIO thin films deposited at 450 °C is found to be 8.887 Å, which is in good agreement with the standard value 8.864 Å (JCPDS 73-2414). However, film deposited at 400 °C has the unit cell dimension of 8.905 Å, which indirectly demonstrates the decrease in density. Density variations in turn increase the microstrain and dislocation density of the film due to the increase of grain boundaries.

The Fourier transform infrared (FTIR) spectrum could provide information on the structure of the oxide since the frequency of the cation–oxygen vibration depends on the mass of the cation, the type of cation–oxygen bond, and the unit lattice parameter a . Interpretation of the FTIR spectrum was carried out according to the vibration frequencies through the tetrahedral cation–oxygen axis, perpendicular vibrations, and octahedral oscillations due to a cation in this environment. Two absorption peaks are observed in the fingerprint region at 561 and 404 cm^{-1} . These peaks can be assigned to the longitudinal optical phonon modes associated with the metal oxide stretching which in turn implies the formation of single phase MgIn_2O_4 films. However, the weak peaks observed at about 1275 cm^{-1} can be assigned to the water-bending vibration mode. Water might have originated from the precursor solvent or may be due to adsorption when the films are exposed to the atmosphere. Also, it is observed that the film prepared at 400 °C is more hydrated, revealing extra peaks in the 3300–3500 cm^{-1} wavenumber region, attributed to the symmetric and asymmetric stretching vibrations of water molecules.

The atomic percentages of magnesium, indium, and oxygen present in the deposited films were calculated from the peak in-

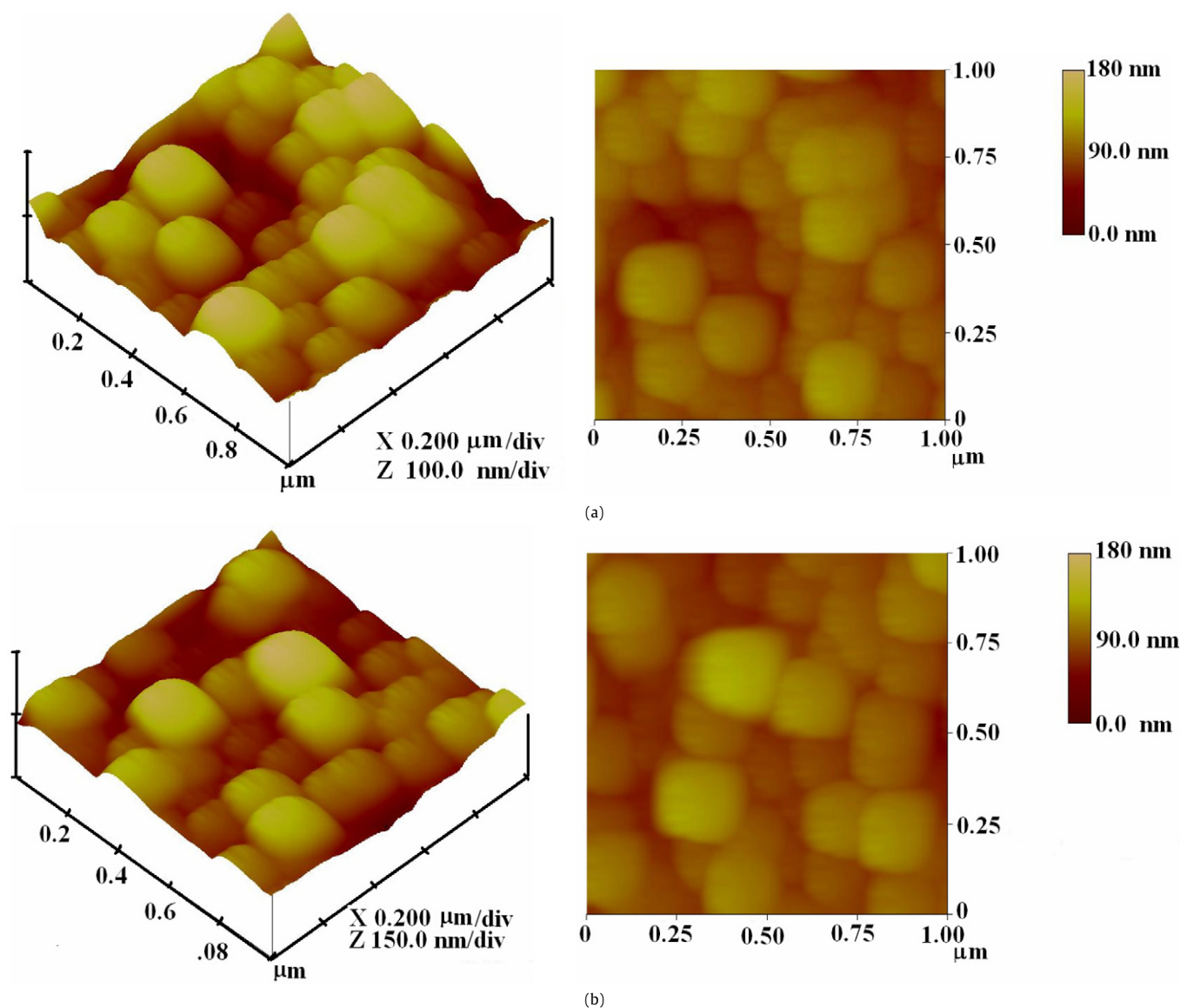


Fig. 6. AFM micrographs of the MgIn_2O_4 films deposited at (a) 400 °C and (b) 450 °C.

tensities and the area under the peak of the corresponding element in the EDAX spectrum. The atomic percentage of magnesium is 31.26%, whereas for indium 68.74% is observed. The atomic ratio of 0.46 thus obtained for the MgIn_2O_4 film synthesized at 450 °C is comparable to the value of the cationic ratio 0.5 in the precursor. On comparing the EDAX spectrum of the prepared film at 400 °C, it is apparent that the film is indium rich and therefore the cationic ratio deviates more from 0.5.

The dc electrical conductivity of the film deposited at 450 °C is found to vary in the order of 1.5×10^{-5} – $1.24 \times 10^{-4} \text{ S cm}^{-1}$ in the measured temperature range (30–150 °C). Such a temperature-dependent conductivity reveals the degenerate semiconducting nature of the films that have very small change in electrical conductivity [24]. However, the conductivity variation may be attributed to carrier generation that strongly depends on the film preparation parameters. At high temperatures, conductivity increases due to the increase of the conduction electrons. The Fermi energy level is therefore believed to be moved upward close to the conduction band that accelerated the conduction behavior of the film. However, the films prepared at 400 °C show a stronger dependence of temperature than that of the films deposited at 450 °C and have very low electrical conductivity in the range of

5.6×10^{-6} – $3.2 \times 10^{-5} \text{ S cm}^{-1}$. These observations show that the resistivity of the MIO films decreases with the increase of substrate temperature. This may be due to the decrease of dislocation density and grain boundary density which reduces the number of carrier-scattering centers leading to enhancement of carrier concentration. Measured conductivity may be fitted to the following expression,

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right), \quad (2)$$

where σ_0 is a constant, k , the Boltzmann constant, T , the temperature, and E_a , the activation energy. From the slope of the curve, the activation energy is found to be 0.75 and 0.57 eV for the MIO films prepared at 400 and 450 °C, respectively. The lower activation energy value of the MgIn_2O_4 films deposited at 450 °C confirms the formation of well-crystallized lattice possessing high conductivity [21].

Even though the conduction electron concentration is high, the MgIn_2O_4 film deposited at 450 °C has low electrical conductivity of about $10^{-5} \text{ S cm}^{-1}$ at RT. The overall lower conductivity value may be attributed to the stoichiometric nature of the film with very low values of carrier mobility in the of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However,

the observed mobility value of $9.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the film deposited at 450°C is higher than that of the films deposited at 400°C whose value is about $0.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Mobility variation is directly related to the observed increase of conductivity with deposition temperature. This observed correlation is similar to the reported electrical behavior of MgIn_2O_4 spinel pellets sintered at 1500°C [22].

The electrical conductivity and their temperature-dependent nature elucidate the presence of oxygen vacancies in the prepared films. The electrical conductivity of oxide semiconductors is mainly determined from the carrier concentration of electrons (n) and their mobility (μ), both being governed by the cation stoichiometry and oxygen vacancy. As far as the MgIn_2O_4 spinel films prepared by the spray pyrolysis technique here, the X-ray results show the formation of stoichiometric and well-crystallized films without the presence of metallic Mg, In, or other MgO or In_2O_3 metal oxide phases. Hence, the observed moderate conductivity values of about 10^{-5} – $10^{-4} \text{ S cm}^{-1}$ may be attributed only to the oxygen vacancies produced at higher temperatures. The oxygen vacancies act as doubly ionized donors and each vacancy contributes two electrons to the electrical conduction as evident from the reaction:



Optical measurement also confirms the changes in optical transmittance of the MIO films with the deposition temperature. Optical transmittance of about 80% is observed for the films deposited at 450°C . The shift in the absorption band to the lower wavelength side in turn increases the optical band gap value to 3.82 eV. This may be attributed to the crystallinity and well-packed structure. Transparency and higher energy gap values make the spray-deposited MgIn_2O_4 film a novel transparent and conducting oxide material for optoelectronic devices. Similar studies have been performed on films deposited at 400°C and the transmittance is found to be about 67% in the visible region and the optical band gap value is about 3.75 eV.

RMS roughness values obtained by averaging the scan of the 2D images for the MgIn_2O_4 film deposited at 450°C markedly decreased up to 5.6 nm compared to the other MgIn_2O_4 films examined. Additional information has been obtained that all columns are of same shape and size. They are of spherical shape with sizes in the range of 150–250 nm. On average, the grain size of the MgIn_2O_4 films deposited at 400 and 450°C are 184 and 234 nm, respectively. This result indicates that the surfaces of the grown films were smooth, homogeneous, and parallel to the substrate surface. Roughness of the film deposited at 400°C is larger than those of the films deposited at 450°C . This observation substantiates the optical transmission results.

5. Summary

Highly crystalline and transparent MgIn_2O_4 thin films have been prepared using the spray pyrolysis technique on glass substrates. Stoichiometric films prepared at 450°C were polycrystalline, single phase and exhibit (311) preferential orientation. The dc electrical conductivity and carrier concentration of these films increase with the increase in substrate temperature from 400 to 450°C . A maximum electrical conductivity of about $1.24 \times 10^{-4} \text{ S cm}^{-1}$ was observed for the MIO films deposited at 450°C . A high electron carrier concentration of $2.7 \times 10^{19} \text{ cm}^{-3}$ was generated in the MgIn_2O_4 crystal lattice and was mainly due to the available oxygen vacancies. However, conductivity in the order of $10^{-4} \text{ S cm}^{-1}$ may be due to the lower mobility of the carriers due to scattering within the grain boundaries. The optical band gap of the deposited films at 450°C is 3.82 eV which is greater than tin-doped indium oxide (ITO) films. Increasing the substrate temperature from 400 to 450°C improved the crystallinity as well as the optical transmittance. From the structural, electrical, optical, and surface morphological results, it is obvious that the MgIn_2O_4 films deposited by the spray pyrolysis technique under the proposed optimized conditions are suitable for optoelectronic applications.

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