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Preparation, characterization, spectroscopic (FT-IR, FT-Raman, UV and visible) studies, optical properties and Kubo gap analysis of In_2O_3 thin films

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HIGHLIGHTS

- Indium oxide thin films are deposited by spray pyrolysis technique making use of indium acetate as precursor solution.
- The physical properties of these films are characterized by XRD, SEM, AFM, UV–visible, PL and Photo acoustic measurements.
- The complete vibrational analysis has been carried out and the HOMO and LUMO and Kubo gap are calculated using HF and DFT.
- The electronic properties; absorption wavelengths, excitation energy, dipole moment, Kubo gap are studied.

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ABSTRACT

Indium oxide (In_2O_3) thin films are successfully deposited on microscopic glass substrate at different temperatures by spray pyrolysis technique using Indium acetate as precursor solution. The physical properties of these films are characterized by XRD, SEM, AFM, UV–visible, PL and Photo acoustic measurements. XRD analysis revealed that the films are polycrystalline in nature having cubic crystal structure with a preferred grain orientation along (222) plane. The average transmittance in the visible region is found to vary from 60% to 93% depending upon the substrate temperature. The complete vibrational analysis has been carried out and the optimized parameters are calculated using HF and DFT (LSDA, B3LYP and B3PW91) methods with 3-21G(d,p) basis set for In_2O_3. The fundamental frequencies are calculated and assigned according to the experimental frequencies. Furthermore, ^{13}C NMR and ^{1}H NMR chemical shifts are calculated by using the gauge independent atomic orbital (GIAO) technique with HF/B3LYP/B3PW91 methods on same basis set. A study of the electronic properties; absorption wavelengths, excitation energy, dipole moment, Kubo gap (HOMO and LUMO) and frontier molecular orbital energies, are performed by HF and DFT methods. Besides frontier molecular orbitals (FMO), molecular electrostatic potential (MEP) is executed. The thermodynamic properties (heat capacity, entropy, and enthalpy) of the compound are calculated in gas phase.

1. Introduction

Indium oxide (In_2O_3) is an important and a well known transparent conducting oxide of n-type semiconductor exhibiting a wide band gap, chemical stability, high electrical conductivity and transparency to visible light. It is frequently used for photovoltaic devices, transparent windows; liquid crystal displays (LCD), light emitting diode (LED), solar cell, gas sensors and anti- reflecting coatings [1].

In_2O_3 thin films were prepared by variety of physical and chemical methods such as spray pyrolysis [2], vacuum evaporation [3], magnetron sputtering [4], dc- sputtering [5], sol gel [6], electron beam evaporation [7], reactive thermal evaporation [8] and pulsed laser deposition [9]. Among these deposition methods, spray pyrolysis is a versatile, most inexpensive, reproducible, commercially viable, simple to manipulate and applicable to large scale area. So far, in many research works [10–15], during the preparation of In_2O_3 thin film various precursors such as indium chloride, indium nitrate as well as indium acetlacetonate were used as starting materials with ethanol derivates and water as solvents. However, up to the knowledge of authors, no work has been reported

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on the deposition of In_2O_3 thin films using indium acetate as precursor by spray pyrolysis method.

In the present work, In_2O_3 thin films were prepared at different substrate temperatures using indium acetate as precursor by spray pyrolysis method. The structural and optical properties of the prepared thin films were characterized by XRD, UV, SEM with EDX, AFM and PL measurements. Moreover, FT-IR and FT-Raman spectra were recorded and FT-IR, FT-Raman, NMR, UV and Visible spectra were simulated and their results were tabulated for comparison. The geometrical parameters and vibrational frequencies were calculated using HF and DFT (LSDA, B3LYP and B3PW91) methods with 3-21G(d,p) basis set and the results were compared with the experimental values.

2. Experimental methods

0.05 M of indium (III) acetate trihydrate $In(CH_3COO)_2.3H_2O$ salt is dissolved in deionized water and sprayed onto the microscopic glass substrates with dimension of 75 × 25 mm^2, at different substrate temperatures (T_s = 350–475 °C). The substrates are first cleaned with water bath, followed by dipped in conc. HCl, acetone and finally rinsed several times with deionised water then allowed to dry in a hot air oven. In spray unit, the substrate temperature is maintained using a heater, controlled by a feedback circuit. During the spray, the substrate temperature is kept constant with an accuracy of ±5 °C. Spray head and substrate heater are kept inside a chamber, provided with an exhaust fan, for removing gaseous by-products and vapors from the solvent. The spray head is allowed to move in the *X*–*Y* plane using a microcontroller stepper motor, in order to achieve a uniform coating on the substrate. The spray head could scan an area of 200 × 200 mm with *X*-movement at a speed of 20 mm/s and *Y*-movement in steps of 5 mm/s simultaneously. The spray rate (20 min) of the solution (2 ml min^{-1}) and the pressure (1 kg cm^{-2}) of the carrier gas are controlled by the microcontroller device which is connected with PC through a serial port. The data of each spray is stored systematically in regular intervals. The distance between spray nozzle and substrate is fixed at 20 cm during the spray process. After the deposition, the films are allowed to cool slowly to room temperature and washed with deionised water and dried.

The structural characterization of the deposited films are carried out using SHIMADZU-6000 X-ray diffractometer equipped with a monochromatic Cu Kα radiation (λ = 1.5406 Å). The XRD patterns are recorded in 2θ interval from 10° to 80° with a step of 0.05°. The thicknesses of the films are measured using Stylus profiler Mitutoyo SJ-301. Morphological and topological surface studies are carried out using JEOL JES-1600 Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDX) and NANONICS MV-1000 Atomic force microscope, respectively. Optical absorption spectra are recorded in the range of 300–1200 nm using JASCO V-670 spectrophotometer. The photoluminescence spectra (PL) are recorded at room temperature using plorolog 3-HORIBA JOBIN-YVON with an excitation source wavelength of 325 nm.

FT-IR and FT-Raman spectra are recorded by KBr disc method in the region of 1000–50 cm^{-1} using Bruker IFS 66 V FT-IR spectrometer equipped with a Globar source, Ge/KBr beam splitter and TGS detector with a spectral resolution is ±2 cm^{-1} and FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line widths with 200 mW power.

3. Computational methods

In the present work, HF and DFT methods; LSDA, B3LYP and B3PW91 are carried out using the basis set 3-21G(d,p). All the calculations are performed using GAUSSIAN 09W program package on Pentium IV processor in personal computer. In DFT methods; local-spin density approximation LSDA [16] generally gives good molecular structures, vibrational frequencies and charge densities in strong bound systems, Becke's three parameter hybrids function combined with the Lee–Yang–Parr correlation function (B3LYP) [17], Becke's three parameter exact exchange-function (B3) [18] combined with gradient-corrected correlation functional of Lee, Yang and Parr (LYP) [19,20] as well as Perdew and Wang (PW91) [21,22] predict the best results for molecular geometry and vibrational frequencies for moderately larger molecules.

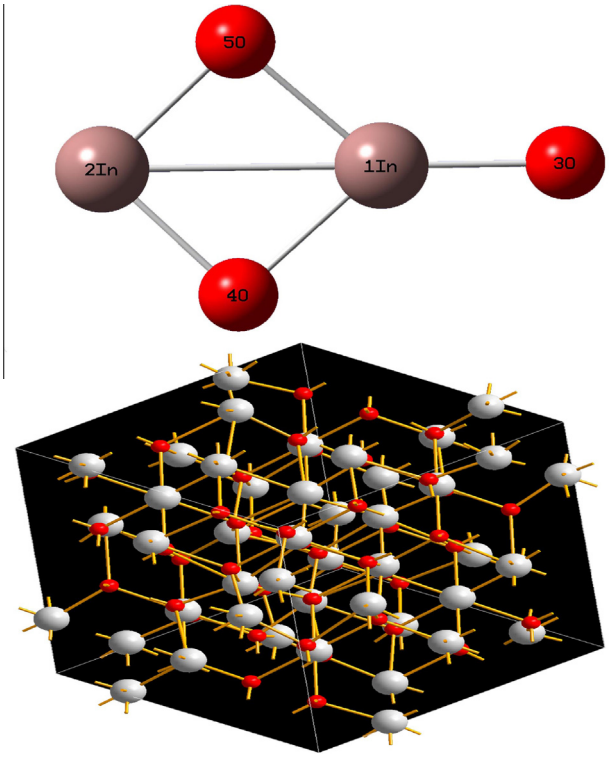

Fig. 1. Crystal structure of indium oxide.

The optimized crystal and molecular structure of In_2O_3 is obtained from Gaussian 09 and Gaussview program and is shown in Fig. 1. The comparative optimized structural parameters such as bond length, bond angle and dihedral angle are presented in Table 1. The observed (FT-IR and FT-Raman) and calculated vibrational frequencies by HF and DFT (LSDA, B3LYP and B3PW91) methods, vibrational assignments and the total energy distribution (TED) for B3PW91 of In_2O_3 are presented in Table 2. Experimental and simulated spectra of IR and Raman in both phases are presented in Figs. 2 and 3, respectively.

The total energy distribution (TED) calculations show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule which enable numerically to describe the character of each mode and are carried out by SQM method [23,24] using the output files created at the end of the frequency calculations. The TED calculations are performed by using PQS program [24].

4. Results and discussion

4.1. Molecular geometry

In_2O_3 compound posses a BCC molecular structure and belong to C_S point group symmetry. The most stable Y-shape structure is