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Indium oxide: A transparent, conducting ferromagnetic semiconductor for spintronic applications

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ABSTRACT

The optical and electrical properties are the two important dimensions of Indium oxide and its derivatives (indium tin oxide) and were well studied to understand the origin of wide electronic band gap and high electrical conductivity at room temperature. In_2O_3 and its derivatives find many applications in electronic and optoelectronic domains based on the above properties. The recent discovery of ferromagnetism in In_2O_3 at room temperature become a third dimension and lead to intensive research on enhancement of ferromagnetic strength by various means such as dopants and synthesis protocols and extrinsic parameters. The research lead to enormous experimental data and theoretical models proliferation over the past one decade with diverse insights into the origin of ferromagnetism in In_2O_3 based dilute magnetic semiconductors. The experimental data and theoretical models of ferromagnetism in In_2O_3 has been thoroughly surveyed in the literature and compiled all the data and presented for easy of understanding in this review. We have identified best chemical composition, geometry and synthesis protocols for strongest ferromagnetic strength and suitable theoretical model of magnetism has been presented in this review.

1. Introduction

Doping magnetic metallic elements into non-magnetic conventional semiconductors yield dilute magnetic semiconductors (DMS). This can be achieved by adding a small quantity of magnetic material into the In_2O_3 lattice and converting it to magnetic material. Such processed materials are called as dilute magnetic semiconductors. The II–VI semiconductor based DMS materials such as transition metal (TM) doped ZnTe, CdTe and CdS were studied extensively and magnetic results were reported in the literature [1–3]. The observed ferromagnetism in these compounds was limited due to low miscibility of the dopant(s). The alloy type of DMS materials such as Mn-doped InAs and GaAs of these materials have been investigated and found that the figure of merit of these materials is not impressive for device fabrication due to high cost of raw materials, stringent material preparation conditions and low Curie temperature (T_c) [4,5].

Generally the characteristics of a dilute magnetic semiconductor are:

- It should have high Curie temperature.
- A close relation between the ferromagnetism and the population of a spin split band of carriers.
- A choice of making either p type or n type.
- Anomalous Hall effect.
- High carrier mobility and long spin diffusion length.

Most of the alloy type of semiconductors are not fulfilling the above all characteristics. The alloy type semiconductors are exhibiting low Curie temperature and limited dopant concentration.

For the cost effective and reliable device fabrication, the DMS material should have low cost, moderate processing conditions and high Curie temperature (above room temperature). For these reasons, much focus is being put on pure and transition metal (TM) doped oxide based DMS materials such as ZnO, TiO_2, SnO_2, In_2O_3 and Cu_2O [6–10]. The advantages in the oxide DMSs are their wide band gap, high carrier concentration, ease of preparation, low cost of material and high Curie temperature (T_c). In oxide magnetic semiconductors, oxygen vacancy has been considered as one of the origins for the room temperature ferromagnetism [11,12]. Moreover, high electronegativity of oxygen atoms may possibly produce a strong *p*, *d* exchange coupling between band carriers and localized spins. Hence oxide semiconductors are better to have above characteristics because oxide semiconductors are exhibiting ferromagnetism at room temperature and above room temperature and having high solubility of impurity ions (> Fe 20%). When compared to other oxide semiconductors, it is challenging if one could achieve ferromagnetism in In_2O_3 matrix.

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For the past few decades, indium oxide (In_2O_3) is one of the best studied and established oxide semiconductors. It is an n-type, degenerate, transparent highly conducting oxide material with band gap (3.5 eV) [13–15]. The thin films of indium oxide exhibit high optical transmittance in the visible region of the solar spectrum, high optical reflectance in the infrared region and high electrical conductivity with wide band gap. The electrical conductivity and optical transmittance of the indium oxide can be controlled by creating off stoichiometry or external doping elements [16,17]. In_2O_3 in thin film form, have electrical resistivity of the order of $10^{-4}\,\Omega$ cm and optical transmittance more than 90% in the visible region of the electromagnetic spectrum [18]. The properties of the In_2O_3 thin films are highly dependent on preparation method. The pure indium oxide can acts as an insulator whereas the same can be converted into conducting by creating defects in it or making off stoichiometry in the composition. In_2O_3 can exhibit considerable non-stoichiometry and show good doping capacity. The doping mechanism in In_2O_3 is more complex since every oxygen vacancy will produce two free electrons.

2. Applications of In_2O_3

Among the different transparent conducting oxide materials (TCOs), In_2O_3 is one of the best transparent conducting oxide which find many applications such as transparent conductive electrodes in solar cells, coating material in optoelectronic devices, photodiodes, gas sensors, touch screens, liquid crystal displays, light emission diodes, photovoltaic devices,transparent contact, antireflection coatings for silicon solar cells, ultraviolet lasers, infrared reflective and electrochromic windows, etc. [19–35]. Different magnetic and non-magnetic ions were doped into the In_2O_3 lattice and studied the physical properties of it. The impurity ions as such as iron (Fe), nickel (Ni), carbon (C), fluorine (F), cobalt (Co), chromium(Cr), manganese (Mn), copper (Cu), molybdenum (Mo), etc were doped into In_2O_3 lattice and reported ferromagnetism. Further the magnetic nanoparticles such as Fe, Co, Mn, Ni, find many biological applications. Recently, significant advances have been achieved in the development of magnetic hydrogels (i.e., the combination of hydrogels with micro- and/or nanomagnetic particles that can quickly respond to an external magnetic field (MF). The hydrogels containing magnetic nanoparticles (MNPs) are more suitable for biomedical applications due to their super-paramagnetic and responsive properties. The development of magnetic hydrogels holds great potential applications in tissue engineering and cell/drug delivery. The magnetic hydrogels find applications in biomedical engineering, tissue engineering, drug delivery and release, enzyme immobilization, cancer therapy and soft actuators [36–40]. Further magnetic nanoparticles are currently being considered in medical applications such as magnetic resonance imaging contrast agents, targeted drug delivery and hyperthermia treatment of cancer [41–49].

Different synthesis methods such as solid state reaction, sol–gel, co-precipitation, solvo-thermal and mechanical alloys were employed for the synthesis of bulk and nanoparticles of pure and doped indium oxide [50–52]. As indium oxide in thin film and nanostructure forms find many optoelectronic applications, many preparation techniques such as such as flash evaporation, activated reactive evaporation, electron beam evaporation, pulsed laser deposition, sputtering, molecular beam epitaxy, sol–gel, spray pyrolysis and reactive ion plating were employed for the preparation of pure and impurities doped indium oxide thin films and nanostructures [53–62]. Each method has its own advantages and limitations. Further, in order to improve the properties of In_2O_3 thin films, effect of air annealing, vacuum annealing, substrate temperatures, doping with different elements, etc. were also employed. It is known that the properties of the material will be different in 1D (nanowire), 2D (nanosheet), 3D (bulk). Moreover, it is known that the decrease in crystallite size lead to the change in their physical properties such as optical transmittance, electrical conductivity, chemical, surface and band gap of the materials that can be attributed to the quantum confinement effect [63].

3. Physical properties of In_2O_3

3.1. Structural properties

Indium oxide (In_2O_3) is one of the most well studied and established oxide semiconductors. The In_2O_3 unit cell of the bixbyite structure has 80 atoms, 48 oxygen atoms and 32 indium atoms (8 formula units, 40 atoms in the primitive unit cell). It occurs in cubic bixbyite symmetric structure with indium (In^{+3}) ions at six fold coordinate site and oxygen (O^{-2}) ions at four fold co-ordinate positions with lattice constant of 10.118 Å. The indium atoms occupy two non-equivalent lattice positions surrounded by oxygen atoms in octahedral and trigonal prismatic coordination, respectively. The indium ions (In^{+3}) occupy Wyckoff positions 8b and 24d and oxygen ions (O^{-2}) occupy Wyckoff position 48e [64,65]. Further, it is known that the cubic bixbyite structure of indium oxide consists of lot of inherent oxygen vacancies which are believed as double donors and responsible for the good electrical conductivity and ferromagnetism. The schematic representation of structure of indium oxide is shown in Fig. 1.

Due to the difference in site symmetry, it is envisaged that the In_2O_3 with the two kinds of sites occupied preferentially by a magnetic dopant are different in magnetic behavior. Studies have been carried out to find the position of dopant element in the host material using Mossbauer and hyperfine interaction studies [66–68]. In_2O_3 exhibits amorphous nature when prepared at lower substrate temperature (>250 °C) and form crystalline cubic structure with (2 2 2) orientation when prepared/annealed above 250 °C. No structural deformations can be found even if the doping concentration is high enough (Fe:50%) [69,70]. The cubic structure of In_2O_3 remains same even when the thin films were annealed at higher temperatures. Its structure can be easily formed any kind of substrates such as YSZ (1 0 0), MgO (0 0 1), STO (0 0 1), glass, quartz, and Si substrates

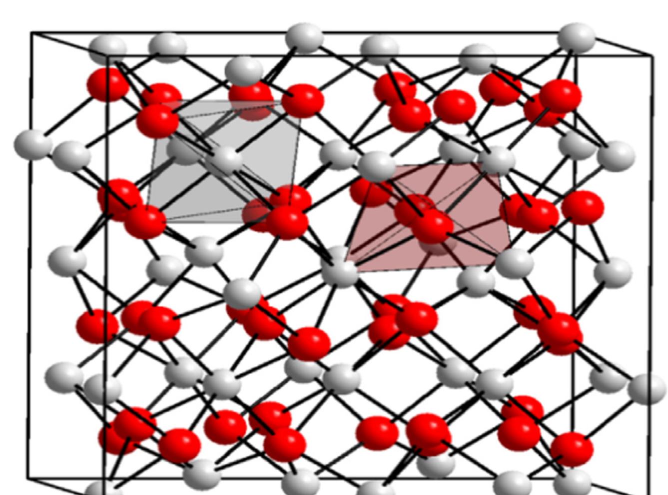

Fig. 1. Cubic bixbyite structure of Indium oxide.