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Physical properties of Fe doped In_2O_3 magnetic semiconductor annealed in hydrogen at different temperature

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ABSTRACT

The effects of hydrogen-annealing at different temperatures (300, 400, 500 and 600 °C) on physical properties of $In_{2-x}Fe_xO_3$ ($x=0.025$) thin film were investigated. The structural measurement using XRD shows that the film has a single In_2O_3 phase structure when annealed in hydrogen at 300–500 °C, however when annealed in hydrogen at 600 °C the film has a mixed phase structure of In_2O_3 and In phases. The electrical measurements show that the carrier concentrations of the films decrease with the increase of hydrogen-annealing temperature in the range 300–500 °C. The optical band gap of the films decreases with increasing hydrogen-annealing temperatures. The saturation magnetisation, Ms, and coercivity of films increase with the increment of hydrogen annealing temperature. The film annealed at 300 °C has the lowest resistivity, $\rho=0.03\ \Omega$ cm, and the highest carrier concentrations, $n=6.8\times10^{19}\ cm^{-3}$, while film annealed at 500 °C has both good electrical ($\rho=0.05\ \Omega$.cm and $n=2.2\times10^{19}\ cm^{-3}$) and magnetic properties, Ms=21 emu/cm^{3}.

1. Introduction

Magnetic behaviour in transition metals doped semiconductor oxides has received a great attention from scientific community. The idea behind this field of research is the manipulation of the charge transport and spin degree of freedom via doping of transition metals in semiconductor oxides may lead to fabrications of novel spintronic devices [1]. The research in this field has been started after the theoretical prediction of room temperature ferromagnetic behaviour (RTFM) in Mn doped ZnO as reported by Dietl et al., which later was followed by the discovery of similar behaviour in Co doped TiO_2 by Matsumoto et al. [2,3]. Ferromagnetic behaviours were then reported in several transition metals doped semiconductor oxides, TiO_2, ZnO, SnO_2 and In_2O_3 [4–9].

The annealing condition has a vital role on the final semiconducting and magnetic properties of transition metals doped semiconducting oxides. For instance, Fe doped In_2O_3 thin film prepared on Al_2O_3 (0001) substrate by PLD technique has been reported. The films were annealed in high vacuum in order to induce multi valence of Fe ions into Fe^{+3} and Fe^{+2} that stands behind the existence of magnetic behaviour in the prepared film [10]. In another study, the decrease of oxygen pressure on film grown by PLD has in turn changed both its magnetic and electrical behaviour. The film grown by PLD at 5 and 1 Pa has paramagnetic and semiconducting behaviour, and was ferromagnetic and semiconducting when grown at 10^{-1} Pa. However, when the pressure was reduced by one and two orders of magnitude i.e. 1×10^{-2} and 1×10^{-3} Pa, the film became ferromagnetic and metallic [11]. In a recent work, An et al. have prepared $(In_{0.93}Fe_{0.07})_2O_3$ film by RF-magnetron sputtering on (001) Si substrate. The as-deposited film exhibited magnetisation of 1.07 emu/cm^3, but this value has dropped off to 0.058 emu/cm^3 when the sample was annealed in air, which was ascribed to higher oxygen vacancies available in as-deposited film than annealed one [12].

The incorporating of H in In_2O_3 system has been theoretically proven to act as shallow donor below conduction band that can add electrons and system conductivity increases [13,14]. On the other hand, ferromagnetic behaviour of Fe doped ZnO system has been enhanced by annealing in the presence of H_2/Ar atmosphere [15]. In another work, the annealing using hydrogen atmosphere was reported to enhance the magnetic saturation and coercivity of Cr doped ZnO nanoparticles [16]. The physical properties of Fe doped In_2O_3 thin film annealed in hydrogen have not been reported yet. Thus, we aimed in this work to study and optimise electrical and magnetic properties of $In_{2-x}Fe_xO_3$, $x=0.025$, thin film by hydrogen-annealing at different temperatures 300–600 °C. The film annealed at 300 °C was found to have the lowest resistivity and highest carrier concentrations while film annealed at 500 °C was found to have both good electrical and magnetic

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properties.

2. Experimental and method

The $In_{1.975}Fe_{0.025}O_3$ films were prepared by sol–gel followed by spin coating as reported elsewhere in our previous work [17]. The films were annealed at 300, 400, 500 and 600 °C for 30 min with hydrogen gas flowing through the furnace tube with a volume flow $\leq$ 1 L/min at 15 psi cylinder pressure. The phase and crystal structure were determined using a Bruker X-ray diffractometer (XRD model D8 advance). The surface morphology and thickness were examined using a field emission scanning electron microscopy (FESEM). The electrical properties parameters were measured using the Hall Effect system and the optical properties of the films were characterized using a UV–vis spectrophotometer (Model Perkin-Elmer Lamda 35). The grain size was measured using a transmission electron microscopy (TEM model Philips Cm12). The electronic and compositions of films were investigated using an X-ray photoelectron spectroscopy (XPS) (esca+ Omicron XPS). The magnetic behaviour of films was investigated using a vibrating sample magnetometer (VSM model Lakeshore 7404), where the distance between the two electromagnetic poles was ~2.5 cm.

3. Result and discussion

3.1. Structure and morphology

Fig. 1 presents the X-ray diffractions of $In_{1.975}Fe_{0.025}O_3$ thin films annealed at 300–600 °C in hydrogen. The In_2O_3 phase starts to form at annealing temperature of 300 °C as evident from the small peaks of (222) and (400) planes. At 400 °C and 500 °C of hydrogen-annealing temperature, the In_2O_3 phase is completely recognised and matches with JCPDS (006-0416) of In_2O_3. However, at 600 °C of hydrogen annealing, three peaks are observed at angle $2\theta = 33°$, 36.5° and 39°, which correspond to In phase. It is believed that at 600 °C, the H_2 as reduction agent become more reactive and reduces the In_2O_3 phase. However, the hydrogen may not react completely with In_2O_3 molecules because the volume flow was slow, as indicated in the experimental section. In addition, hydrogen is a light element. This causes some of the In_2O_3 molecules to lose completely the oxygen and convert to In phase while others tend to lose some of oxygen and hence creating oxygen vacancy. The percentages of In_2O_3 and In phases in the film annealed at 600 °C, calculated using Eq. (1), are 73% and 27%, respectively,

$$In_2O_3\,\% = \frac{\sum I_{In2O3}}{\sum I_{In2O3} + \sum I_{In}}, \tag{1}$$

where I_{In2O3} and I_{In} are the intensity of peak corresponding to In_2O_3 and In phase, respectively. The intensity of XRD peaks increases gradually with the increase of annealing temperature. The peak with highest intensity is along (222) direction when annealed at 600 °C. This behaviour could be due to the increase of annealing temperature that improves films' crystallinity and possibly due to the change in oxygen content in lattice of $In_{1.975}Fe_{0.025}O_3$ films caused by annealing in hydrogen. Table 1 summarizes the lattice parameters of films. The lattice parameter of film annealed at 300 °C is 10.13 Å, and it decreases to 10.11 Å and it remains as such for films annealed at 400, 500, 600 °C.

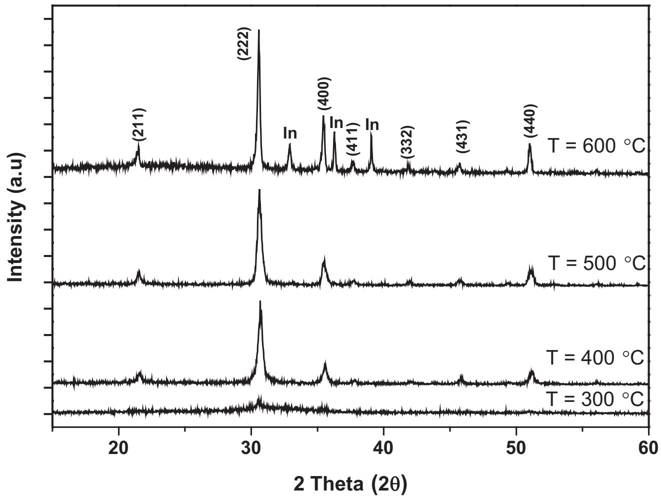

Fig. 1. XRD of $In_{1.975}Fe_{0.025}O_3$ films annealed in hydrogen at (300–600 °C).

Table 1
Lattice parameters *a*, relative reliability R/R_0 and crystallite size of $In_{1.975}Fe_{0.025}O_3$ films anneal at 300, 400, 500 and 600 °C.

Annealing temperature (°C)	a-axis (Å)	R/R_0	Thickness (nm)	Optical band gap (eV)	Grain size from TEM (nm)
300	10.130	1.5	82	3.86 ± 0.06	5.8 ± 1.7
400	10.110	1.4	100	3.80 ± 0.05	8.7 ± 2.8
500	10.111	1.5	57	3.50 ± 0.03	14 ± 4.0
600	10.111	1.4	53	2.60 ± 0.03	72 ± 36.0

Fig. 2 demonstrates the surface morphology and thickness of $In_{1.975}Fe_{0.025}O_3$ films annealed in hydrogen at 300 and 600 °C. It is noted that the thickness of films tends to decrease with increasing hydrogen-annealing temperature until it reaches 53 nm for film annealed at 600 °C. From another angle, the films' grains tend to agglomerate conforming bigger, irregular shaped particles when annealed at 600 °C.

Fig. 3 shows the TEM micrographs of $In_{1.975}Fe_{0.025}O_3$ grains annealed in hydrogen at 300–600 °C. The average grains size of films are listed in Table 1. At low annealing temperature of 300 °C, the grain size is small, 5.8 ± 1.70 nm. With the increase of the annealing temperature the grains tend to grow up forming bigger grains. The average grain size of films annealed at 400, 500 and 600 °C are 8.7 ± 2.8 nm, 14 ± 4.0 nm and 72 nm, respectively. Possibly the grains tend to combine and finally increasing the grain size with the increase of annealing temperature.

3.2. Electrical properties

Table 2 summarizes the electrical properties of $In_{1.975}Fe_{0.025}O_3$ films annealed in hydrogen at 300, 400, 500 °C. The resistivity increases from 0.032 Ω cm to 0.23 Ω cm when the annealing temperature increases from 300 to 400 °C. On the other hand, it decreases to 0.053 Ω.cm for film annealed at 500 °C. The film annealed at 600 °C become insulators and its resistivity could not be measured. This could be due to the mixed phase of In_2O_3 and In observed from XRD result of the film. The carrier concentration decreases with the increase of hydrogen-annealing temperature. The carrier concentration of film annealed at 500 °C is 57 times higher than that of the same film annealed in air which agree with previous study that proposed the hydrogen to act as shallow donor in oxide that provides additional carrier to conduction band [13,14].

3.3. Optical properties

The optical band gaps of the films calculated from the