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Ion beam studies on reactive DC sputtered manganese doped indium tin oxide thin films

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Abstract

Indium based transparent conducting oxides doped with magnetic elements have been studied intensively in recent years with a view to develop novel ferromagnetic semiconductors for spin-based electronics. In the present work, we have grown manganese doped indium tin oxide (Mn:ITO) thin films, onto Si and Si/SiO_2 substrates by DC reactive sputtering of a composite target containing indium–tin alloy and manganese, in a gas mixture of oxygen and argon. Glancing angle X-ray diffraction (GXRD) studies reveal the polycrystalline nature of the films. Magnetic measurements carried out using vibrating sample magnetometer (VSM) suggest that the films are ferromagnetic at room temperature, with a saturation magnetization of $\sim$22.8 emu/cm^3. The atomic percentages of In, Sn, Mn and O, as estimated using Rutherford backscattering spectrometry (RBS) are 37.0, 4.0, 1.6 and 57.4, respectively. RBS measurements reveal that the interface of the films with Si substrate has a $\sim$30 nm thick intermediate layer. This layer consists of oxygen, silicon, indium, tin and manganese, in the ratio 1:0.56:0.21:0.07:0.03, indicative of diffusion of elements across the interface. The films on Si/SiO_2, on the other hand, have a sharp interface.

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Keywords: TCO; Thin films; DMS; Interface

1. Introduction

Novel ferromagnetic semiconductors are being developed for applications in spintronics [1] and optical waveguide technology [2]. The search for room temperature ferromagnetism in diluted magnetic semiconductors has gained impetus following the theoretical prediction by Dietl et al. [3]. Recently, different groups have successfully demonstrated ferromagnetism above room temperature in various transition metal doped oxide semiconducting thin films. The observed ferromagnetism is found to depend critically on the concentration of the dopants as well as on the growth and post-growth processing conditions. ITO is a transparent oxide semiconductor with high carrier concentration and single-phase crystal structure [4], which makes it a perfect host for magnetic dopants. ITO films doped with magnetic elements have properties which make them viable for use as spin injectors in spintronic devices [5]. The interface of these films with technologically important substrates like Si and Si/SiO_2 will play a crucial role in the applicability of these films, in practical devices.

In the present work, we have grown Mn:ITO films onto Si and Si/SiO_2 substrates at high temperature, by reactive DC sputtering. The films have been characterized using GXRD for phase purity, and VSM for magnetic properties. RBS has been used for compositional characterization of the films as well as for interface analysis.

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2. Experimental details

2.1. Growth, phase identification and magnetization studies

Mn:ITO films were deposited on to p-Si(100) and Si/SiO_2 substrates using reactive DC sputtering of a composite target containing In–Sn alloy and Mn, in a gas mixture of oxygen and argon. The target was made from a melt quenched In–Sn alloy containing nearly 10 at.% tin. Uniformly planted Mn pellets on the target surface acted as source for Mn doping. By varying the number of Mn pellets, the ratio of the area covered by the Mn pellets to that of the In–Sn alloy could be altered, thereby varying the concentration of Mn in the films. In order to ensure uniform distribution of Mn in the films, a rotating substrate holder with 120 rpm was employed. Films grown without the rotation arrangement were non uniform with regions of varying Mn concentration. The vacuum chamber was evacuated to a pressure of 2×10^{-6} Torr, before allowing in oxygen and argon gas in the ratio 1:1000. Sputtering was done at a pressure of 6×10^{-2} Torr, at a constant power of 100 W. These conditions were arrived at after optimization for optically high transparent films on glass substrates. During sputtering, the temperature of the substrate, held at a distance of 30 mm from the target, always reached 675 K [6]. The rate of deposition of the films was ~0.7 nm s^{-1}. The Si/SiO_2 substrate was prepared by thermally oxidizing p-Si(100) wafer in dry oxygen, at 1273 K for 5 h inside a quartz tube. Thickness of SiO_2 layer was ~300 nm.

The phase purity of the sputtered films was analyzed by GXRD using a PANalytical X'Pert Pro diffractometer. The incident angle of X-ray beam was kept fixed at 1.5° to the plane of the film. Magnetic properties of the films grown on Si/SiO_2 substrate were studied using a VSM, with the magnetic field applied perpendicular to the plane of the film.

2.2. RBS studies

RBS measurements were carried out using the CIBA Singletron 3 MV accelerator facility at NUS, Singapore. The measurements were carried out using a $^4He^+$ beam of energy 2 MeV under a chamber pressure below 5×10^{-6} mbar. The backscattered particles from the films were collected by a surface barrier detector, at an angle of 160°. Theoretical simulation to the experimental data was performed using the software XRUMP [7].

3. Results and discussion

3.1. GXRD and magnetization results

Fig. 1 shows the GXRD pattern of Mn:ITO films on Si and Si/SiO_2 substrates. The peaks marked as 's' in Fig. 1(b) were from the Si/SiO_2 substrate. The pattern could be indexed based on a cubic bixbyite structure of indium oxide as no peaks corresponding to elemental Mn or its oxides

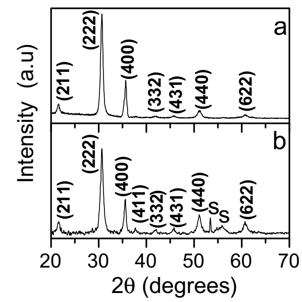

Fig. 1. GXRD pattern of Mn:ITO films deposited on (a) Si and (b) Si/SiO_2 substrates.

could be detected. The films were polycrystalline with a mean crystallite size of ~40 nm as calculated using Scherrer formula. The lattice constant was calculated to be 10.10 Å, which is slightly lower in comparison to that reported for indium oxide (10.118 Å). This is in agreement with the reported value for Mn:ITO film grown on Si/SiO_2 substrate by co-evaporation [5]. The slightly lower lattice constant is attributed to the lower ionic radii, 0.83 and 0.8 Å, respectively, of Sn(IV) and Mn(II) ions which are expected to substitute for the In(III) ions having higher ionic radius (0.94 Å), in an octahedral configuration. The fact that the presence of dopant does not give rise to additional reflections in XRD pattern of many doped oxide semiconductors, but is manifested only as a change in lattice constant has been reported by several workers [5,8,9] as well.

Fig. 2 shows the variation of magnetization (M) with the applied filed (H), at 300 K, where the diamagnetic background due to the substrate has been subtracted. A well defined hysteresis loop is observed, with a saturation magnetization of ~22.8 emu/cm^3, at a field of 5000 Oe applied perpendicular to the plane of the film. Fig. 3 shows the variation of M as a function of temperature (T), at a field of 5000 Oe. The curve is typical of ferromagnetic films, with a Curie temperature well above 300 K.

3.2. RBS results

Fig. 4 shows the RBS spectra of Mn:ITO film on Si substrate. In Fig. 4, symbols correspond to the experimental

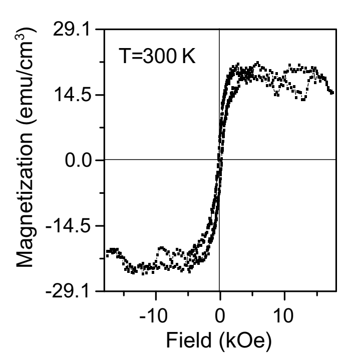

Fig. 2. M–H curve of Mn:ITO film on Si/SiO_2 substrate.

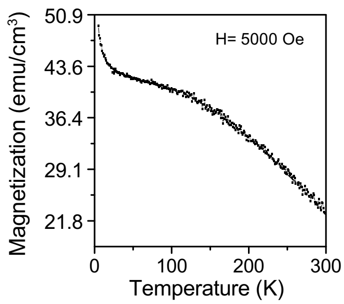

Fig. 3. *M–T* plot of Mn:ITO film on Si/SiO_2 substrate.

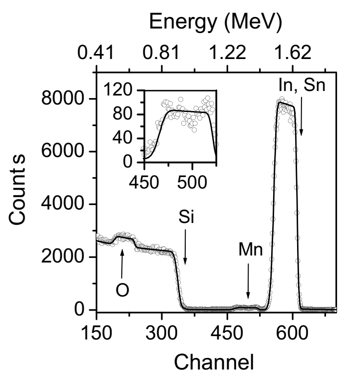

Fig. 4. RBS spectra of Mn:ITO film on Si substrate.

data and the continuous line, the simulated curve. The distinct peak appearing on the high energy side is due to In and Sn from Mn:ITO. Since the atomic numbers of In ($Z = 49$) and Sn ($Z = 50$) are comparable, RBS cannot uniquely distinguish between the two. Therefore, composition of these elements in the film is usually taken as that in the source material [5] and we have followed the same procedure here. The small peak that lies to the left of the peak due to In and Sn corresponds to Mn from Mn:ITO and is shown as inset to Fig. 4. The concentration of Mn in the film is low and hence the yield due to Mn is less, as evidenced by the small height of the peak. Oxygen due to the Mn:ITO film is seen towards the low energy side, as a superimposed peak on the Si plateau which extends to lower energies. The composition of the film was evaluated to be 37.0 at.% In, 4.0 at.% Sn, 1.6 at.% Mn and 57.4 at.% O. The errors in the estimated concentration of the elements are 0.5%, 2.8%, 2.3% and 4.3%, respectively, for In, Sn, Mn and O. The ratio of oxygen to the other constituents of the film is ~1.3, evidently less than 1.5, expected for stoichiometric indium oxide. This suggests that the semiconducting films are deficient of oxygen and hence n-type. The simulation that reproduced the experimental data best could be obtained only by incorporating a 300 Å thick intermediate layer between the film and Si substrate. This layer was assumed to be homogeneous, consisting of oxygen, silicon, indium, tin and manganese in the ratio 1:0.56:0.21:0.07:0.03. This indicates finite diffusion of elements across the interface. Fig. 5 shows the trailing

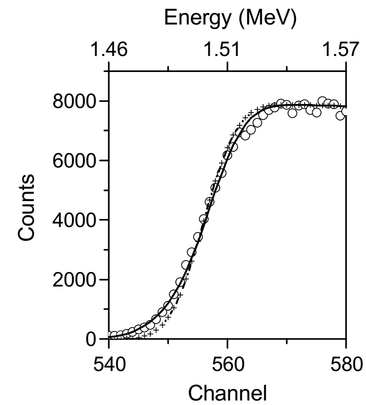

Fig. 5. Low energy edge of the In–Sn peak in Fig. 4 on an expanded scale. Open circles denote experimental data, solid line, the curve simulated by incorporating an intermediate layer and dotted line, the curve simulated without incorporating the intermediated layer.

edge of the In–Sn peak on an expanded scale along with the curves simulated with and without incorporating the intermediate layer. The interface layer is attributed to the oxidation of silicon at the expense of Mn:ITO during the initial stages of film formation [6].

RBS spectra of Mn:ITO film on Si/SiO_2 substrate is shown in Fig. 6. The presence of SiO_2 layer between Mn:ITO film and Si is clearly seen from the two separate edges for both Si and oxygen. The edge occurring at higher energy accounts for Si from SiO_2 layer while the other is due to Si from the Si substrate. The high energy edge for oxygen corresponds to oxygen from the Mn:ITO film, whereas the low energy one accounts for oxygen from SiO_2 layer. The peak corresponding to Mn is shown on an expanded scale as inset to Fig. 6. The film on Si/SiO_2 substrate is found to have nearly the same composition as the film on Si substrate. The simulated curve which reproduced the experimental data best could be obtained by assuming a sharp interface between the film and SiO_2 layer. This is in contrast to the presence of an interface layer, observed in the case of Mn:ITO film on Si substrate.

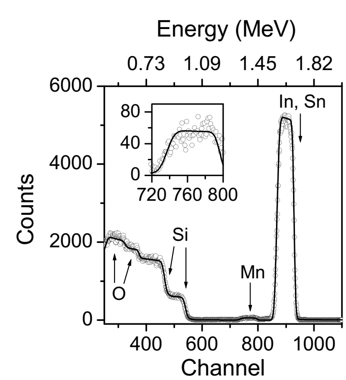

Fig. 6. RBS spectra of Mn:ITO film on Si/SiO_2 substrate.

4. Conclusion

In summary, polycrystalline films of Mn:ITO that show ferromagnetism at room temperature have been deposited on to Si and Si/SiO_2 substrates. The concentration of Mn in the films was 1.6 at.%. Interface analysis using RBS revealed the presence of an intermediate layer between the film and Si substrate, while the interface of the film with Si/SiO_2 substrate was found to be sharp.

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