Journal of Magnetism and Magnetic Materials 324 (2012) 2932–2935

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Effect of vacuum-annealing on the d^0 ferromagnetism of undoped In_2O_3 films

Shaohua Sun, Ping Wu, Pengfei Xing *

Department of Applied Physics, Institute of Advanced Materials Physics, Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Faculty of Science, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Article history:
Received 14 December 2011
Received in revised form
23 April 2012
Available online 8 May 2012

Keywords:
d^0 ferromagnetism
Indium oxide
Vacuum-annealing
Oxygen vacancy
Radiofrequency magnetron sputtering

ABSTRACT

Vacuum-annealing was carried out on the pure indium oxide films deposited on Si (100) substrates by radiofrequency magnetron sputtering. Oxygen-deficiency states and room temperature d^0 ferromagnetism were both detected in the as-grown and vacuum-annealed films. With more oxygen vacancies appeared through vacuum-annealing, the saturation magnetization increased rapidly from 0.5 to 5.5 emu/cm^3. The connection between the highly oxygen-deficiency states and the strong magnetic moment suggests that oxygen vacancies play a crucial role in mediating the ferromagnetism in In_2O_3 films. We think that this d^0 ferromagnetism mainly stems from V_O^+ and oxygen vacancy clusters in the interfaces or grain boundaries.

1. Introduction

Since ferromagnetism with T_C above 300 K in Mn-doped ZnO was theoretically predicted by Dietl et al. [1], diluted magnetic oxide semiconductors (DMOSs) with possibility to simultaneously control spin and charge have gained much attention due to their potential applications in spintronics [2–5]. Room-temperature ferromagnetism (RTFM) has been discovered by some groups in transition-metal (TM)-doped oxide semiconductors, such as ZnO, In_2O_3, SnO_2, etc. But the probability that the ferromagnetism originates from ferromagnetic clusters or secondary phases [6] is hard to be removed due to the low solubility of the TM elements in the oxide lattice. Recently, the discovery of d^0 ferromagnetism in pure HfO_2 opens up a new way for magnetic semiconductors [7]. As there is no magnetic-doping in the d^0 system, the probable impact induced by TM-doping can be effectively ruled out. d^0 ferromagnetism has also been observed in pure TiO_2 [8], CeO_2 [9], In_2O_3 [10,11], nonstoichiometric CaB_6 [12] and ZnO powders [13], nanoparticles [14,15], nanowires [5,16], thin films [3,4], etc. There are suggestions that point defects serve as possible origins for the d^0 ferromagnetism [17]. Experimentally, Banerjee et al. [13] and Xing et al. [16] attribute the ferromagnetism obtained in pure ZnO powders and nanostructures to oxygen vacancy (V_O). Singhal et al. [8] attribute the ferromagnetism in TiO_2 to three factors: Ti 3d-O 2p hybridization, V_O^+ (the electrons in singly occupied oxygen vacancies) and oxygen vacancy assisted fragmentation of grains. Theoretically, Kim et al. [18] predict the sizable magnetic moment in rutile TiO_2 stems from the lattice distortion due to oxygen vacancies. The ab initio calculations performed by Rahman et al. [19] on SnO_2 and Pemmaraju and Sanvito [20] on HfO_2 indicate that cation vacancies can induce local moments in surrounded O atoms, while calculations to the Hubbard U of defects carried out by Chakrabarty and Patterson [21] attribute the arise of ferromagnetism in ZnO films to V_{ZnO}^- and V_{Zn}^-. Although the ferromagnetism observed in undoped oxides mentioned above is consistently attributed to the existence of native defects (oxygen vacancy, cation vacancy and other complex structures of defects), further and systematic researches are still needed to define when a specific kind of defect plays a role and how the coupling happens.

As a transparent and wide gap oxide, In_2O_3 has a variety of practical applications in transparent conducting films, solar cells, flat-panel displays, etc. Meanwhile, as a base-material for magnetic semiconductors, it is also expected to be made as a multi-functional material with properties of magnetism, optics and conduction together. However, till now, only a few works [10,11,22,23] have been proceeded on the d^0 ferromagnetism of pure In_2O_3. The corresponding d^0 ferromagnetism origin and its underlying physics in this system are poorly understood. In this paper, we report an enhancement on the d^0 ferromagnetism of pure In_2O_3 films by vacuum-annealing. The connection between the highly oxygen-deficiency states and the enhanced ferromagnetism indicates that oxygen vacancies play a crucial role in mediating the d^0 ferromagnetism in the pure In_2O_3 films.

2. Experimental details

In_2O_3 films were deposited on (100) single crystal silicon substrates by radiofrequency magnetron sputtering using a ceramic In_2O_3 target (99.99%, Φ60 mm). The chamber was firstly

* Corresponding author. Tel.: +86 22 27403488; fax: +86 22 27406852.
E-mail address: pfxing@tju.edu.cn (P. Xing).

0304-8853/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2012.04.050

evacuated to a base pressure of 8.7×10^{-5} Pa. During deposition, the sputtering pressure and substrate temperature were maintained at 1 Pa and 700 °C. High purity O_2 and Ar with a constant flux of 5 sccm and 25 sccm were introduced, serving as reactive and sputtering gases, respectively. After deposition for 1 h, we got the as-grown (AG) In_2O_3 film with a thickness of 110 nm. Thereafter, by annealing the as-grown film in vacuum at 650 °C for 6 h, we got a vacuum-annealed (VA) film, and by further annealing the VA film in air, we got an air-annealed (AA) film. The relatively lower annealing temperature is to avoid any significant changes in the crystal structure.

The surface topography and grown quality were investigated by a scanning electron microscope (SEM). The crystal structure and phase identification were studied by X-ray diffraction (XRD) using a diffractometer D/max-2500 with Cu Kα radiation. The valence and effective concentration of elements were characterized with an X-ray photoelectron spectroscopy (XPS). And the magnetization measurements were conducted using a high sensitivity Quantum Design MPMS magnetometer.

3. Results and discussion

Fig. 1(a) shows the SEM pattern of the AG In_2O_3 film, from which we can see that the as-grown film has a neat and clean surface without any impurity precipitates. Cubic-grown grains are well-distributed in the film with the grain size of about 25 nm. XRD patterns for the films before and after vacuum-annealing are shown in Fig. 1(b). From the patterns, we can see that all diffraction peaks are indexed well to a cubic bixbyite In_2O_3 structure (space group Ia3 (206)). No peaks of impurities or other indium-related secondary phases are detected within the detection limit. Both the two films have a strong diffraction peak along (222), indicating that films before and after vacuum-annealing both have a strong texture structure along (222) direction. As a result of the vacuum-annealing, the position of the (222) peak moves from 30.580° to 30.661° (inset in Fig. 1). The corresponding lattice constant decreases from 10.092 Å to 10.089 Å. This is mainly caused by the oxygen atoms escaping from the lattice or the interstitial positions during vacuum annealing. Meanwhile, the full width at half maximum (FWHM) of the (222) peak decreases from 0.364° to 0.302°. The corresponding grain size calculated by the Scherrer formulation increases from 22.4 nm to 27.0 nm. That's to say phase transformation does not occur during the vacuum-annealing process, but the crystal quality is improved to some extent, with the lattice more compact and the grain size a little bigger.

Fig. 2 shows the XPS spectrum of the AG In_2O_3 film depicting a full range scan from 0 to 1200 eV. Similar spectrum is also obtained for the VA In_2O_3 film which is not shown here. Peaks such as O 1s, In 3s, In 3d, In 3p, In 4s, In 4p, In 4d and C are detected. No other magnetic impurity peaks are detected in the detection limit, indicating that both our AG and the VA samples are clean without any contamination. Fig. 3 shows the In 3d spectra for the AG and VA In_2O_3 films. The peaks at 444.2 eV and 451.8 eV represent the core levels of In $3d_{5/2}$ and In $3d_{3/2}$, respectively. The energy difference between the two peaks is coincident with the standard reference value of In_2O_3, indicating that the In element is in a +3 valence state. For the VA film, the peaks have a tiny shift toward lower energy and become sharper after vacuum-annealing, which manifest the evidence that the surroundings of In have been changed due to the creation of oxygen vacancies [3]. However, from the tiny change in the intensity of In 3d spectrum, it is hard to determine the presence of In vacancies.

Fig. 4 shows the spectra of O 1s of the AG and VA In_2O_3 films. The peaks are asymmetric in shape, indicating the presence of surface contamination [8,14,15], and they can be fitted with two

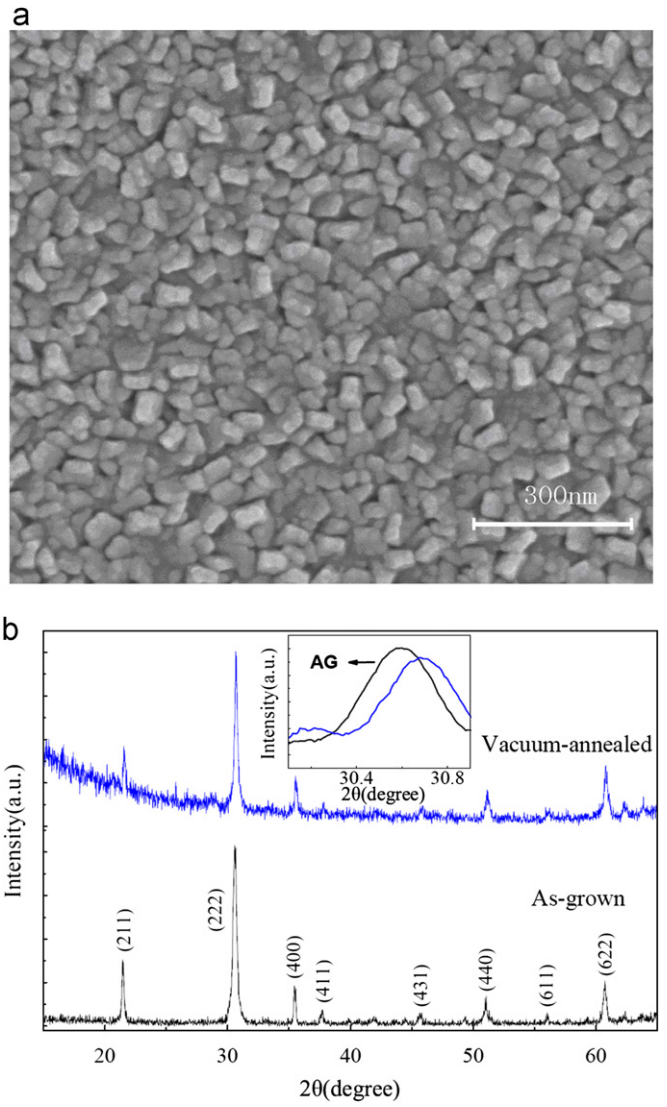

Fig. 1. (a) SEM pattern of the as-grown In_2O_3 film. (b) XRD spectra for the as-grown and vacuum-annealed In_2O_3 films. The inset shows the magnified part of (222) peaks.

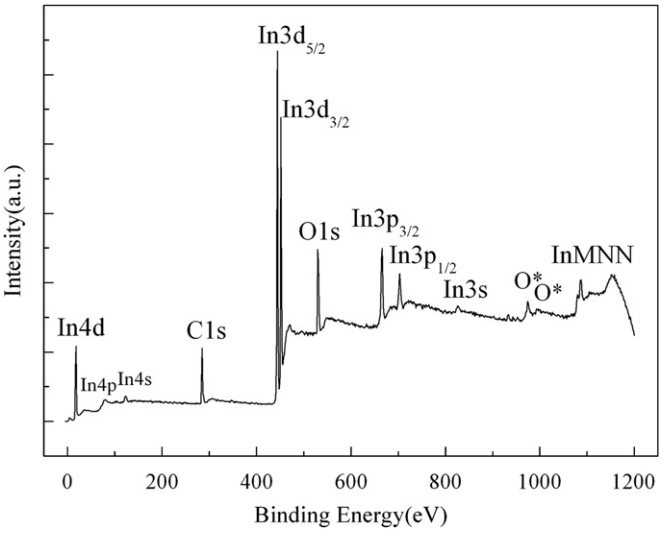

Fig. 2. XPS survey spectrum of the as-grown In_2O_3 film. Similar spectrum was also obtained for the vacuum-annealed In_2O_3 film.