Journal of Magnetism and Magnetic Materials 426 (2017) 545–549

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Origin of room temperature ferromagnetism in SnO_2 films

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ARTICLE INFO

Keywords:
Room temperature ferromagnetism
Oxygen vacancies
Thin film growth
Pulsed laser deposition
SnO_2

ABSTRACT

SnO_2 films exhibiting room temperature ferromagnetism (RTFM) have been prepared on Si (001) by pulsed laser deposition. The saturation magnetization (M_s) of the films experiences a decreasing trend followed by increasing with the growth temperature increased from RT to 400 ℃. The growth temperature affects both the concentration and the location of the oxygen vacancies as the origin of the RTFM. With lower growth temperatures (< 300 ℃), more oxygen vacancies exist in the inner film for the samples with less crystallinity, resulting in enhanced magnetism. Higher deposition temperature leads to less oxygen vacancies in the inner film but more oxygen defects at the film surface, which is also beneficial to achieve greater magnetism. Various oxygen pressures during growth and post-annealing have also been used to confirm the role of oxygen vacancies. The study demonstrates that the surface oxygen defects and the positively charged monovalent O vacancies (V_O^+) in the inner film are the origin of the magnetism in SnO_2 films.

1. Introduction

Dilute magnetic semiconductors (DMSs) have attracted intensive interest due to their potential application in spintronics devices [1]. Since the discovery of room temperature ferromagnetism (RTFM) in Co-doped TiO_2 [2], numerous investigations have been focused on realizing RTFM in doped oxides, including ZnO [3–5], TiO_2 [6,7] In_2O_3 [8–10] and SnO_2 [11–13], etc. Previous studies suggested that the ferromagnetism originated from interactions between the dopant moments and carrier spins and that the doping was critical to achieve RTFM [7,14–16]. Later observations of RTFM in undoped oxides challenge the conventional understanding on the origin of the ferromagnetism [17,18]. As the *d* shells of the cationic elements of the oxides are either empty or full, such phenomenon is called d° ferromagnetism [19]. Various studies have been stimulated to reveal the mechanism behind the RTFM in d° oxides and defects have usually been considered as an important factor.

SnO_2 as a chemically stable oxide with a wide band gap (3.62 eV) has been intensively investigated as a DMS [20–22]. The origin of its RTFM, however remains controversial. It has been suggested that oxygen vacancies (V_o) [23–25] or Sn vacancies (V_{Sn}) [26] can exhibit localized moments, whereas other defects such as Sn interstitials (Sn_i) are nonmagnetic [23,25]. Since it is energetically difficult for V_{Sn} to form in the SnO_2 according to first-principles calculations [27], V_o have been considered to induce ferromagnetic ordering in pure SnO_2. Details on the type and location of the oxygen vacancies and their effects on the magnetic properties of the SnO_2 thin films are still limited. In this work, we report study of the RTFM in the pristine SnO_2 thin films prepared under different temperatures and oxygen pressures. Correlating the evolution of the defects with the RTFM indicates that both the surface oxygen defects and the V_o in the inner film are responsible for the ferromagnetic ordering in the SnO_2 thin films.

2. Experimental methods

SnO_2 thin films were grown on Si (001) substrates by pulsed laser deposition (PLD) with a KrF excimer laser (λ=248 nm, 10 Hz). The Si substrates were cleaned by dilute HF acid solution to obtain oxide-free surface before introducing into the vacuum chamber which was then evacuated to the base pressure (10^{-7} Torr). The SnO_2 films were deposited by ablating a sintered SnO_2 target with a target-to-substrate distance of 60 mm. Thickness of the SnO_2films was measured by cross sectional scanning electron microscopy (SEM, S-4800, Hitachi). The structure and crystallinity of the films were examined using x-ray diffraction (XRD, PANalytical X′Pert PRO) with a Cu Kα radiation source. Atomic Force microscopy (AFM) was used to examine the surface morphology of the films. A superconducting quantum interference device magnetometer (SQUID, Quantum Design MPMS-XL) was used to reveal the magnetic performance of the thin films. The chemical state of the film was investigated with X-ray photoelectron

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http://dx.doi.org/10.1016/j.jmmm.2016.12.002
Received 26 July 2016; Received in revised form 15 November 2016; Accepted 1 December 2016
Available online 02 December 2016
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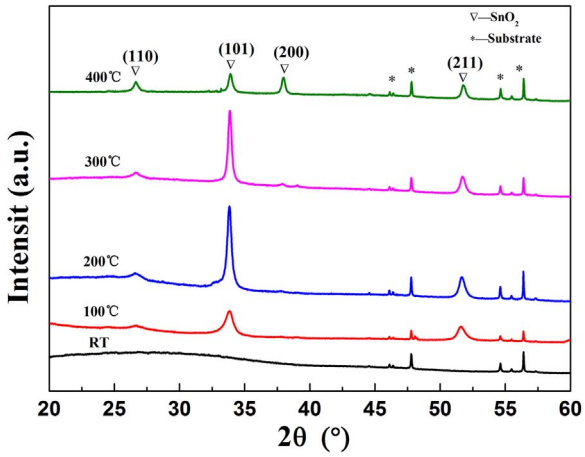

Fig. 1. XRD data of the SnO_2 films grown at temperatures ranged from room temperature to 400 ℃.

spectroscopy (XPS, Escalab 250Xi) using monochromatized Al Kα radiation (1486.6 eV). The surface of the sample was etched for 15 s to remove any absorbed oxygen. The optical properties were investigated by photoluminescence (PL, Edinburgh Instruments F900).

3. Results and discussion

Fig. 1 shows the XRD curves of the SnO_2 films with the growth temperature varied from room temperature (RT) to 400 ℃. The SnO_2 film deposited at RT exhibits amorphous feature with only peaks of the substrate observed. XRD peaks corresponding to the SnO_2 rutile phase appear for the films grown at elevated temperatures. Enhanced crystallinity is achieved by raising the growth temperature. With the temperature increased from 100 ℃ to 300 ℃, the SnO_2 films grow preferentially along the (101) direction and small peaks corresponding to (110) and (211) orientations are also detected. Multiple crystal directions including (110), (101), (200) and (211) without any obvious preference are observed for the SnO_2film deposited at 400 ℃, according to the reference pattern (Powder Diffraction File No. 41–1445) of tin oxide. Temperature above 300 ℃ has previously been identified as a prerequisite to produce polycrystalline SnO_2films [28], which agrees with our study that polycrystalline SnO_2film is obtained when deposited at 400 ℃. By Debye-Scherrer formula, the average crystallite sizes of the thin films are estimated to be around 10.6 nm, 20.5 nm, 23.7 nm and 24.8 nm for the films deposited at 100, 200, 300 and 400 ℃, respectively.

Fig. 2a and b present typical AFM images showing the morphology of the SnO_2film deposited at 400 ℃ with a scan size of 2 μm×2 μm. Surface of the film is relatively smooth with rms roughness of approx. 4.8 nm. Cross-sectional SEM has been used to identify the thickness (~80 nm) of the SnO_2film as shown in Fig. 2c. The surface of the film is

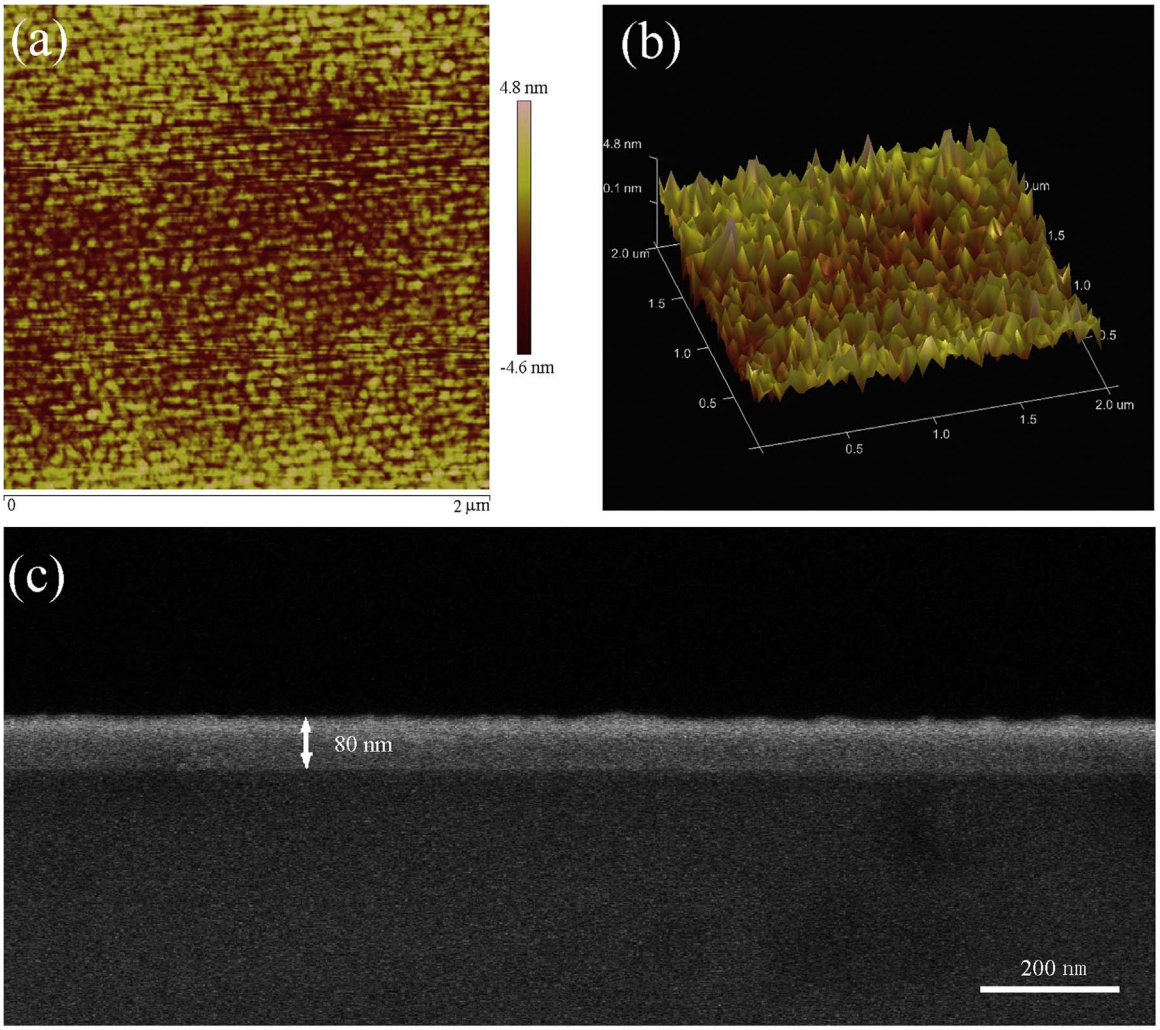

Fig. 2. Typical AFM images showing the surface (a) morphology and (b) roughness of the SnO_2 film. (c) Cross sectional SEM image demonstrating the thickness of the film.