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Nano-precipitates induced room temperature ferromagnetism in heavily Nb-doped titania thin films

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ABSTRACT

Room temperature ferromagnetism (FM) is observed for annealed heavily niobium doped titania (TNO) thin films on silicon substrates and on glass nanospheres. Precipitation of ~10–30 nm-diameter Nb_2O_5 nanoparticles occurs in the TNO films air-annealed at 600 °C or above and enhances their saturation magnetization (M_s). The largest M_s is found in the 800 °C annealed 40 nm-thick TNO films on glass nanospheres (~6×10^4 A/m) and the M_s reduces as films increased in thickness or deposited on flat Si substrates or annealed at lower temperature or in hydrogen. This work demonstrates that nano-precipitates and interfaces are both significant factors in achieving enhanced FM in the titania based thin films.

1. Introduction

Dilute magnetic semiconducting oxides have been widely studied during recent years [1–3]. Materials such as pristine and doped ZnO, SnO_2, In_2O_3 and TiO_2 have been investigated on the development of room-temperature ferromagnetism (FM). Titania (TiO_2) has gained the most attention among the oxides because of its outstanding properties useful for applications such as FM, photocatalysis, transparent conducting oxide and solar cells [4,5]. Beginning with the discovery of FM in Co-doped TiO_2 thin films [2], some studies have indicated that the detected room temperature FM is due to the formation of Co clusters [6–8]. However, it is observed that such magnetic properties are sensitive to sample preparation, which led to some experimental studies giving evidence that the origin of FM is from the Co-doped TiO_2 matrix itself [9,10]. Numerous studies on transition element doped TiO2 films have been carried out and reported including substituting V, Cr, Mn, Fe, Co, and Ni partially for Ti in TiO_2 and ferromagnetism above room temperature in films with good crystallinity [1,3].

The microscopic mechanism of long-range order magnetic behavior for pristine and doped oxides is still an open problem. Several theoretical models have been proposed to give an explanation, however, the origin of this magnetic property is still not clear. One of the models is based on the carrier-induced Ruderman–Kittel–Kasuya–Yoshida (RKKY) model which claims the carriers presented in the host lattice will interact with the local magnetic moment of the dopants and result in long-range ferromagnetic order [11]. But it is likely that the magnetic property does not originate solely from the RKKY interaction, it may also come from the defects and oxygen vacancies in the thin film [12–16]. Other reports of room temperature FM in pure oxides including HfO_2 films have shown that the intrinsic magnetic property in the films arises from the lattice defects from the film/substrate interface [1,17,18]. Despite the persistent controversy on the possibility of granular precipitates of magnetic materials in doped oxides as a possible cause of the observed FM, there are other reports about magnetic properties induced by nanoparticles or quantum dots. The effect of surfaces is significant for quantum dots due to their large surface-to-volume ratio. Surface passivation is generally used to eliminate these dangling bonds and to ensure the good confinement of electrons inside the quantum dot. The resulting quantum confinement along with reduced coordination number, local symmetry, localized unpaired spins, and surface effects may give rise to magnetism in quantum dots. For example, room-temperature FM has been reported for non-magnetic semiconductors [19–22], metallic [23–26] and oxide nanoparticles [27] and carbon nanostructures [28].

Nb-doped titania (denoted as TNO) films have been studied extensively for its excellent transparent conducting behaviors [29]. In contrast, studies of the magnetic properties of TNO are relatively few, since niobium is not exactly regarded as a classic magnetic metal, neither should its oxides exhibit ferromagnetic-like behavior. Zhang has reported the magnetic effect in a transparent nonmagnetic oxide doped with a nonmagnetic dopant ($Ti_{1-x}Nb_xO_2$) and suggested that the possible origins of local magnetic moments in the Nb-doped

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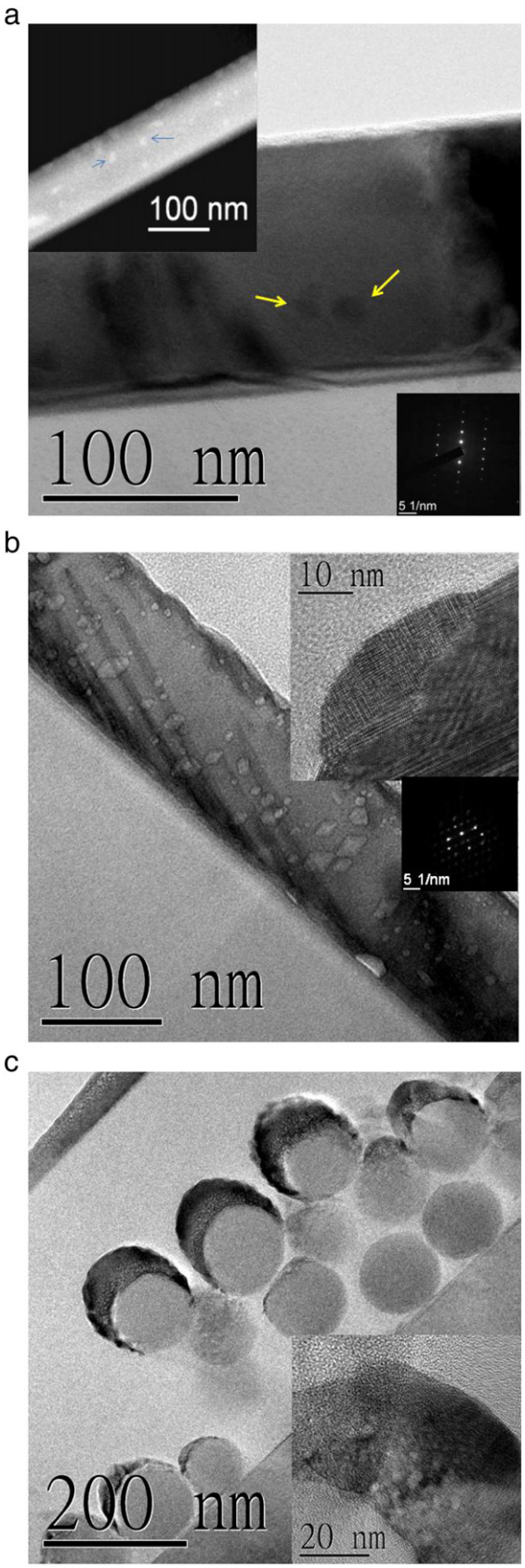
TiO_2 samples are specific cation valence states or other defects states [30]. Zheng has studied the magnetoresistance of two anatase Nb-doped TiO_2 films and revealed ferromagnetic characteristics, which proves the existence of localized magnetic moment in $Ti_{1-x}Nb_xO_2$ compounds [31].



More recently, Yang reported that room temperature ferromagnetism was obtained in Nb:TiO_2 grown on LaAlO3 (100) substrates by pulsed laser deposition and suggested the existence of Ti^{3+} and Nb^{4+} ions, which had one unpaired d electron, responsible for the local magnetic moments [32].

In this paper, we prepare heavily doped Nb-doped TiO_2 thin films by magnetron sputtering technique. Through annealing under air atmosphere, we minimize the influence of oxygen vacancies and allow Nb_2O_5 nanoparticles to precipitate and generate extra interfaces in the thin film. The effect of nano-precipitates and interfaces on the room temperature FM in the TNO thin films is deeply observed and discussed.

2. Experimental details

TNO thin films were deposited on substrates of silicon and of a two-dimensional (2D) layer of glass-nanospheres (GNS) on silicon by reactive co-sputtering of pure Ti and Nb metal targets in a plasma of argon and oxygen using a 5-cathode magnetron sputtering system (AJA Inc. MA, USA)[29]. The densely packed 2D layer of GNS of 100 nm in diameter, purchased from Duke Scientific and diluted with distilled water in a 1:100 ratio by volume) was prepared by spin-coating (Chemat Tech., KW-4 A) onto Si substrates at ca. 600 rpm. The deposition conditions of the TNO films are essentially the same as those reported in reference [29]. Three sputtering guns with a DC power of 200 W were set for the Ti targets, and a single gun with RF power of 120 W was set for the Nb target. The purity of both target metals is over 99.9%. Gas flows of 20 sccm of Ar and 6 sccm of O_2 were introduced during deposition. The working temperature and the working pressure were controlled at 100 °C and 0.4 Pa (3 mTorr), respectively, with the substrate holder rotation at 5 rpm. The total deposition time was 10 min. and 30 min. to fabricate the TNO thin films with two different thicknesses of ~40 and ~120 nm, respectively. The as-deposited films are homogeneous and amorphous oxide of titanium and niobium with about 70 % oxygen content and 30% metal, in which the ratio of Nb/(Ti + Nb) is 0.35.

After deposition, the TNO thin films were annealed for one hour in air at 400, 600 and 800 °C and in hydrogen at 600 °C using a rapid thermal annealing furnance (Mila300, Ulvac Company, Tokyo, Japan). The samples were elevated to the designed temperature in 10 seconds and held for 1 hour, then, cooled down to room temperature in 30 seconds. The surface composition and electron binding energy of Ti2p, Nb3d and O1s orbit are measured by X-ray photoelectron spectrometer (XPS, Thermo K-Alpha) using Al-Kα X-ray (1486.6 eV) at 15 kV and 100 W, and we choose C1s at 284.8 eV as a standard for calibration when analyzing the data. The film structure was characterized using an X-ray diffractometer (XRD, Rigaku Co., Tokyo, Japan) with Cu Kα radiation at 40 kV and 150 mA, also an incident angle at 3°. Observation of the plan view and the cross-sectional view of the samples was achieved using a field emission scanning electron microscope (FE-SEM, JEOL JSM-6500 F) operating at 15 kV and a transmission electron microscope (TEM, JEOL JEM-2100 Field Emission TEM) operating at 200 kV. The cross-sectional TEM samples were prepared first by mechanical thinning and followed by ion milling with 6 kV Ar ion beam at an etching angle around 4°. A Vibrating Sample Magnetometer (VSM, Lake Shore 7407) was used to characterize the magnetic properties of the

Fig. 1. (a) Cross-sectional TEM image of the 120 nm-thick TNO thin film annealed in air at 600 °C. The top left inset shows the scanning TEM image of the film. The inset at the bottom right shows the selected electron diffraction of the matrix. (b) Image of the 120 nm-thick TNO film annealed in air at 800 °C. Precipitation of Nb_2O_5 nano-particles was observed. The inset is a close up view of the Nb_2O_5 on the surface with selected electron diffraction in this region. (c) Image of the 40 nm-thick TNO film deposited on glass nanospheres and air-annealed at 600 °C showing discontinuity of the TNO film. The inset is the close up view of the TNO film.