Structures and magnetic behaviours of TiO_2–Mn–TiO_2 multilayers*

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The TiO_2–Mn–TiO_2 multilayers are successfully grown on glass and silicon substrates by alternately using radio frequency reactive magnetron sputtering and direct current magnetron sputtering. The structures and the magnetic behaviours of these films are characterised with x-ray diffraction, transmission electron microscope (TEM), vibrating sample magnetometer, and superconducting quantum interference device (SQUID). It is shown that the multi-film consists of a mixture of anatase and rutile TiO_2 with an embedded Mn nano-film. It is found that there are two turning points from ferromagnetic phase to antiferromagnetic phase. One is at 42 K attributed to interface coupling between ferromagnetic Mn_3O_4 and antiferromagnetic Mn_2O_3, and the other is at 97 K owing to the interface coupling between ferromagnetic Mn and antiferromagnetic MnO. The samples are shown to have ferromagnetic behaviours at room temperature from hysteresis in the M–H loops, and their ferromagnetism is found to vary with the thickness of Mn nano-film. Moreover, the Mn nano-film has a critical thickness of about 18.5 nm, which makes the coercivity of the multi-film reach a maximum of about 3.965×10^{-2} T.

Keywords: magnetron sputtering, TiO_2–Mn–TiO_2 multilayers, transmission electron microscope, ferromagnetic properties

PACC: 8115C, 6116D, 7550D, 6170T

1. Introduction

Many researchers have focused on the study of transition-metal doped semiconductor oxide thin film to seek for a new compound for industrial applications in spintronics since Matsumoto *et al.*[1] first experimentally investigated the room temperature ferromagnetism (FM) in Co-doped TiO_2 thin films. However, a little work[2,3] has been done on Mn–TiO_2 multilayers, and the mechanisms responsible for FM in diluted semiconductor oxides are still under debate. Recently we grew a Mn nano-film sandwiched between TiO_2 films by alternately using radio frequency reactive magnetron sputtering and direct current magnetron sputtering. In this paper, the structures of the TiO_2–Mn–TiO_2 multilayers are measured on an X' Pert Pro x-ray diffraction (XRD) system and a JEM-2010 high resolution transmission electron microscopy (HRTEM). The magnetic behaviours of the TiO_2–Mn–TiO_2 multilayers are investigated by an LDJ-model 9600 vibrating sample magnetometers (VSM) at room temperature and a superconducting quantum interference device (SQUID) in a temperature range of 5–400 K with a maximum applied field of 5×10^{-2} T. For a quantitative determination of sample magnetisation, both VSM and SQUID are applied to the same sample.

2. Experiment

The TiO_2–Mn–TiO_2 multilayers were deposited by alternately using radio frequency reactive magnetron sputtering and direct current magnetron sputtering. Glass and silicon substrates (20 mm×20 mm) were ultrasonically washed successively in acetone, alcohol, and deionised water to obtain a clean surface before being placed in a vacuum chamber. And the substrate was further inversely sputtered for 5 min before the film deposition. The target was separated from the substrate by 5 cm. First, a TiO_2 thin film

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was deposited by radio frequency reactive magnetron sputtering. When the chamber was evacuated to a pressure of 5×10^{-5} Pa high-purity (99.9999%) argon and oxygen (99.999 %) gases were introduced. The ratio of argon and oxygen is maintained at 50/5.0. A high-purity (99.999%) Ti plate with 60 mm in diameter and 3 mm in thickness was used as the target. The voltage applied to the radio frequency sputter gun was 1020 V. During sputtering, the chamber pressure was maintained at 2 Pa. Then, the film was heated *in situ* at various temperatures (100 °C∼700 °C) to ensure good-quality TiO_2 film. And then, a Mn nano-film was grown onto TiO_2 layer by direct current magnetron sputtering. A high-purity (99.98%) Mn plate with 60 mm in diameter and 3 mm in thickness was used as target. When the chamber was evaluated to a pressure of 5×10^{-5} Pa again, only high-purity (99.9999%) argon gas was introduced. The direct current sputtering power was about 26 W. And finally, another TiO_2 thin film was also grown by radio frequency reactive magnetron sputtering as mentioned above in order to form the TiO_2–Mn–TiO_2 multilayers. The film thickness d was determined by surface profilometry using a DEKTAK 3 Alpha-step instrument. The deposition rate was obtained as a ratio of thickness d to sputtering time. In our experiment, the sputtering rate of TiO_2 was as large as $\sim$ 2.5 nm / min, and sputtering rate of Mn was about 0.28 nm/s. The sputtering system was controlled by computer.

The TiO_2–Mn–TiO_2 multilayers were characterised by XRD and HRTEM. The XRD studies were carried out on an X'Pert Pro XRD system with x-ray Mirror PFX at an operating voltage of 40 kV and a current of 40 mA. The HRTEM micrographs were obtained by a JEM-2010 TEM. The magnetic properties were measured by an LDJ-model 9600 vibrating sample magnetometer at room temperature. The magnetic properties were investigated by a SQUID magnetometer (MPMS5, Quantum Design) in a temperature range of 5–400 K with a maximum applied field of 5×10^{-2} T.

3. Results and discussion

3.1. Structure and morphologies

Figure 1 shows XRD studies on a pure anatase TiO_2 thin film prepared by radio frequency reactive magnetron sputtering and a TiO_2–Mn–TiO_2 multi-film prepared by the alternate use of radio frequency reactive magnetron sputtering and direct current magnetron sputtering. From Fig. 1(b), one can see that the TiO_2–Mn–TiO_2 multi-film consists of anatase and rutile TiO_2[4] and contains a little Mn_3O_4,[5] and the strength of x-ray diffraction of rutile TiO_2 is higher than that of anatase TiO_2.

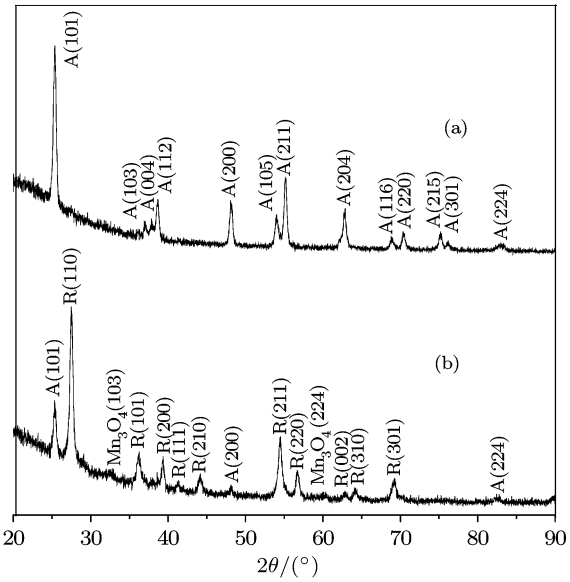


Fig. 1. XRD patterns of (a) pure antase TiO_2 film and (b) TiO_2–Mn–TiO_2 multilayer.

Figure 2 shows the TEM image of the TiO_2–Mn–TiO_2 multi-film in cross section. One can obviously see that the composite film consists of an 80 nm TiO_2, a 7 nm Mn and a 144 nm TiO_2.

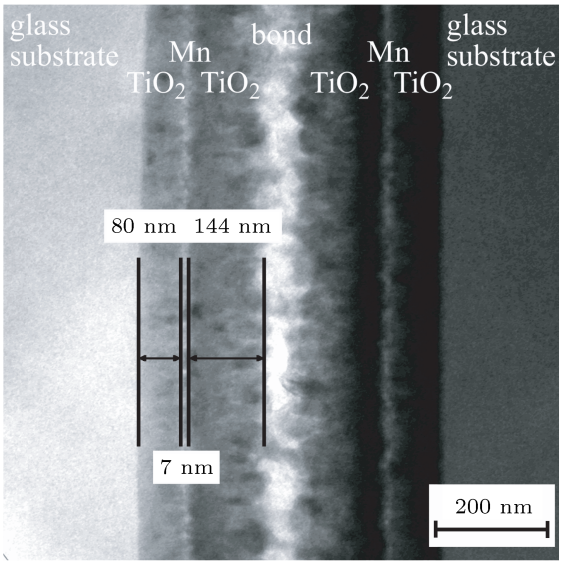


Fig. 2. A typical low resolution TEM image of TiO_2–Mn–TiO_2 multi-film. The thickness of each layer is marked.

Figure 3 shows the high-resolution TEM images of the TiO_2–Mn–TiO_2 multi-film in cross section. Fig-

ure 3(a) shows the TiO_2 thin film on glass substrate.

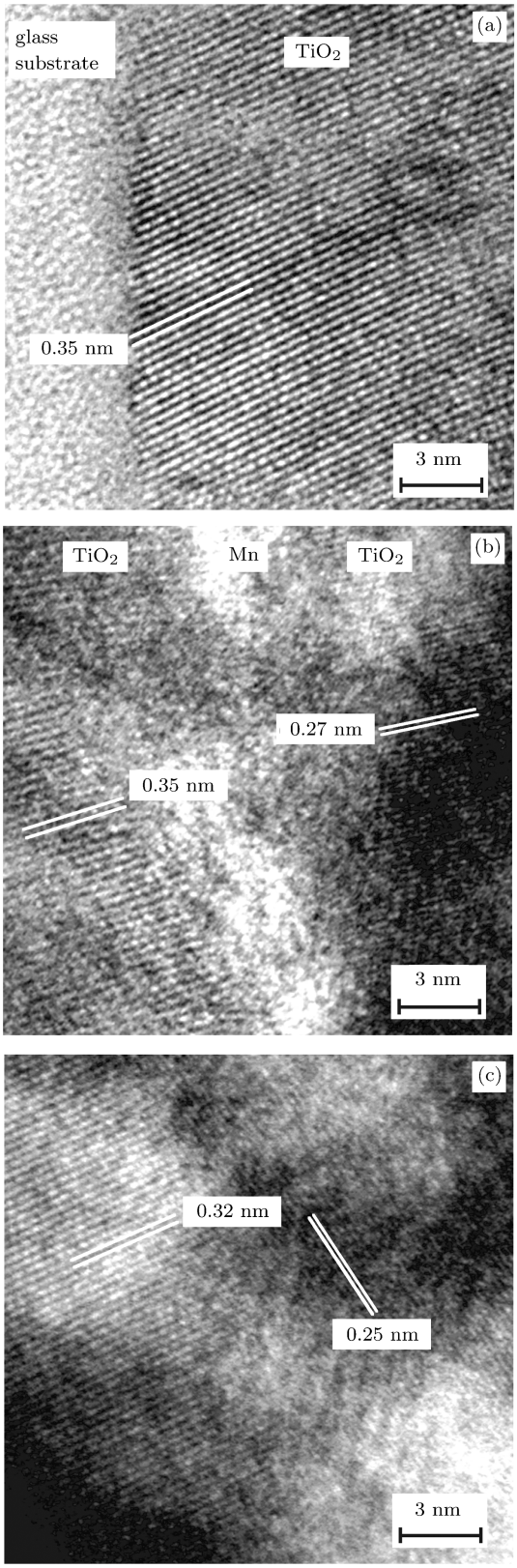


Fig. 3. High-resolution TEM images of the TiO_2–Mn–TiO_2 multi-film. (a) at the interface between the glass substrate and the TiO_2 thin film; (b) near the Mn layer; (c) at the top TiO_2 layer of the multi-film.

One can see that the adjacent fringe spacing, 0.35 nm, is marked, and is consistent with the inter-planar distance of (101) crystal planes of anatase TiO_2. Figure 3(b) shows the interlayer film of Mn and its oxide. It is shown that the Mn layer is amorphous, and the thickness is not homogenous. According to PDF card #80-0382, the adjacent fringe spacing, 0.27 nm, is consistent with the inter-planar distance of (103) crystal planes of the hausmannite Mn_3O_4. The 0.35 nm refers to the (101) crystal planes of anatase TiO_2. It can be indicated that the Mn layer has diffused into the TiO_2 layer, and has been oxidated into Mn_3O_4. Figure 3(c) shows the top TiO_2 layer of multi-film. One can see that the adjacent fringe spacings, 0.32 nm and 0.25 nm, are marked, and are consistent with the inter-planar distances of (110) and (101) crystal planes of rutile TiO_2, respectively. It is interesting to see that the phase of the top TiO_2 layer is different from that of the bottom layer.

3.2. Magnetic properties

Figure 4 shows a typical hysteresis loop for the TiO_2–Mn–TiO_2 sandwich film obtained by an LDJ-model 9600 vibrating sample magnetometer at room temperature. The magnetic field is set to be parallel to the film plane. It is found that the coercivity is about 3.836×10^{-2} T when the thickness of Mn is about 25.2 nm between the two TiO_2 films.

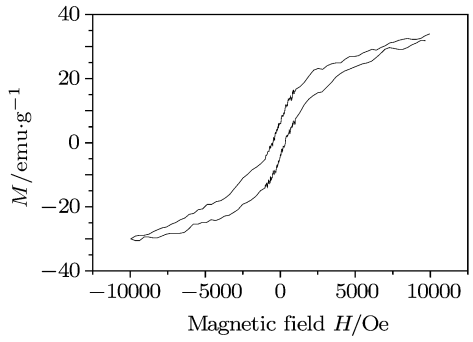


Fig. 4. Hysteresis loop for TiO_2–Mn–TiO_2 sandwich film with a 25.2 nm-thick Mn film in magnetic field parallel to the film plane. (1 Oe=79.5775 A/m, 1 eum=10^3 A·m^2).

The hysteresis loops were measured by VSM for TiO_2–Mn–TiO_2 multilayers in magnetic field parallel to the film plane at room temperature. The relation between the coercivity of the TiO_2–Mn–TiO_2 multilayer and the thickness of the Mn film is shown in Fig. 5, where the solid squares represent the experimental data, and solid line is of the Gaussian fitting. One can see from Fig. 5 that the thickness about

18.5 nm, called the optimal coupling thickness, is the critical thickness of the TiO_2–Mn–TiO_2 system.

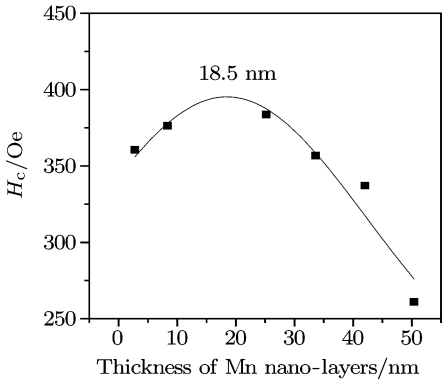


Fig. 5. Coercivity versus thickness of Mn thin film in the TiO_2–Mn–TiO_2 multilayer.

Figure 6 shows the magnetisation of the TiO_2–Mn–TiO_2 multilayer against temperature, which is

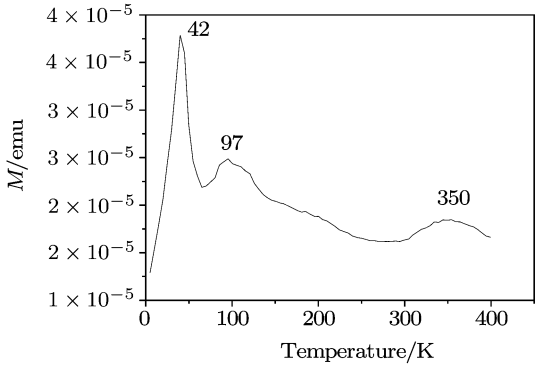


Fig. 6. Magnetization of the TiO_2–Mn–TiO_2 multilayer versus temperature, measured by a SQUID in a temperature range of 5–400 K with a maximum applied field of 5×10^{-2} T.

measured by a SQUID in a temperature range of 5–400 K with a maximum applied field of 5×10^{-2} T parallel to the sample surface. It shows the behaviour of ferromagnetic-to-antiferromagnetic phase transition when the temperature is at 42 K attributed to the interface coupling between ferromagnetic Mn_3O_4 and anti-ferromagnetic Mn_2O_3,[5,6] and the phase transition at about 97 K originates from the interface coupling between ferromagnetic Mn and anti-ferromagnetic MnO, resulting in magnetic exchange bias below the Néel temperature (110 K) of MnO.[7,8]

And it has the behaviour of paramagnetic-to-ferromagnetic transition when the temperature increases from 320 to 350 K. The TiO_2–Mn–TiO_2 multilayers are of anti-ferromagnetic properties when the temperature is higher than 350 K. These originate from the strong interface coupling and the defect.

4. Conclusions

The TiO_2–Mn–TiO_2 multilayers are successfully deposited on the glass and silicon substrates by alternately using RF magnetron sputtering and DC magnetron sputtering. The structures of the multilayers are characterised and they consist of a mixture of anatase and rutile TiO_2 with an embedded Mn nano-film. Two turning points of ferromagnetic-to-antiferromagnetic phase transition are found. One is at 42 K which is attributed to interface coupling between ferromagnetic Mn_3O_4 and antiferromagnetic Mn_2O_3, and the other is at 97 K owing to the interface coupling between ferromagnetic Mn and antiferromagnetic MnO. Ferromagnetic behaviour at room temperature, obtained from hysteresis loops, varies with the thickness of the Mn nano-film. The maximum of coercivity, 3.965×10^{-2} T, appears in the sample with the Mn nano-film which has a critical thickness of about 18.5 nm.

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