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Magnetic and transport properties of magnetite thin films

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Abstract

Magnetite (Fe_3O_4) films were prepared by DC reactive magnetron sputtering at various oxygen partial pressures with the ratio γ of oxygen to argon changing from 0.50:50 to 0.70:50 at room temperature, and then the Fe_3O_4 films were annealed at 480 °C for 80 min. The properties of the films were studied by X-ray diffraction, scanning electron microscopy, magnetic hysteresis loops, magnetoresistance (MR), etc. The results showed when γ increased, resistivity of magnetite films were increased exponentially, and only these magnetite films of $\gamma > 0.60:50$ showed MR effects. After annealing, the resistivity decreased about one order; and all magnetite films showed MR effects. The Verwey transition of the magnetite films was confirmed by MR–T curves. XRD and SEM showed that the films were composed of Fe_3O_4 nanoparticles with highly preferential orientation and the best conditions for high-quality magnetite films were $\gamma = 0.65:50$ and 0.675:50. The magnetic transport properties of the films infer that strong coupling between Fe_3O_4 nanoparticles originated from RKKY exchange interaction and dipolar interaction, this made the films differ from metallic granular ones and higher-order terms of $(M/M_s)^2$, such as $(M/M_s)^4$ and $(M/M_s)^6$, should be added to the fitting functions of the MR–(M/M_s) curves.

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Keywords: Magnetite thin film; Nanoparticle; Magnetic property; Transport property; Reactive magnetron sputtering

1. Introduction

Magnetic transition metal oxides with mixed valence are very important materials with applications in magnetic and various spin-electronic devices [1–5], especially the magnetite (Fe_3O_4) because of its rather unique and interesting set of

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transport and magnetic properties [6–11]. Since band-structure calculations indicate a half-metallic structure with a gap in the density of state of majority carriers, magnetite has high negative spin polarization ($SP = -100\%$) of conduction electrons, and has drawn a great deal of interest as promising candidates for application in tunnel magnetoresistance (TMR) device [12–17]. Fe_3O_4 has high Curie temperature T_C of 858 K compared to LSMO ($T_C = 360$ K) or CrO_2 ($T_C = 395$ K) and thus presents a better perspective for large TMR at RT [12,15,18], however, the most experimentally observed TMR is disappointingly small, casting doubt on the half-metallic nature of magnetite [13,16]. In Fe_3O_4, the conduction is supposed to be due to hopping between those Fe^{2+} and Fe^{3+} ions in the octahedral site (B site) of Fe_3O_4, so the electric resistivity ρ at RT of bulk Fe_3O_4 crystal is about 10 mΩ cm, which is not so large [9,19]. For the net magnetic moment arises only from the Fe^{2+} ions, the saturation magnetization M_s at RT of bulk Fe_3O_4 is 477 emu/cm^3 [20]. Upon cooling, Fe_3O_4 undergoes a semiconductor–insulator transition which is defined as Verwey transition at temperature of $T_V = 120$ K associated with the freezing of the electron hopping, and the resistivity, magnetization, magnetoresistance ratio and susceptibility show a sharp jump at T_v that marks a structural transition from a cubic high-temperature to monoclinic low-temperature phase [7–8,10,18,21–23].

In this report, we mainly studied the magnetoresistance of magnetite films sputtering at various oxygen partial pressure, and compared it with the giant magnetoresistance (GMR) effect seen in metallic granular solids with magnetic granules embedded in a nonmagnetic matrix [24–26].

2. Experiment

In this report, magnetite thin films of 480 nm in thickness were DC reactive magnetron sputter deposited on thermally oxidized-silicon-wafer and glass substrates from a pure Fe target (99.9%) with Ar–O_2 mixture gas flow at room temperature (RT). The vacuum chamber was evacuated to less than 2×10^{-4} Pa before deposition. The working gas pressure was kept at a constant value of $P = 0.8$ Pa, and the oxygen partial pressure was varied by changing $\gamma = F(O_2):F(Ar)$ from 0.50:50, 0.55:50, 0.60:50, 0.65:50, 0.675:50 to 0.70:50, which $F(O_2)$ and F(Ar) were the flow rate of oxygen and argon, respectively. Then these magnetite thin films were annealed at 480 °C for 80 min in high vacuum. The structure of the films was analyzed by the θ–2θ scanning of X-ray diffraction (XRD, Rigaku, D/max-RB) with using a Cu K_α radiation. Scanning electron microscope (SEM, XL30 S-FEG) images of magnetite thin films were shown for $\gamma \geqslant 0.60{:}50$ before and after annealing, respectively. The magnetic hysteresis loops were measured by alternating gradient force magnetometer (AGM, Model 2900-4C) with a maximum applied field of 2.0 T. Resistivity and temperature dependence of the resistance was measured using the standard four-probe technique. Magnetoresistance (MR) and the temperature dependence of MR ratio were measured in a maximum applied magnetic field of $H = 6300$ Oe.

3. Results and discussion

Resistivity ρ of the magnetite films were measured using the standard four-terminal technique at room temperature. With γ increased from 0.50:50 to 0.70:50, the resistivities were about 0.114, 0.285, 0.669, 1.70, 7.11 and 10.4 Ω cm, respectively. The resistivity for $\gamma = 0.70:50$ was three order higher than the bulk one ($\rho_{bulk} = 10$ mΩ cm), probably there had excessive oxygen in the film. After annealing, the resistivities decreased one order or so, and were 0.021, 0.030, 0.048, 0.118, 0.409, 1.10 Ω cm, respectively.

XRD showed small difference in the crystal structure before and after annealing. The intensity of XRD peaks was enhanced and the full-width at half-maximum (FWHM) of XRD peaks was decreased after annealing. Fig. 1 showed the X-ray diffraction patterns of the magnetite films after annealing. Interestingly, for $\gamma = 0.50:50$, $0.55:50$, $0.60:50$, there were two main peaks (2 2 0) and (4 4 0), which indicated the growth direction of the films was mainly [1 1 0]