

ELECTRODEPOSITED Fe₃O₄ FILMS AND NANOWIRES: MAGNETIC, ELECTRICAL AND MAGNETOTRANSPORT INVESTIGATIONS

Subhash C. KASHYAP, Mamraj Singh, Sujeet Chaudhary, and Dinesh Pandya

Thin Film Laboratory, Indian Institute of Technology Delhi, New Delhi 110016, INDIA

Introduction

Magnetite (Fe₃O₄) is of great scientific and technological interest because of its important magnetic properties and its half-metallic nature. The later characteristic is quite promising for its applications in spintronics. The theoretical 100 % spin-polarization, together with the high Curie temperature (858 K)[1], might be exploited in a variety of advanced devices including highly sensitive magnetic sensors. Ideally, 1D structure of Fe₃O₄ nanowires with obvious perpendicular magneto-anisotropy can be employed for high-density magnetic recording media

There are a number of deposition techniques to grow thin films and nanowires of magnetite, such as molecular beam epitaxy (MBE), pulse laser deposition (PLD), iron oxidation, sputtering and so on. In contrast to these methods, the electrodeposition is a simple and economic technique. The motivation of this work was to investigate magnetite (Fe₃O₄) thin films and nanowires grown *via* an electrochemical route.

Experimental

The electrodeposition was performed using CH-Electrochemical Analyzer (Model-1100A) in a three electrode cell consisting of a saturated calomel reference electrode (Hg/HgCl₂/KCl), and a Pt counter electrode. The potential windows for electrodepositing thin films and nanowires were identified by cyclic voltametry.

The magnetite film was electrodeposited on to ITO coated glass substrates at 65°C for 300 sec using an alkaline aqueous bath (pH=12.48) of Fe₂(SO₄)₃ complexed with triethanolamine (TEA). The concentration of the bath was 0.18M Fe(III), 0.10M TEA, and 2.00M NaOH [2, 3]. A constant potential difference of -1.16 V was applied to the working electrode with respect to SCE. In another bath, an aqueous solution containing 3g/L

of (NH₄)₂SO₄·FeSO₄·6H₂O, 3g/L of KNO₃, few drops per liter of HCl and N₂H₄·H₂O with a pH of 5.58 was used to synthesize Fe₃O₄ nanowires [4]. In this case, a constant voltage of -0.86 V was applied (w.r.t. SCE) to the conducting surface of the working electrode e.g. Ag coated Polycarbonate template (PCT). These PCTs have an average pore size of 50 nm and pore length of 6 μm, and the electrodeposition was carried out at 80°C for 1400 sec. The process has been carried out by bubbling Ar gas inside the electrolyte to prevent the decomposition of Fe₃O₄.

The synthesized Fe₃O₄ thin films were characterized by Philips X-ray diffractometer (Model X'Pert PRO) using Cu-K_α radiation (λ=1.5406 Å). The electrical and magnetoresistive transport measurements were done by a dc two-probe method using current source (Keithley 224) and a nanovoltmeter (Keithley 181). The study of room temperature magnetic properties of the film and nanowires was carried out by a vibrating sample magnetometer (VSM-EG&G Princeton Applied Research, Model-155).

Results and Discussions

The glancing angle X-ray diffractogram (GAXRD) of Fe₃O₄ thin film, and the calculated value of lattice parameter (8.39Å) are in good agreement with standard values for the Fe₃O₄ cubic phase (JCPDS 79-0418). The average diameter of Fe₃O₄ nanowires is estimated (by TEM) to be ~100 nm, which is higher than the average pore diameter of the PCT.

We have observed nonlinear current vs. voltage (I-V) characteristics of electrodeposited Fe₃O₄ film (Fig.1) at room temperature. The observed I-V behavior suggests that the conduction mechanism in Fe₃O₄ film is predominantly governed by spin polarized tunneling across the Fe₃O₄ grains with finite contributions arising due to carrier hopping via localized states.

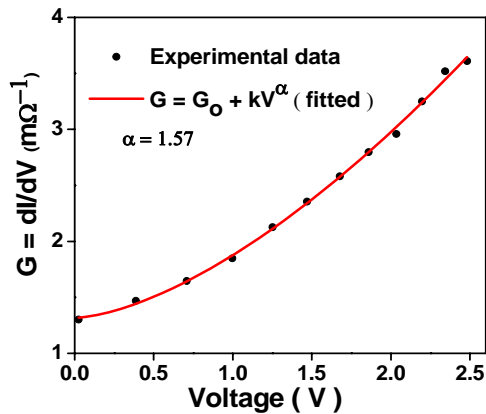


Fig. 1 Conductance (G - V) plots for Fe_3O_4 film at 27°C (Solid line is fit to the data as shown)

The hysteresis (M - H) loops (Figs.2 and 3) of the electrodeposited Fe_3O_4 film/nanowires, recorded at RT, exhibited shape anisotropy. The coercivity is estimated to be 66 and 197 Oe with field H applied parallel and normal to film, respectively. In the case of nanowires the corresponding values are 84 and 135 Oe, respectively.

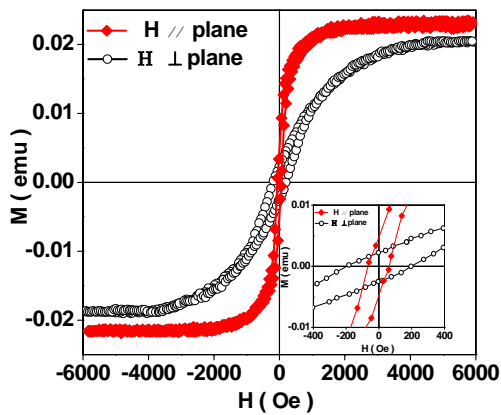


Fig. 2 Room temperature M - H hysteresis loops recorded with the H applied parallel and perpendicular to Fe_3O_4 film surface. The Inset shows the expanded curve near the origin.

A large negative longitudinal magnetoresistance of 4.3% (at 2.3 kOe, 27°C) was observed. The shape of MR curves showed a reduced hysteresis loop with low coercivity (112 Oe) of Fe_3O_4 film.

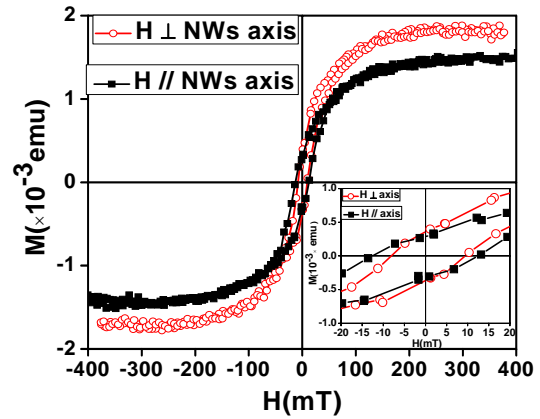


Fig. 3 Room temperature M - H hysteresis loops recorded with the H applied parallel and perpendicular to nanowire-axis. The Inset shows the expanded curve near the origin.

Conclusions

Thin films and nanowires of Fe_3O_4 have been synthesised using electrodeposition. The conduction mechanism in these Fe_3O_4 film is predominantly governed by spin polarized tunneling across the Fe_3O_4 grains with finite contributions arising due to carrier hopping. The observed magneto-anisotropy and MR value (4.3% at 1.3 kOe) in Fe_3O_4 films/nanowires suggest that Fe_3O_4 is a potential candidate for high-density magnetic recording media and magnetic sensor applications.

References

1. Coey, J. M. D., and Chien, C. L. Half-Metallic Ferromagnetic Oxides. *MRS Bull.*, (2003) 720-724.
2. Kothari, H. M., Kulp, E. A., Limmer, S. J., Poizot, P., Bohannan, E. W. and Switzer, J. A. Electrochemical Deposition and Characterization of Fe_3O_4 Films Produced by the Reduction of Fe(III) -triethanolamine. *J. Mater. Res.*, **21** (2006) 293-301.
3. Mitra, S., Poizot, P., Finke, A. and Tarascon, J. M., Growth and Electrochemical Characterization versus Lithium of Fe_3O_4 Electrode Made via Electrodeposition. *Adv. Funct. Mater.*, **16** (2006) 2281-2287.
4. Terrier, C., Abid, M., Arm, C., Serrano-Guisan, S., Gravier, L., and Ansermet, J.-Ph. Fe_3O_4 Nanowires Synthesized by Electroprecipitation in Templates. *J. Appl. Phys.*, **98** (2005) 086102, 1-3.