Journal of Alloys and Compounds 550 (2013) 365–369

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Spin-dependent transport properties of oleic acid molecule self-assembled $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles

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ARTICLE INFO

Article history:
Received 4 June 2012
Received in revised form 11 October 2012
Accepted 17 October 2012
Available online 5 November 2012

Keywords:
Low-field magnetoresistance
Tunneling
Molecules
Organic barrier

ABSTRACT

Spin-dependent transport property through molecules is investigated using a monolayer of oleic acid molecule self-assembled half metallic $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) nanoparticles, which was synthesized using a coprecipitation method. Fourier transform infrared spectroscopy was used to confirm that one-monolayer oleic acid molecules chemically bond to the LSMO nanoparticles. The transport properties and magnetoresistance (MR) effect of the oleic acid molecule coated LSMO nanoparticles were measured by a direct current four probes method using a Cu/nanoparticle assembly/elargol electrode sandwich device with various temperatures and bias voltages. The non-linear *I–V* curve indicates a tunneling type transport properties. The tunnel barrier height around 1.3 ± 0.15 eV was obtained by fitting the *I–V* curve according to the Simmons equation. The magnetoresistance curves can be divided to high-field MR and low-field MR (LFMR) parts. The former is ascribed to the influence of spin disorder or canting within the LSMO nanoparticle surface and the latter one with strong bias dependence is attributed to the spin-dependent tunneling effect through the insulating surface layer of LSMO and oleic acid molecules. The enhanced LFMR effect for oleic acid coated LSMO with respect to the bare LSMO was attributed to the enhanced tunneling transport and weak spin scattering in oleic acid molecule barrier.

1. Introduction

Since 1994, magnetic tunnel junctions with insulating AlO_x or MgO as spacers between the ferromagnetic electrodes have attracted intensive investigation due to its successful application not only in information storage but also for fundamental physics. Recently, ferromagnetic metal/organic molecules/ferromagnetic metal junctions and ferromagnetic material–molecule composites have attracted much attention due to the observation of rather large tunnel magnetoresistance (MR) in these sandwich devices. For example, Seiji Sakai etc. reported about 30% TMR in Co–C_{60} composites [1–3], Clément Barraud etc. reported −30% TMR in LSMO/Alq_3/Co [4], Gobbi reported 5% TMR in Co/AlO_x/C_{60}/Py at RT [5]. The successful observation of large MR in molecule based magnetic tunnel junctions was attributed to the long life time of the spin polarized electrons in molecules, due to the weak spin–orbit coupling of the carbon and hydrogen atoms. According to the prediction of Jullier's model on TMR value, the half metals have much advantage to improve the TMR value due to its 100% spin polarization. Among all kinds of half metals, half metallic ferromagnetic oxides are expected to be superior to pure metals as a spin injection source because of the easy connection between the oxide electrode and carbon material, which has the advantages including high spin polarization, environmental stability, and efficient spin injection [6]. Previous studies indicate that enhanced low field MR (LFMR) can be achieved in manganite–inorganic insulator composites due to the spin-dependent inter-granular tunneling process [7–13]. However, there is few report on the bias-voltage dependent spin transport properties on the ferromagnets/molecule composites. In this work, the spin-dependent transport properties of molecule self-assembled half-metallic $La_{0.7}Sr_{0.3}MnO_3$/oleic acid molecule composites with the variation of bias-voltages and temperatures were reported.

2. Experiment details

In this article, $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles were synthesized using coprecipitation way [14,15]. The first step was the decomposition and coprecipitation of the La, Sr and Mn precursors. The solution of precursors $La(NO_3)_3{\cdot}6H_2O$ (8.4 mmol), $Sr(NO_3)_2$ (3.6 mmol) and $Mn(NO_3)_3{\cdot}4H_2O$ (12 mmol) was prepared in 200 ml deionized water, NaOH (36 mmol) were dissolved in 800 ml deionized water to obtain the alkaline solution. The NaOH solution was slowly dropped into the precursors' solution with the stirring of glass rod under ultrasound condition. The pH value of the solution was kept more than 12 in order to make sure the desired ions were completely precipitated. After reaction, the solution was filtered by a filter paper to obtain the residue. The second step was to dry the residue in vacuum. The third step was to anneal the powder at 800 °C for 200 min to obtain LSMO nanoparticles. Afterward, the mixture of LSMO and oleic acid was heated to 70 °C. The length of oleic acid is about 2 nm [12]. After about 3 h self-assembly growth, the nanoparticles were separated via centrifugation and thoroughly washed with ethanol to remove any physically absorbed oleic acid. The obtained sample was named as LSMO/oleic acid.

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http://dx.doi.org/10.1016/j.jallcom.2012.10.126

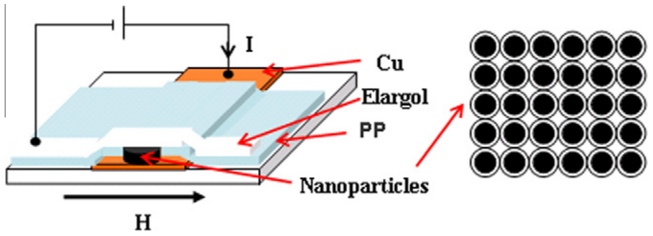

Fig. 1. Schematic diagram of a Cu/nanoparticle assembly/elargol electrodes sandwich device.

The concentration of the LSMO sample with atomic ratio of La:Sr:Mn around 0.73:0.27:1.06 was characterized by Inductively Coupled Plasma instrument. The crystal structure and microstructure of the samples was characterized by a Rigaku D/Max-2400 powder X-ray diffraction (XRD) using Cu Kα radiation and a FEI G2 F30S transmission electron microscope (TEM) with an accelerating voltage of 300 kV. Fourier transform infrared spectroscopy (FTIR) was used to detect the bonding state of the molecules on $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles. The static magnetic properties were characterized by a Lakeshore 7304 vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID).

The transport properties of nanoparticles was investigated at various temperatures, applied fields and biases through a Cu/nanoparticle assembly/elargol electrodes sandwich device as shown in Fig. 1. The detailed sandwich device preparation procedure is described as follows. First, a copper-clad plate bottom electrode was prepared. Second, an insulating photographic paper (PP) was adhered to the middle of the bottom electrode, then a hole of about 1 mm in diameter in the middle of PP was drilled to place the nanoparticle sample. Third, a burette was used to drop one drop of nanoparticles and ethanol mixture in the hole. Then the incomplete device was dried in a vacuum baker for several hours to get rid of the ethanol and water. Repeating the above procedure until the hole was fulfilled. After several cycles, the dropped nanoparticles were naturally coalesced by the van der Waals force with resistance around a few mega ohms. At last, a layer of elargol covered the hole was spread and the top electrode was formed. A direct current four-terminals method was used to carry on the transport measurement. A Keithley 220 current source was used to apply a constant current between the top and bottom electrode. A Keithley 2000 multimeter was used to detect the voltage between another two top and bottom electrodes.

3. Results and discussion

To investigate the crystal structure and microstructure of the LSMO nanoparticles, several different kinds of techniques were utilized to characterize the samples. Fig. 2 shows the XRD patterns of LSMO and LSMO/oleic acid particles. All diffraction peaks match well-defined $La_{0.7}Sr_{0.3}MnO_3$ perovskite structure with rhombohedral symmetry described in a hexagonal cell. According to Bragg's formula and the diffraction peak positions, the lattice constant of LSMO was calculated with $a = 5.477$ Å and $c = 13.45$ Å, which is fitting well with JCPDS PDF# 510409 ($a = 5.490$ Å and $c = 13.32$ Å). All the diffraction peak positions of LSMO/oleic acid is nearly the same with those of LSMO, implying no change of crystal structure of LSMO nanoparticles during chemical absorption of oleic acid molecules procedure. The broaden peak widths were consistent with nanosized crystallites. According to Scherrer's formula and the full width at half maximum (FWHM) of the (110)/(104) peak, the grain size of LSMO is estimated to be about 16 nm.

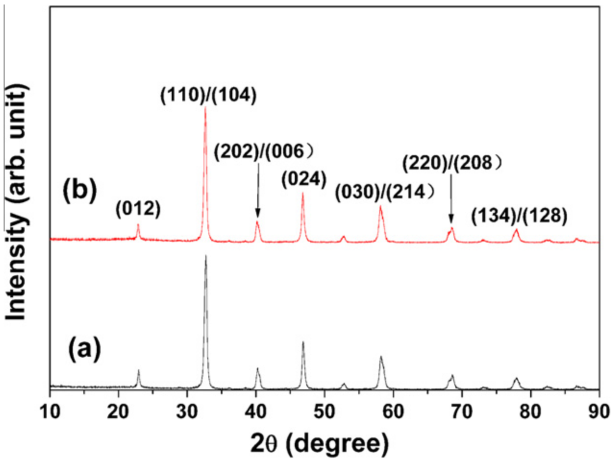

Fig. 2. XRD patterns of (a) LSMO and (b) LSMO/oleic acid.

Fig. 3 shows the TEM and HRTEM images of LSMO nanoparticles. As shown, the particle size of LSMO is in the range of 50–100 nm. Fig. 3(b) shows a high-resolution TEM image of one LSMO particle, from which one can see the two dimensional illustration of atomic array of LSMO. The distance between two nearby arrays is equal to the interplanar spacing of the (110) and (104) planes of the LSMO. Fig. 3(c) shows the magnification of the small block area, one can clearly see the ordered arrangement of atoms. It is worthy to note that the ordered atoms arrangement disappears near the surface margin of LSMO nanoparticles. It may be an evidence of the formation of an insulating disordered shell on the surface of LSMO nanoparticles [16]. Fig. 3(d) gives the Fourier transformation of the large block area of Fig. 3(b), whose pattern is consistent with the structural feature of a rhombohedral symmetry single crystal. TEM observation is consistent with the result of XRD investigation.

Fourier transform infrared spectroscopy (FTIR) was used to study the bonding of oleic acid on $La_{0.7}Sr_{0.3}MnO_3$ in a pressed KBr pellet. Fig. 4 shows the FTIR spectra of LSMO, LSMO/oleic acid composites and pure oleic acid. The FTIR spectra of LSMO and LSMO/oleic acid composites all show a strong wide absorption band around 609 cm^{-1}. The band centered at 609 cm^{-1} does not show on pure oleic acid spectrum and is related to the inorganic manganite core as it is assigned to Mn–O–Mn symmetric stretching vibrations [17,18]. This indicates both samples strongly contain the metal–oxygen bonds which involves the internal motion of a change in Mn–O–Mn bond length. The stretching mode is related to the change of Mn–O–Mn length while the bending mode involves the change of Mn–O–Mn bond angle. The FTIR spectrum of the pure oleic acid exhibits a series of characteristic peaks of the carboxylic head group (–COOH) vibration at 1708 (C=O stretching), 1463 (C–O stretching), and 1285 cm^{-1} (O–H bending). The remarkable features at 2857 and 2919 cm^{-1} are due to the symmetric and asymmetric CH_2 stretching. After self-assembly with oleic acid, the FTIR spectrum of LSMO/oleic acid changes a little from LSMO and is quite different from pure oleic acid, indicating there is no physically absorbed oleic acid in the surface of LSMO particles. Furthermore, there appear two little peaks located at 2852 and 2922 cm^{-1}, which may be coming from the oleic acid molecules with the CH_2 stretching. However there is absent the –COOH characteristic peaks of oleic acid. Thus, we may conclude that the surface of $La_{0.7}Sr_{0.3}MnO_3$ nanoparticles are chemically absorbed a circle of oleic acid molecules and there is nonexistence of the physically absorbed oleic acid molecules.

The magnetic properties of LSMO and LSMO/oleic acid were investigated by VSM. Fig. 5 shows hysteresis loops of sample at room temperature and 10 K. The hysteresis loop exhibits the typical shape of powder ferromagnetic materials with low remanence and low coercivity (H_c). The room temperature saturation magnetization (M_s) of LSMO is about 38.49 emu/g, while the room temperature M_s of LSMO/oleic acid is around 37.94 emu/g. The coercivities and remanence ratios of LSMO and LSMO/oleic acid are both around 64 Oe and 0.16, respectively. There is no significant variation of M_s indicating the quite thin layer of oleic acid molecules absorbed on the surface of LSMO nanoparticles. It also indicates that the surface state of LSMO nanoparticles almost has not changed during self-assembly procedure. As the temperature decreases to 10 K, M_s and H_c of LSMO and LSMO/oleic acid were increased to 69.52 and 68.63 emu/g, 275 and 240 Oe, respectively. The remanence ratios of them are both increased to about 0.26.