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(54) Title: HIGHLY SENSITIVE MAGNETIC TUNABLE HETEROJUNCTION DEVICE FOR RESISTIVE SWITCHING

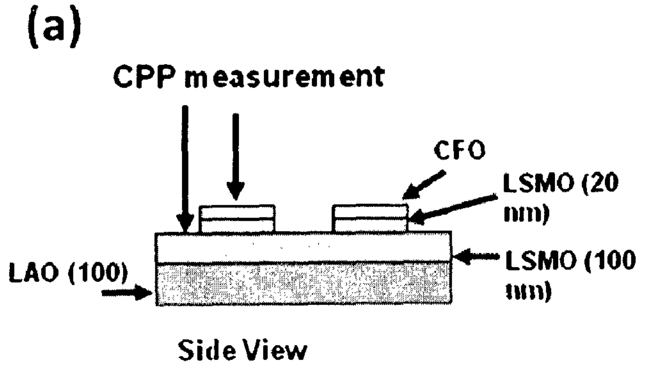

Fig 1

(57) **Abstract**: The present invention discloses highly sensitive magnetic heterojunction device consisting of a composite comprising ferromagnetic ($La_{0.66}Sr_{0.34}MnO_3$) LSMO layer with ultra-thin ferrimagnetic $CoFe_2O_4$ (CFO) layer capable of giant resistive switching (RS) which can be tuned at micro tesla magnetic field at room temperature.

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HIGHLY SENSITIVE MAGNETIC TUNABLE HETEROJUNCTION DEVICE FOR RESISTIVE SWITCHING

The following specification particularly describes the invention and the manner in which it is to be performed:

FIELD OF THE INVENTION

The invention relates to highly sensitive magnetic heterojunction device of ultrathin $CoFe_2O_4$ (CFO) on $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) capable of resistive switching (RS) which is tunable at micro tesla magnetic field.

BACKGROUND AND PRIOR ART OF THE INVENTION

Metal oxides, particularly mixed-valent manganites are at the focus of scientific attention in recent times in view of their peculiar properties emanating from a competition between different attendant energies (charge, spin, orbital and lattice). The high carrier densities in such functional oxide systems are considered a big plus in their potential for future electronics at the nanoscale where silicon based systems face carrier statistics problems. Therefore extensive research work is being done on exploring the properties of hetero-structures and multi-layers involving these and other lattice-matched oxide systems seeking novel phenomena. Recently, some unique, unusual and novel physical properties have been reported in the domains of transport and magnetism in such oxide based interface systems. Uni polar and bipolar switching has been observed in different film and interface systems, and mechanisms based on filamentary path formation or field induced interface barrier modification have been proposed.

Resistive switching (RS) is an especially interesting phenomenon that has attracted recent attention in view of its potential for alternative high density non-volatile memory application. Unipolar and bipolar switching has been observed in different film and interface systems, and mechanisms based on filamentary path formation or field induced interface barrier modification have been proposed [*J. Maier, Nature Mater.* 4, 805 (2005);R Waser, R Dittmann, G Staikov, and K Szot, *Adv. Mater.* 21, 2632 (2009)]. In manganites, resistive switching (RS) was first reported in Pr_xCa_{1-}

$_{x}MnO_3$ (PCMO, a charge ordered (CO) insulator) in the hole doping regime (x = 0.1-1.0) having lowest bandwidth amongst the manganite family. The melting of the CO state with concurrent appearance of ferromagnetic nuclei under external perturbations (electric/magnetic fields, current, temperature etc) led to a large resistance reduction. Subsequent studies have brought out the significance of interfacial effects in RS in manganites and various related models have also been proposed.

There is one previous report by Das et al [S. Das, S. Majumdar, S. Giri, *J. Phys. Chem. C* **114**, 6671 (2010)] on low field magnetic tuning of RS in very thick (83 nm) sol-gel deposited NiO films but only at low temperature.

An article titled "Room Temperature Magnetic Barrier Layers in Magnetic Tunnel Junctions" by B. B. Nelson-Cheeseman, F. J. Wong et.al in APS Journals, *Phys. Rev. B* Volume 81, Issue 21 relates to the spin transport and interfacial magnetism of magnetic tunnel junctions with highly spin polarized LSMO and Fe_3O_4 electrodes and a ferrimagnetic $NiFe_2O_4$ (NFO) barrier layer. The spin dependent transport is explained in terms of magnon-assisted spin dependent tunneling where the magnons are excited in the barrier layer itself. Tri layers of LSMO (25 nm)/NFO (3 nm)/Fe_3O_4(25 nm) were grown by pulsed laser deposition on (110)-oriented $SrTiO_3$ (STO) substrates. Magnetization is induced at +/- 1.5 Tesla and the magnetic field applied is in the range of -2000 to +2000 Oe.

Article titled "Current switching of resistive states in magnetic resistive manganites" by A. Asamitsu discloses crystals of $Pr_{1-x}Ca_xMnO_3$ (x = 0.3) which were melt-grown by a floating-zone method. The crystals showed the switching phenomenon in a much higher magnetic field of approx. 4 tesla.

Though, resistive switching is demonstrated in other metal oxides systems and their interfaces and shown to be tuned under magnetic fields, however the "magnetic" aspect of magnetic oxides has not been emphasized especially in terms of low field tenability.

OBJECTIVE OF THE INVENTION

Main objective of the present invention is to provide a highly sensitive magnetic heterojunction device of ultra thin $CoFe_2O_4$ (CFO) on $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) capable of resistive switching (RS) which is tunable at micro tesla magnetic field.

Another objective of the present invention is to provide a magnetic heterojunction device to tune the resistive switching at very low magnetic field with high sensitivity.

SUMMARY OF THE INVENTION

Accordingly, present invention provides a highly sensitive magnetic heterojunction device comprising substrate of single crystal (001) $LaAlO_3$ (LAO), ferromagnetic $La_{0.66}Sr_{0.34}MnO_3$ layer (LSMO) and ferrimagnetic $CoFe_2O_4$ (CFO) layer.

In an embodiment of the present invention, said device is capable of giant resistive switching (RS) at the interfaces of LSMO and CFO at 2 to 100 mT magnetic field at temperature in the range of 25 to 30°C for alternative high density non-volatile memory application.

In another embodiment of the present invention, the thickness of the substrate is 450 to 550 μm.

Yet another embodiment of the present invention, the thickness of the LSMO layer is in the range of 100 to 130 nm.

Yet another embodiment of the present invention, the thickness of the CFO is in the range of 2 to 6 nm.

Yet another embodiment of the present invention, device exhibits resistive switching voltage in the range of 0.7 to 2V for 2 to 6 nm CFO in the presence of 72 mT magnetic field at temperature in the range of 25 to 30°C.

Yet another embodiment of the present invention, the device is magneto restrictive and senses magnetic field.

Yet another embodiment of the present invention, the process for the preparation of heterojunction device comprising the steps of:

a. depositing 100 to 130 nm ($La_{0.66}Sr_{0.34}MnO_3$) LSMO film on 450 to 550 μm single crystal (001) $LaAlO_3$ (LAO) substrate by Pulse layer deposition (PLD) at 700°C in 100 mTorr oxygen pressure;

b. masking part of the film as obtained in step (a) followed by growing of 15 to 25 nm LSMO onto the masked surface by PLD at 700°C in 100 mTorr oxygen pressure to form a thin film; and

c. depositing 2 to 6 μm film of CFO on to the LSMO film as obtained in step (b) by PLD at 700°C in 100mTorr oxygen pressure followed by cooling till temperature in the range o f 25 to 30°C at oxygen pressure of 400 torr;

Yet another embodiment of the present invention, a method of detecting a magnetic field using CFO/LSMO comprises;

a. providing Highly sensitive magnetic heterojunction device;

b. exposing the device to a magnetic field so as to detect the magnetic field.

Yet another embodiment of the present invention, a method of inducing a magnetic field using CFO/LSMO comprises;

a. providing Highly sensitive magnetic heterojunction device;

b. Exposing the device at an electrical current to induce a magnetic field.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1a represents the ultrathin heterojunction device comprised of a single crystal (001) $LaAlO_3$ (LAO) substrate (500 μm), a $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) film (100 nm), and freshly grown heterostructure of LSMO (20 nm, as bottom layer) and $CoFe_2O_4$ (CFO) of different thickness (2 nm, 4 nm, 6 nm, as top layers). The arrows in CPP measurement indicate where the voltage probes were put so as to perform current-voltage measurements.

Figure 1b represents Cross sectional Transmission electron microscopy (TEM) image of 4 nm CFO/ LSMO interface.

Figure 1c represents conducting AFM (Atomic Force Microscopy) image of 4 nm CFO/LSMO interface.

Figure 1d represents typical I-V curves noted in the absence of magnetic field across LSMO-CFO interface in current perpendicular to plane (CPP) mode for different CFO thicknesses (Black for 2 nm, Red for 4 nm, and Green for 6 nm), Inset shows RS (Resistive switching) curves for two different device areas, namely 2mm × 3mm and 500μm × 500μm.

Figure 2a represents I-V characteristics of the samples of CFO thicknesses (2 nm) under finely tuned magnetic field, showing a systematic variation of threshold voltage with magnetic field. Insets: I-V curves at log scale.

Figure 2b represents I-V characteristics of the samples of CFO thicknesses (4 nm) under finely tuned magnetic field, showing a systematic variation of threshold voltage with magnetic field. Insets: I-V curves at log scale.

Figure 2c represents I-V characteristics of the samples of CFO thickness (6 nm) under finely tuned magnetic field, showing a systematic variation of threshold switching voltage (switching voltage) with magnetic field. Insets: I-V curves at log scale.

Figure 3a represents the systematic variation of threshold switching voltage (V_{th}) with magnetic field for different CFO thicknesses.

Figure 3b represents effect of magnetic field direction on resistive switching.

Figure 4a represents the magnetization curve of bare CFO thin film (100 nm).

Figure 4b represents the magnetization curves of bare LSMO thin film (120 nm) and

Figure 4c represents the magnetization curves of LSMO-CFO junction for 2 nm (Black curve) and 6 nm (Blue curve) thickness of CFO.

Figure 5a represents threshold switching voltage (V_{th}) as a function of reverse bias voltage $|V_{rb}|$ for 4nm CFO.

Figure 5b represents resistance plotted as a function of magnetic field in High resistance state (HRS) (Black solid circle) and low resistance state (LRS) (Red square).

Figure 6 represents schematic showing (a) unbiased interfacial barrier formed at LSMO/CFO interface as a result of oxygen vacancies in HRS, (b) under forward bias before switching in the absence of external magnetic field (c) under forward bias after switching (crossing) from HRS to LRS, (d) under forward bias HRS in the presence of external magnetic field.

DETAILED DESCRIPTION OF INVENTION

The invention relates to highly sensitive magnetic heterojunction device consisting of ultrathin ferrimagnetic $CoFe_2O_4$ (CFO) and ferromagnetic $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) capable of giant resistive switching (RS) which is tunable at micro tesla magnetic field (at much lower field) at room temperature.

In an aspect, there is provided a novel heterojunction device of ultrathin $CoFe_2O_4$ (CFO) on $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) which are grown by pulsed laser deposition (PLD) and examined for the current-voltage (I-V) characteristics in the current perpendicular to plane (CPP) geometry. These measurements on such an *in situ* grown interface reveal rectifying nature with a giant resistive switching. The switching voltage is magnetically tunable at much lower fields with high sensitivity.

The device exhibit rectifying characteristics in CPP and the threshold voltage for resistive switching as well as the conductance at switching show systematic and synergistic variation with magnetic field.

The term 'magnetic tunable Resistive switching' described herein the specification refers and means to the physical phenomena where a dielectric suddenly changes its (two terminal) resistance switching under the action of applied voltage and this voltage essential to switch the device changes in the presence of magnetic field. The change of resistance is non-volatile and reversible.

The term 'heterojunction' or 'interface system' refers and means to the interface that occurs between CFO and LMSO layers or regions.

The term 'Switching voltage' refers to the maximum signal voltage across switch module necessary to switch its resistance state.

CFO is a ferrimagnetic insulator which is known for its very high magnetostriction coefficient [R. Bozorth, E. Tilden & A. Williams, *Phys. Rev.* 99, 1788 (1955).] ($\lambda \sim 800 \times 10^{-6}$) and a very efficient spin filtering effect [A. Ramos, M. -J. Guittet, J. -B. Moussyet, R. Mattana, C. Deranlot, F. Petroff, C. Gatel, *Appl. Phys. Lett.* 91, 122107 (2007)] at room temperature.

$La_{1-x}Sr_xMnO_3$ (x = 0.34, as determined by Rutherford Backscattering) is a ferromagnetic conductor at room temperature due to large bandwidth and nearly linear Mn^{3+}-O-Mn^{4+} bond. Small changes in the Mn-O-Mn bond properties at an interface can however change the transport and magnetic properties significantly. [A. Rana, Kashinath Bogle, Onkar Game, Shankar Patil, Nagarajan Valanoor, Satishchandra Ogale, *Appl. Phys. Lett.* 96, 263108 (2010); A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, *Phys. Rev. B* 51, 14103 (1995).]

The heterojunction device of the instant invention comprising of ultra-thin $CoFe_2O_4$ / $La_{0.66}Sr_{0.34}MnO_3$ displays an interface system for resistive switching (RS) and shows a very sharp (bipolar) transition at room temperature (27 °C) that can be gated with high sensitivity by low magnetic fields. The said device is thus senses magnetic fields. The interfaces of $La_{0.66}Sr_{0.34}MnO_3$ (LSMO) and ultrathin $CoFe_2O_4$ (CFO) show very unique and interesting magneto-electronic coupling in the resistive switching phenomenon with remarkably high magnetic field sensitivity at micro Tesla level in the range of 2-100 mT at room temperature (27 °C).

The device consisits of magentorestrictive film $CoFe_2O_4$ (CFO) layer grown on LSMO (120 nm) layer with a thickness in the range of 2-6 nm.

The observed change in resistive switching voltage in the presence of magnetic field is ~ 2 V at 72 mT at the interface of LSMO/CFO (2 nm CFO case) at room temperature (27°C) in the heterojunction device of the instant invention.

The heterojunction device composite consisting of two materials is grown by Pulse layer deposition (PLD) technique, which is known for deposition layer by atomic layer, using KrF excimer (laser, λ=248 nm, 20 ns pulse). The laser ablation was carried out at energy density of 2 J/cm^2 and a repetition rate of 10 Hz. The upper layer is CFO (which acts as ferrimagnetic insulator) and the bottom layer is $La_{1-x}Sr_xMnO_3$ (x=0.34) which is a ferromagnetic conductor at room temperature due to broader bandwidth and nearly linear Mn^{3+}-O-Mn^{4+} bond.

The process for the preparation of heterojunction device of ultrathin $CoFe_2O_4$ / $La_{0.66}Sr_{0.34}MnO_3$ comprises;

1. Depositing ($La_{0.66}Sr_{0.34}MnO_3$) LSMO film [Abhimanyu Rana, Kashinath Bogle, Onkar Game, Shankar Patil, Nagarajan Valanoor, and Satishchandra Ogale, *Appl. Phys. Lett.* 96, 263108 (2010)] on a single crystal (001) $LaAlO_3$ (LAO) substrate by PLD (Pulsed laser deposition) at 700°C in 100 mTorr oxygen pressure;
2. Masking part of the film of step (1) followed by growing of LSMO onto the masked surface by PLD at 700°C in 100mTorr oxygen pressure to form a thin film;

3. Depositing a thin film (2 to 6 nm) of CFO on to the LSMO film of step (2) by PLD at 700°C in 100mTorr oxygen pressure and cooling at oxygen pressure of 400 torr.

According to the process described above, a 100 nm uniform LSMO film is deposited on a single crystal (001) $LaAlO_3$ (LAO) substrate by PLD at 700°C in 100 mTorr oxygen pressure. Subsequently, a mask is put on part of the 100 nm film surface, and a 20 nm LSMO film is grown through the mask (to create a fresh LSMO surface) by PLD technique at same temperature and oxygen pressure. This is immediately followed by deposition of a few nm thick (2 to 6 nm) CFO film by PLD at 700°C in 100mTorr oxygen pressure, cooled at oxygen pressure of 400 torr to obtain the desired ultra-thin heterojunction device. The ultrathin heterojunction device is shown in Fig 1 (a). The ultra-thin heterojunction is characterized by TEM as described in [Fig 1 (b)], Atomic force microscopy (AFM) in Fig 1 (c). The Transmission electron Microscopy (TEM) cross section image [Fig. 1 (b)] of CFO/LSMO heterostructure shows parallel lattice planes, thickness uniformity and high degree of surface smoothness Atomic force microscopy (AFM) topographic image [Root mean square (RMS) roughness of ~ 0.4 nm] and concurrently acquired conducting-AFM (CAFM) image at negative sample bias of -3.5 V is described in [Fig. 1 (c)]. The spatial distribution of current, measured by CAFM in CPP configuration, is observed to be uniform throughout the interface with a nanoscale modulation of current near grain boundaries.

The present invention further relates to a method of detecting a magnetic field using CFO/LSMO comprises;

1. Providing the ultra -thin heterojunction device comprising of CFO and LSMO which is capable of resistive switching and resistive switching is magnetically tunable;
2. Exposing the device to a magnetic field while the current-voltage measurement will be performed simultaneously. As the magnetic field is changed; the resistive switching voltage will also change which is nothing but a measure of applied external magnetic field.
3. Current –voltage measurements will be performed in a current perpendicular to plane (CPP) geometry as shown in Fig. 1 (a).

The rectifying characteristics in CPP across LSMO-CFO interface for different CFO thicknesses (2 nm, 4 nm, 6 nm) and the threshold voltage for different CFO thicknesses in absence of magnetic field are described below:

Fig. 1 (d), shows typical I-V curves obtained for different CFO thickness values. A large RS is seen towards positive polarity (LSMO +ve terminal) at a threshold voltage ~ 4.45 V (±0.05) for all the CFO thicknesses (2 nm, 4 nm and 6 nm). A reverse transition occurs from LRS to HRS in the negative bias cycle, though it is not as sharp as the positive cycle. Independence of RS switching voltage on CFO layer thickness implies that it is a purely interfacial phenomenon. The inset to Fig. 1(d) shows RS curves for two different device areas, namely 2mm × 3mm and 500μm × 500μm. It is clearly observed that the resistance values for the HRS & LRS increase with decreasing lateral area which is completely consistent with the interfacial type resistive switching.

The current perpendicular to plane (CPP) transport is studied across these interfaces in which the voltage is varied in a sweeping cycle (- 5 V→0V→ 5V→ 0V→-5 V) with a sweep rate of 1.0 V/s and a step of 0.05 V and the current is recorded. Surprisingly, a giant resistive switching is observed invariably across all of these interfaces. (In the CPP transport the top contact for the I-V measurements is Indium).

Figure 2a shows typical I-V curves noted across an interface for CFO thicknesses of 2 nm. It shows a systematic reduction of Resistive switching voltage with increasing magnetic field.

The diode-like rectifying characteristics observed above for the present interfacial type is commonly seen in p-n junction interfaces of doped manganites. The higher current values in LRS state can be attributed to the transport of current through CFO grain boundaries as evident from CAFM image discussed above. The mechanism for such rectification is attributed to the formation of Schottky barrier which is seen at the metal-manganite interfaces, particularly in the case of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO)[A. Sawa, T. Fujii, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* 85, 4073 (2004); A. Sawa, T. Fujii, M. Kawasaki, Y. Tokura, *Appl. Phys. Lett.* 88, 232112 (2006)] which showed rectifying character only after depositing a few unit cells of insulating $Sm_{0.7}Ca_{0.3}MnO_3$ (SCMO) on LSMO. Therefore, it can be concluded that the insulating nature of CFO layer and its band alignment play an important role in the surface electronic barrier modification that can lead to Schottky type rectification.

In another embodiment, the high sensitive magnetic tunable resistive switching of the novel ultra-thin heterostructure across magnetic ($La_{0.66}Sr_{0.34}MnO_3$) LSMO and $CoFe_2O_4$ (CFO) hetero-junction is described herein below:

Figure 2 (b), (c) show the resistive switching curve for 4 nm and 6 nm CFO thicknesses as a function of magnetic field applied up to 72 mT in steps The switching voltage is seen to be reduced substantially with increasing magnetic field used for all the cases of CFO thicknesses at fairly low fields without losing the sharpness of the transition. Most remarkably the switching voltage shift depends rather strongly on the CFO thickness in the presence of magnetic field

Further, Figure 3 (a), shows the variation of resistive switching voltage (V_{th}) as a function of applied magnetic field. It is also observed that the effect of magnetic field variation reduces with increasing CFO thickness which indicates a strong and interesting coupling between the magnetic field and the phenomena governing the switching electric field value. The observed shift in resistive switching voltage at 72mT is ~2V, ~1.4 V, and ~0.7V for 2 nm, 4 nm and 6 nm CFO cases respectively.

The reversal of magnetic field direction does not seem to be affecting the trend of RS voltage shift [Fig. 3(b)].

Clearly the mechanism in the present invention, which involves a large bandwidth manganite interfaced with high-resistivity CFO, is very different as discussed later. It is also useful to state that magnetization measurements Fig. 4 (a)-(c), revealed anti-ferromagnetic coupling between LSMO and CFO.

The RS phenomenon was also studied by changing reverse bias voltage (V_{rb}) from 0 V, -1V, -2V to -7V before the positive sweep [Fig. 5 (a)]. It was observed that the threshold voltage (V_{th}) required to switch the device from High resistance state (HRS) to Low resistance state (LRS) increases with increasing negative bias. This observation implies that the entity governing the RS is influenced not just by the polarity of applied electric field but also by its strength. This suggests the role of oxygen vacancies in the modification of Schottky barrier leading to RS and also rules out possible role of Joule heating effect because in that case the reduction of V_{rb} would have made the device to switch at higher V_{th}.[H. Peng, G. P. Li, J. Y. Ye, Z. P.

Wei, Z. Zhang, D. D. Wang, G. Z. Xing and T. Wu, *Appl. Phys. Lett.* 96, 192113 (2010), S. X. Wu, L. M. Xu, X. J. Xing, S. M. Chen, Y. B. Yuan, Y. J. Liu, Y. P. Yu, X. Y. Li, and S. W. Lia, *Appl. Phys. Lett.* 93, 043502 (2008)]

Another related important observation is the increase of device resistance in HRS with increasing magnetic field [Fig.5 (b)]. Positive Magneto-resistance (MR) has been previously reported for LSMO in contact with Nb-doped SrTiO3 (Nb-STO) where the electronic interactions at the interface of the junction are suggested to be responsible. [K. Jin, Hui-bin Lu, Qing-li Zhou, Kun Zhao, Bo-lin Cheng, Zheng-hao Chen, Yue-liang Zhou, and Guo-Zhen Yang, *Phys. Rev. B*, 71, 184428 (2005)]. On the other hand in LRS the resistance is seen to decrease with increasing magnetic field (negative MR), a behavior of the bulk LSMO. This observation implies that in HRS the interface defines and controls the transport, while in LRS the bulk of LSMO controls the transport.

The possible explanation for the above observation is that in the LSMO/CFO device, bulk LSMO away from interface is metallic at room temperature while the interfacial LSMO and the CFO layer are expected to contribute significantly to the device resistance. As suggested by the weak CFO thickness dependence of the switching voltage, the LSMO layer near the interface dominates the resistance in the HRS [Fig. 6 (a)]. Under forward bias the voltage is primarily shared by the CFO and the interfacial LSMO layer. As external voltage increases, voltage drop across the interfacial LSMO layer increases reaching a threshold value which pushes the positively charged oxygen vacancies into the CFO layer [Fig.6 (b)]. Exclusion of oxygen vacancies from the interfacial LSMO increases its metallicity, thereby quenching the insulating interfacial barrier leading to switching from the HRS to the LRS [Fig.6 (c)]. Similarly, when device is reverse biased the oxygen vacancies revert back into the interfacial LSMO layer, eventually making it insulating, and switching the device back again from the LRS to HRS.

If V is the external applied voltage at which the device switches from HRS to LRS in the absence of magnetic field, the voltage drops across the interfacial LSMO and CFO is V_1 and V_2, respectively, in proportion to their resistance values, such that $V = V_1 + V_2$. Thus V_1 is the actual voltage essential to push oxygen vacancies into CFO and switch the device from HRS to LRS. Remembering that the HRS resistance of the interfacial LSMO layer is increased by the magnetic field (positive MR) the relative voltage drop across it must increase [Fig. 6 (d)]. Since the minimum essential voltage for switching of the LSMO interfacial layer is fixed, the device will now switch from HRS to LRS at lesser applied voltage in the presence of magnetic field, as observed here. The key element in this argument is the possible origin of the positive MR of the interfacial LSMO layer which forms a junction with the lower resistivity metallic LSMO. A clue in this respect can be obtained from the work of Jin *et al.* [K. Jin, Hui-bin Lu, Qing-li Zhou, Kun Zhao, Bo-lin Cheng, Zheng-hao Chen, Yue-liang Zhou, and Guo-Zhen Yang, *Phys. Rev. B* 71, 184428 (2005)] on the Nb:STO/LSMO interface wherein the authors discuss how the relative spin polarization of the electrons around the Fermi level in each region of the junction determines how its MR is affected. In the LSMO system the t_{2g} spin up band is full and e_g spin up band is partially filled. The t_{2g} spin down band is higher in energy and hence unfilled. Now in the Schottky junction formation process electrons spill over in to the interfacial LSMO and initially fill the partially filled e_g band followed by partial filling of t_{2g} spin down band leading to band bending until the Fermi levels match. In the CPP transport process it is the spin scattering of spin up electrons by the t_{2g} spin down electrons in this region that can lead to positive MR.

The observed phenomenon of resistive switching ultimately leads to switching current that may be utilized to fabricate electromagnets at micro and nano scale. This can also be used for various applications like nanofabricating ferromagnetic domains with STM-tip in antiferromagnetic films, which can also be used for Radio-frequency identification (RFID) [A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, *Nature* 388, 50–52 (1997)].

The present invention provides a giant resistive switching at room temperature in CFO/LSMO heterostructures (grown by pulsed laser deposition, PLD) which is magnetically tunable with high sensitivity at fairly low magnetic fields. Remarkably, the switching does not show significant CFO thickness dependence in the absence of magnetic field, but a strong CFO thickness dependence under applied magnetic field. The devices exhibit rectifying characteristics in CPP geometry and the threshold voltage for resistive switching as well as the conductance at switching show systematic and synergistic variation with magnetic field.

Examples

Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

Example 1

Preparation of the heterojunction device of ultra–thin $CoFe_2O_4$ / $La_{0.66}Sr_{0.34}MnO_3$

A 100 nm uniform LSMO film is deposited on a single crystal (001) $LaAlO_3$ (LAO) substrate (substrate thickness is 500 μm) from 99.9 % purity LSMO target by PLD at 700°C in 100mTorr oxygen pressure. Subsequently, a mask is put on part of the 100 nm film surface, and a 20 nm LSMO film is grown through the mask (to create a fresh LSMO surface) by PLD technique at same temperature and oxygen pressure. This is immediately followed by deposition of a 2 to 6 nm CFO film from 99.9% pure CFO target by PLD at 700°C in 100mTorr oxygen pressure to obtain the desired ultra- thin heterojunction device. The films were cooled up to room temperature at oxygen pressure of 400 torr.

Example 2

Magnetization studies

Magnetization studies were performed by a superconducting quantum interference device- Vibrating sample magnetometer (SQUID-VSM), an accepted well known technique for determination of magnetic properties of a material.

ADVANTAGES OF THE INVENTION

1. Magnetic switching disclosed herein finds application in memory devices, sensing magnetic fields.
2. It can be used for induction of magnetic field at micro or nano level.
3. The heterojunction is a simple device that elicits this effect of tuning of resistive switching with magnetic field.

We claim

1. Highly sensitive magnetic heterojunction device comprising substrate of single crystal (001) $LaAlO_3$ (LAO), ferromagnetic $La_{0.66}Sr_{0.34}MnO_3$ layer (LSMO) and ferrimagnetic $CoFe_2O_4$ (CFO) layer.
2. The device as claimed in claim 1, wherein said device is capable of giant resistive switching (RS) at the interfaces of LSMO and CFO at 2 to 100 mT magnetic field at temperature in the range of 25 to 30°C for alternative high density non-volatile memory application.
3. The heterojunction device as claimed in claim 1, wherein the thickness of the substrate is 450 to 550 µm.
4. The heterojunction device as claimed in claim 1, wherein the thickness of the LSMO layer is in the range of 100 to 130 nm.
5. The heterojunction device as claimed in claim 1, wherein the thickness of the CFO is in the range of 2 to 6 nm.
6. The heterojunction device as claimed in claim 1, wherein device exhibits resistive switching voltage in the range of 0.7 to 2V for 2 to 6 nm CFO in the presence of 72 mT magnetic field at temperature in the range of 25 to 30°C.
7. The heterojunction device as claimed in claim 1, wherein the device is magneto restrictive and senses magnetic field.
8. A process for the preparation of heterojunction device, comprising the steps of:
   a. depositing 100 to 130 nm ($La_{0.66}Sr_{0.34}MnO_3$) LSMO film on 450 to 550 µm single crystal (001) $LaAlO_3$ (LAO) substrate by Pulse layer deposition (PLD) at about 700°C in about 100 mTorr oxygen pressure;
   b. masking part of the film as obtained in step (a) followed by growing of 15 to 25 nm LSMO onto the masked surface by PLD at about 700°C in about 100 mTorr oxygen pressure to form a thin film; and
   c. depositing 2 to 6 µm film of CFO on to the LSMO film as obtained in step (b) by PLD at about 700°C in about 100mTorr oxygen pressure followed by cooling till temperature in the range of 25 to 30°C at oxygen pressure of about 400 torr;

9. A method of detecting a magnetic field using CFO/LSMO comprises;
    a. providing Highly sensitive magnetic heterojunction device as claimed in claim 1;
    b. exposing the device to a magnetic field so as to detect the magnetic field.
10. A method of inducing a magnetic field using CFO/LSMO comprises;
    a. providing Highly sensitive magnetic heterojunction device as claimed in claim 1;
    b. Exposing the device at an electrical current to induce a magnetic field.

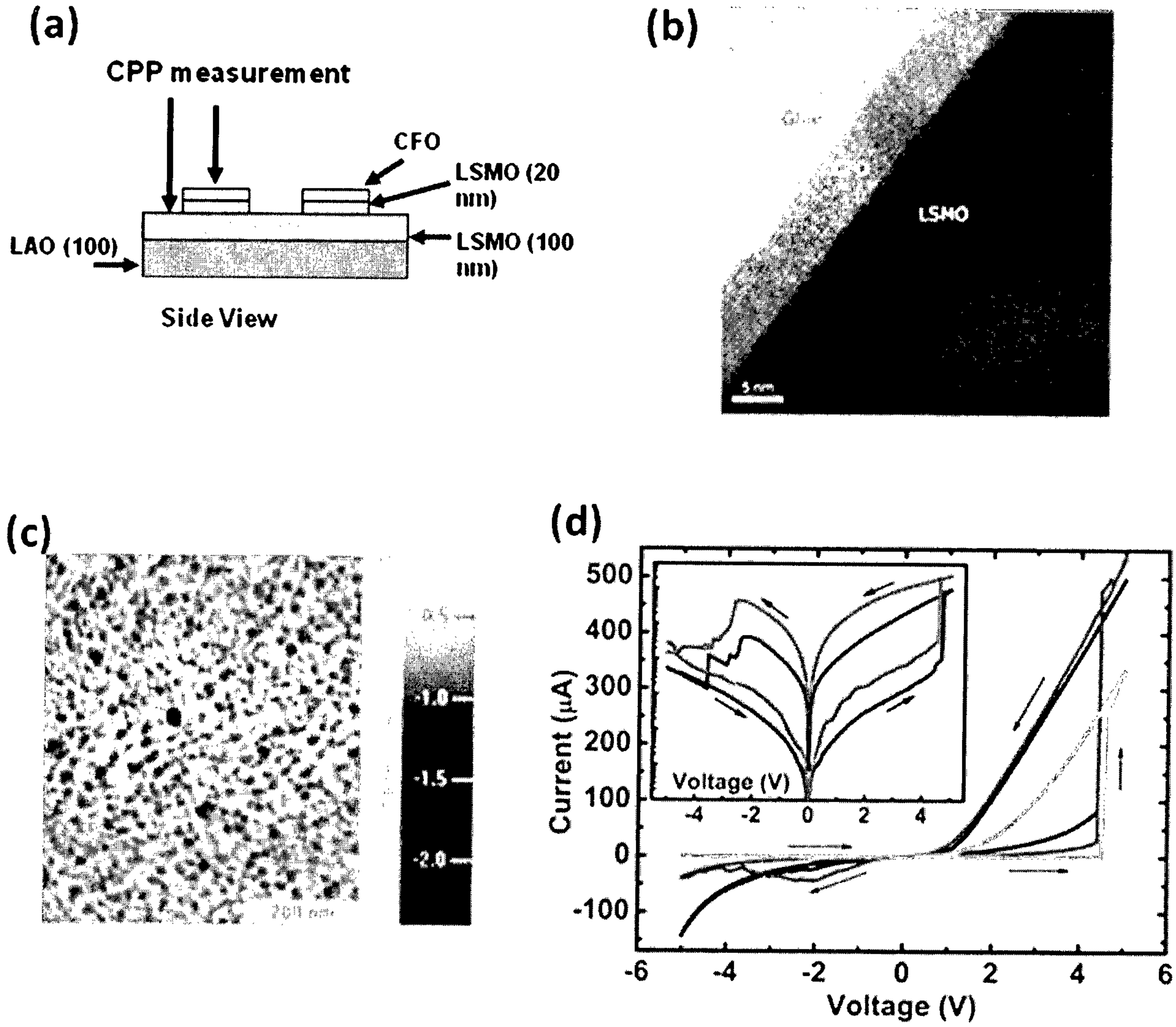

(a)
CPP measurement
CFO
LSMO (20 nm)
LAO (100)
LSMO (100 nm)
Side View
(b)
LSMO
5 nm
(c)
-1.0
-1.5
-2.0
(d)
Current (μA)
Voltage (V)
500
400
300
200
100
0
-100
-6
-4
-2
0
2
4
6

Fig 1

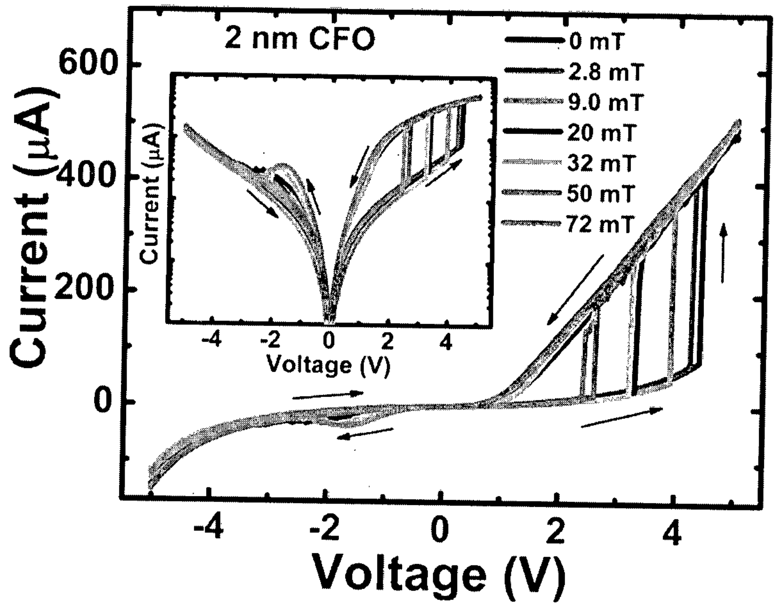
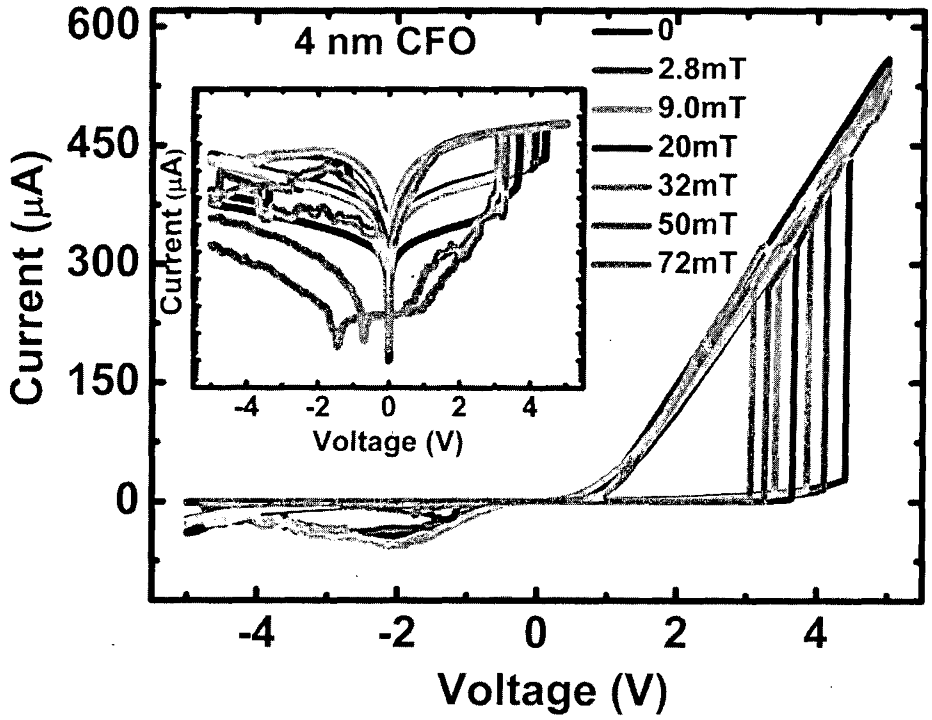
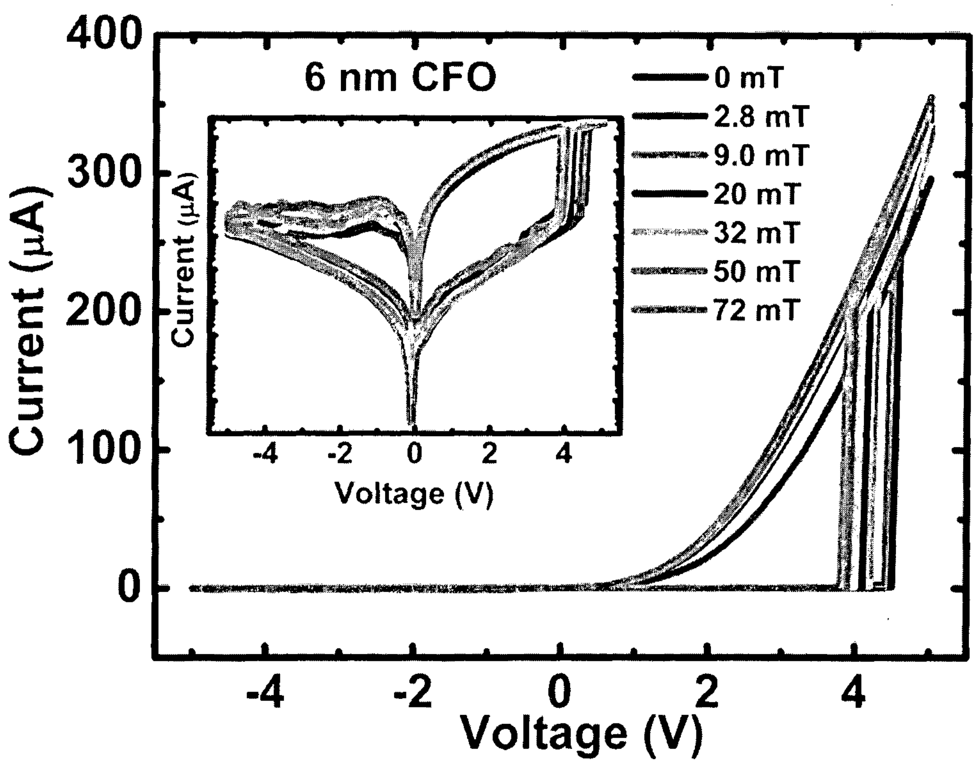

2 nm CFO
0 mT
2.8 mT
9.0 mT
20 mT
32 mT
50 mT
72 mT
Current (μA)
Voltage (V)
600
400
200
0
-4
-2
0
2
4

Fig 2 (a)



4 nm CFO
0
2.8mT
9.0mT
20mT
32mT
50mT
72mT
Current (μA)
Voltage (V)
600
450
300
150
0
-4
-2
0
2
4

Fig 2 (b)



6 nm CFO
0 mT
2.8 mT
9.0 mT
20 mT
32 mT
50 mT
72 mT
Current (μA)
Voltage (V)
400
300
200
100
0
-4
-2
0
2
4

Fig 2 (c)

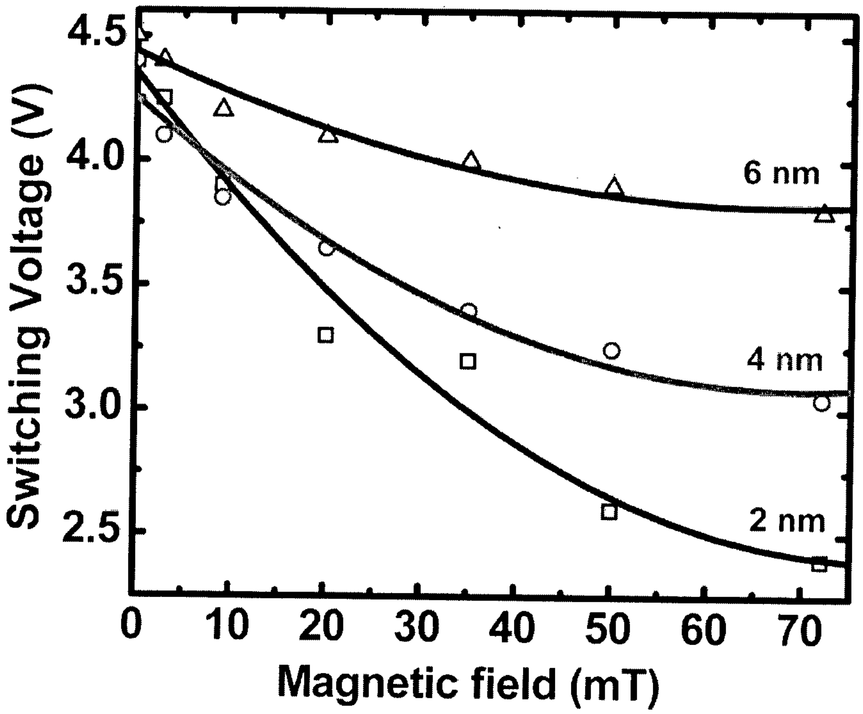

4.5
4.0
3.5
3.0
2.5
Switching Voltage (V)
6 nm
4 nm
2 nm
0
10
20
30
40
50
60
70
Magnetic field (mT)

Fig 3 (a)

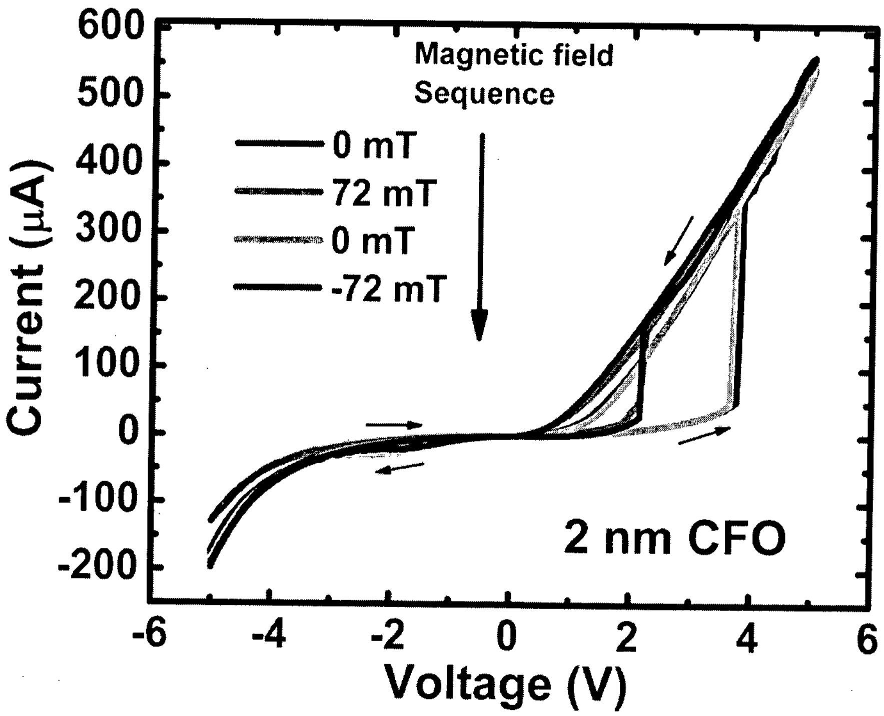

600
500
400
300
200
100
0
-100
-200
Current (μA)
Magnetic field
Sequence
0 mT
72 mT
0 mT
-72 mT
2 nm CFO
-6
-4
-2
0
2
4
6
Voltage (V)

Fig 3 (b)

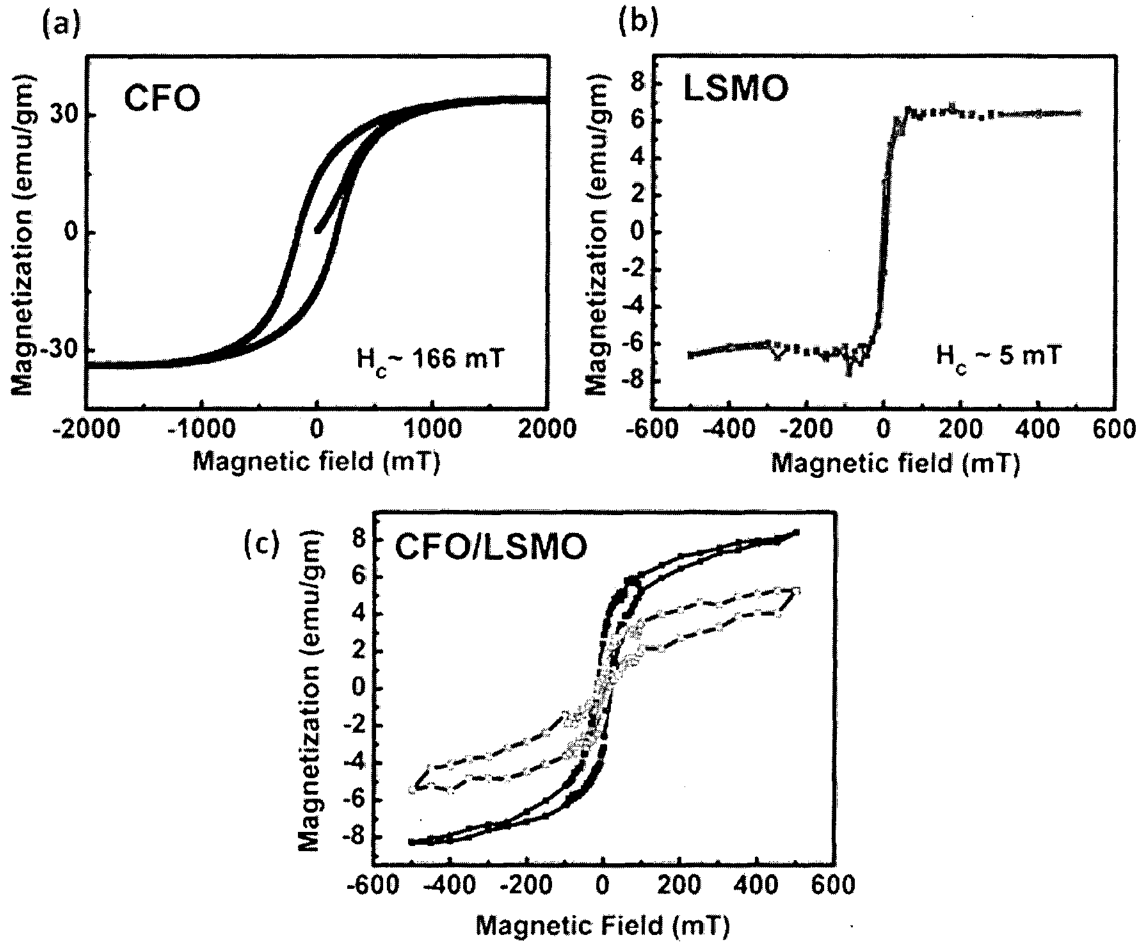

(a)
CFO
Magnetization (emu/gm)
30
0
-30
H_c~ 166 mT
-2000
-1000
0
1000
2000
Magnetic field (mT)
(b)
LSMO
Magnetization (emu/gm)
8
6
4
2
0
-2
-4
-6
-8
H_c ~ 5 mT
-600
-400
-200
0
200
400
600
Magnetic field (mT)
(c)
CFO/LSMO
Magnetization (emu/gm)
8
6
4
2
0
-2
-4
-6
-8
-600
-400
-200
0
200
400
600
Magnetic Field (mT)

Fig 4

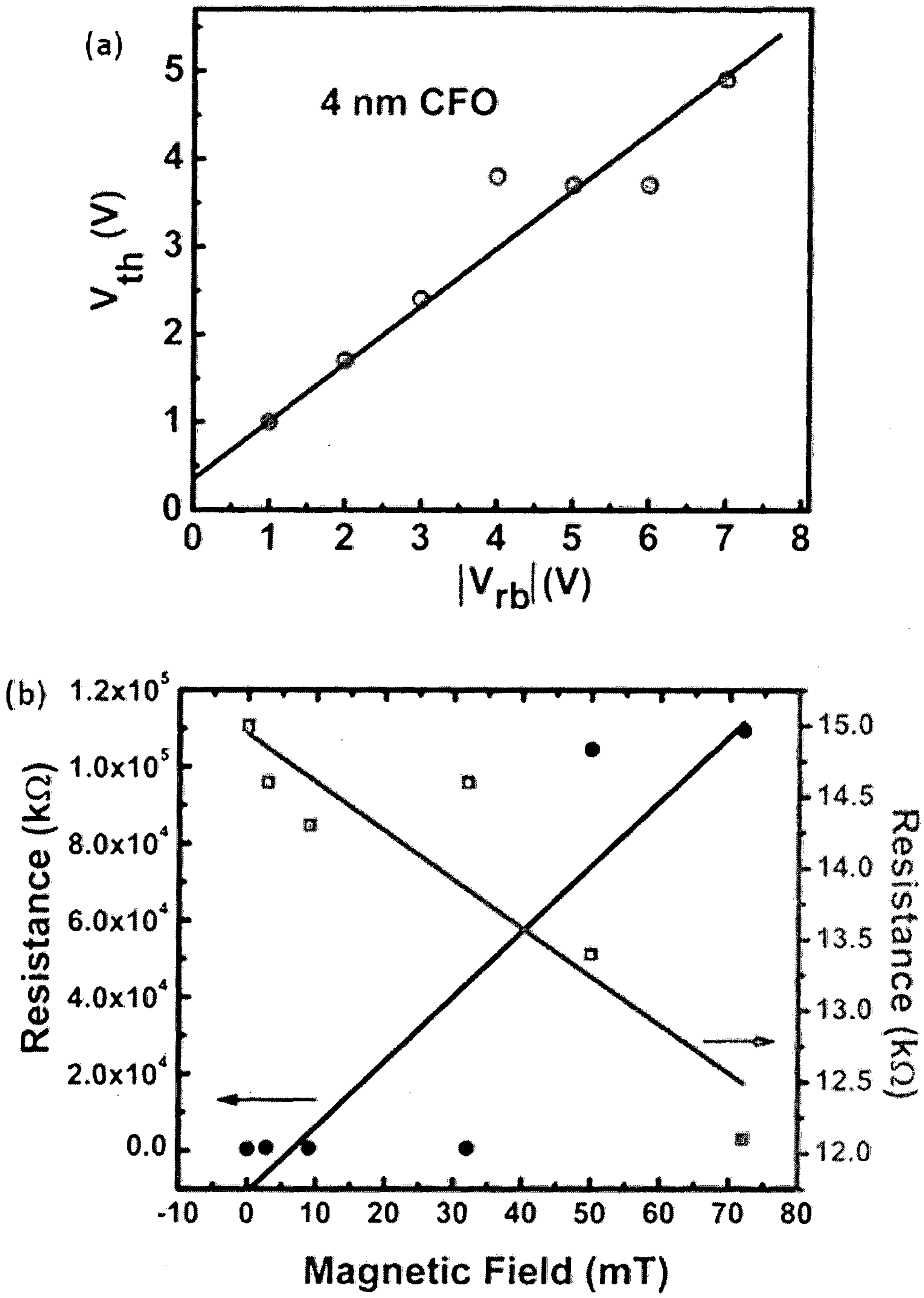

(a)
4 nm CFO
V_{th} (V)
$|V_{rb}|$ (V)
0
1
2
3
4
5
6
7
8
(b)
Resistance (kΩ)
Resistance (kΩ)
1.2x10^5
1.0x10^5
8.0x10^4
6.0x10^4
4.0x10^4
2.0x10^4
0.0
15.0
14.5
14.0
13.5
13.0
12.5
12.0
-10
0
10
20
30
40
50
60
70
80
Magnetic Field (mT)

Fig 5

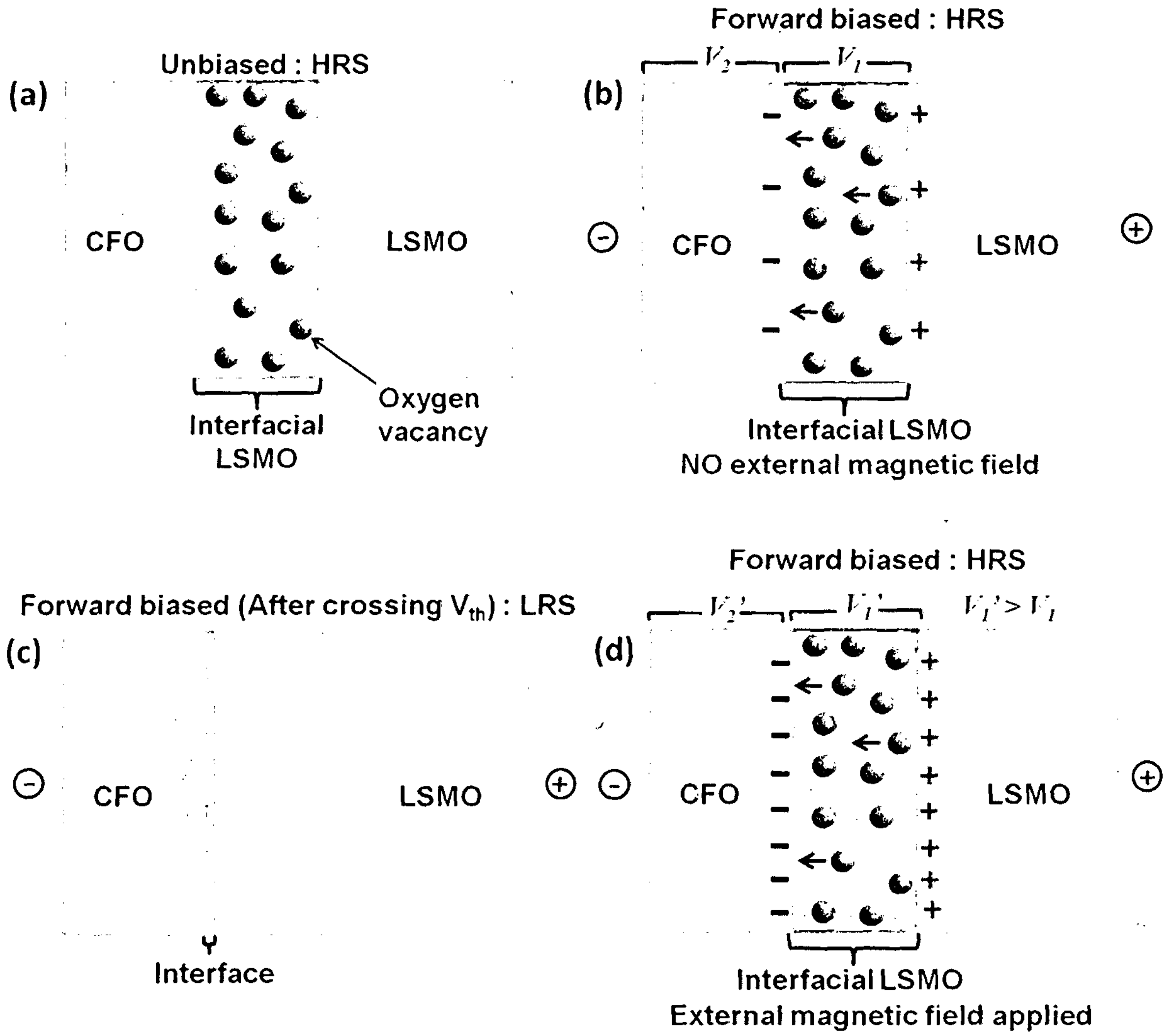

Unbiased : HRS
(a)
CFO
LSMO
Oxygen vacancy
Interfacial LSMO
Forward biased : HRS
(b)
V_2
V_1
CFO
LSMO
Interfacial LSMO
NO external magnetic field
Forward biased (After crossing V_{th}) : LRS
(c)
CFO
LSMO
Interface
Forward biased : HRS
(d)
V_2'
V_1'
$V_1' > V_1$
CFO
LSMO
Interfacial LSMO
External magnetic field applied

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/001259

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01L29/24 H01L43/08 H01L29/82
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	B. B. NELSON-CHEESEMAN; F. J. WONG: "Room Temperature Magnetic Barrier Layers in Magnetic Tunnel Junctions", APS JOURNALS, PHYS. REV. B, vol. 81, 2010, page 21, XP002684425, cited in the application the whole document -----	1-10

-/--

[X] Further documents are listed in the continuation of Box C.

[ ] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 October 2012	11/10/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Baillet, Bernard

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FRITSCH D ET AL: "Strain effects in spinel ferrite thin films from first principles calculations", JOURNAL OF PHYSICS: CONFERENCE SERIES, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 292, no. 1, 15 April 2011 (2011-04-15), page 12014, XP020189463, ISSN: 1742-6596, DOI: 10.1088/1742-6596/292/1/012014 the whole document -----	1-10
Y	TSUCHIYA T ET AL: "Influence of the laser wavelength on the epitaxial growth and electrical properties of La0.8Sr0.2MnO3 films grown by excimer laser-assisted MOD", APPLIED SURFACE SCIENCE, ELSEVIER, AMSTERDAM, NL, vol. 255, no. 24, 30 September 2009 (2009-09-30), pages 9804-9807, XP026675116, ISSN: 0169-4332, DOI: 10.1016/J.APSUSC.2009.04.094 [retrieved on 2009-04-22] the whole document -----	1-10
A	TSUCHIYA T ET AL: "Epitaxial growth of LSMO film prepared by excimer laser-assisted metal organic deposition (ELAMOD)", KEY ENGINEERING MATERIALS, TRANS TECH PUBLICATIONS LTD., STAFA-ZURICH, CH, vol. 388, 1 January 2009 (2009-01-01), pages 133-136, XP008156852, ISSN: 1013-9826 ISBN: 978-0-87849-310-4 [retrieved on 2008-09-24] the whole document -----	1-10