All-spinel oxide Josephson junctions for high-efficiency spin filtering

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Abstract

Obtaining high efficiency spin filtering at room temperature using spinel ferromagnetic tunnel barriers has been hampered by the formation of antiphase boundaries due to their difference in lattice parameters between barrier and electrodes. In this work we demonstrate the use of LiTi2O4 thin films as electrodes in an all-spinel oxide CoFe2O4-based spin filter devices. These structures show nearly perfect epitaxy maintained throughout the structure and so minimise the potential for APBs formation. The LiTi2O4 in these devices is superconducting and so measurements at low temperature have been used to explore details of the tunnelling and Josephson junction behaviour.

Keywords: spintronics, oxides, thin films, superconductivity, pulsed laser deposition

(Some figures may appear in colour only in the online journal)

Introduction

The broad spectrum of electronic and optical properties exhibited by functional oxides offers many opportunities for microelectronic devices. In particular, the experimental growth of epitaxial oxide heterostructures has increased the development of promising novel functionalities and device concepts [1]. However, the integration of complex oxides into multi-layer structures is often challenging. Lattice mismatch, structural differences and different optimum growth conditions between the oxide layers hamper the epitaxial growth of heterostructures. Of particular relevance to this paper, ultrathin films of ferromagnetic insulators (FIs) can form tunnel barriers that generate nearly 100% spin-polarised currents by selectively filtering electrons according to their spins [2]. This spin-filtering process is in contrast to the classic magnetic tunnel junctions in which a non-magnetic tunnel barrier is sandwiched between two ferromagnetic electrodes [3].

The majority of FIs have Curie temperatures \( T_{\text{Curie}} \) well below room temperature and so, although high efficiency (~100%) spin-filtering has already been reported in a range of materials including Eu-chalcogenides [4–6], perovskites [7–10] and GdN [11, 12], potential applications are limited by the low temperatures required. In the last few years, interest has focused on spinel ferrites FIs (e.g. NiFe2O4, CoFe2O4, MnFe2O4) due to their \( T_{\text{Curie}} \) being well above room temperature [13–15]. Spin polarization of ~4–8% at room temperature has been recently reported in spinel ferrite CoFe2O4-based tunnel junctions [16, 17].

The likely reason for such low values is the formation of antiphase boundaries (APBs) in the spinel thin film barrier [18, 19], which are detrimental to spin-filter efficiency as they dramatically affect magnetic behaviour and barrier height [20, 21]. Such defects are formed due to spinels having a lattice parameter \( (a = 0.83–0.85 \text{ nm}) [22] \), almost double that of the metallic layers (Au, Pt, LaNiO3, La2/3Sr1/3MnO3) and substrates conventionally used in spin-filter devices. Achieving high spin-filter efficiencies at room temperature may therefore...
be dependent on overcoming structural and chemical defects in ultra-thin (<5 nm) epitaxial spinel ferrite films to be used in complex oxide heterostructures.

APBs can be reduced by using a spinel structure substrate (MgAl2O4) and LiTi2O4 as non-magnetic electrodes for a spin filter tunnel junction [23]. One of the few conducting spinels, LiTi2O4, is a metallic and superconducting [24] spinel (critical temperature \(T_C \sim 13\) K) with a lattice parameter \(a = 0.8405\) nm closely-lattice matched to those of the spinel CoFe2O4 ferrite and of the spinel MgAl2O4 (\(a = 0.8080\) nm) substrate. The lattice mismatch to the latter is -3.8% while to CoFe2O4 \((a = 0.8392\) nm) is only +0.2%.

The growth of high quality single crystal thin films by pulsed laser deposition (PLD) depends on the oxygen partial pressure \(P_{O_2}\) in the chamber [23, 25–27]. LiTi2O4 has a spinel structure with equal numbers of trivalent and quadrivalent Ti cations and for \(P_{O_2}\) higher than 1 × 10⁻⁵ Torr, Ti³⁺ ions readily oxidise to Ti⁴⁺, leading to the formation of Li₄Ti₅O₁₂, a transparent insulator phase [26]. Conversely, oxygen deficiencies are deleterious to the magnetic properties of spinel ferrite thin films [28] because the oxygen ions mediate the superexchange interaction between the magnetic ions in the spinel structure, producing the net magnetic moment in the ferrites. Thus any oxygen deficiency due to a growth at low \(P_{O_2}\), reduces the exchange interaction between the magnetic ions, and hence, the saturation magnetization of the CoFe₂O₄ films. As a consequence, integrating LiTi₂O₄ into spinel ferrite-based spin filter junctions requires a fine tuning of the growth conditions of these two materials, requiring very different oxygen partial pressures.

In this paper we demonstrate the successful growth of CoFe₂O₄/LiTi₂O₄ bilayers in which LiTi₂O₄ maintains its metallic and superconducting properties and CoFe₂O₄ its insulating ferromagnetic characteristics. LiTi₂O₄/CoFe₂O₄/LiTi₂O₄ trilayers were processed into all-spinel oxide symmetric superconductor-insulator-superconductor (SIS) tunnel junctions. The measured current–voltage characteristics show conclusive evidence of the tunnel nature of these junctions, proving that LiTi₂O₄ can be used as bottom electrode in an almost APBs free tunnel junction.

**Methods**

LiTi₂O₄ and CoFe₂O₄ thin-films were grown by pulsed laser ablation of polycrystalline ceramic targets prepared from a mixture of Li₂CO₃ (Alfa-Aesar) and TiO₂ (Alfa-Aesar), for Li₄Ti₅O₁₂ [29], and from cobalt iron oxide nanopowders (Sigma-Aldrich), for CoFe₂O₄. The higher Li/Ti ratio (0.8) of the Li₄Ti₅O₁₂ target was designed to compensate for the high loss of Li during the ablation process [30]. The PLD system (KrF excimer, \(\lambda = 248\) nm) was operated at an energy density of 0.7 J cm⁻² and at a repetition rate of 5 Hz for LiTi₂O₄, and 2.5 J cm⁻² and 1 Hz and for CoFe₂O₄.

Structural analysis was done using x-ray diffraction (XRD, PANalytical high resolution x-ray diffractometer) with monochromatised CuKα₂ radiation (0.154 nm). The deposition rate was determined by measuring the thickness of ultra-thin films by x-ray reflectivity analysis, allowing the controlled deposition of thicker films. The films’ transport measurements were performed by four-wire method between 300 K and 4.2 K by direct Al-bonding to unpatterned films. Magnetic properties of the films were measured using a vibrating sample magnetometer (VSM) with a maximum dc magnetic field of 1 T.

The SIS trilayers were patterned into square pillars (size ranging from 2 × 2 \(\mu\)m² to 4 × 4 \(\mu\)m²) by optical laser lithography, ion-milling and lift-off steps. The ion milling procedure was performed using a self-aligned process for junction fabrication [31] in a Nordiko 3600 ion beam deposition system [32] with an Ar⁺ beam (current density ~340 \(\mu\)A cm⁻²), first at an angle with respect to the substrate of 70° down to the CoFe₂O₄ barrier and subsequently at 40° until it penetrated the bottom LiTi₂O₄ electrode. This ensured a barrier with steep profile and well controlled nominal size, while avoiding material re-deposition on the sidewalls [33, 34]. A 100 nm-thick Al₂O₃ layer was deposited by RF sputtering for passivation and lateral insulation of the pillars. The top electrode (Au(100nm)/Cr(10nm)) was deposited in an Alcatel SCM450 multi-target DC magnetron sputtering system. Before the patterning process, the structure was covered with a 15 nm-thick Ta anti-reflection layer, deposited by ion beam deposition in a Nordiko 3000 system [35], to reduce specular reflections of the laser during the lithography process.

Device transport properties were measured with a four-probe dc current-biased method in a closed-cycle helium cryostat. A differential conductance spectrum was obtained by numerically differentiating the \(I–V\) characteristic after applying a moving average window to smooth the data.

**Results and discussion**

**Bilayer characterisation**

PLD-growth of LiTi₂O₄ requires reducting conditions, and thus during film growth, the deposition chamber was evacuated to 1 × 10⁻⁶ Torr and the substrate temperature was kept at 800 °C; this is the optimal temperature to reduce Li segregation at the surface [23]. During the subsequent growth of CoFe₂O₄, the temperature of the substrate was lowered to 450 °C to avoid any unfavourable oxidation of the deposited LiTi₂O₄ layer. Thereafter high purity oxygen was injected into the chamber and the \(P_{O_2}\) maintained at 2.5 × 10⁻⁴ Torr, to limit the formation of oxygen deficiencies in the magnetic layer. In this way, the chemical potential of oxygen ions was lower and the oxidation of Ti⁴⁺ into Ti³⁺ could be avoided, keeping LiTi₂O₄ in its metallic, superconducting phase. To verify epitaxy and bulk phase purity of the deposited films, we measured out-of-plane XRD patterns for a CoFe₂O₄(60nm)/LiTi₂O₄(200nm) bilayer.

The XRD pattern (figure 1) shows clear (1 1 1) and (2 2 2) Bragg reflection peaks of the films and those of the underlying MgAl₂O₄(1 1 1) substrate. No undesired phase or orientation of either LiTi₂O₄ or CoFe₂O₄ is observed in the pattern, demonstrating that both layers are in single phase and highly oriented. The overlap of the reflection peaks of the two films forming the bilayer, due to their close lattice match, is clear in the inset of figure 1 where the (2 2 2) reflection peak of the bilayer is compared with the reflections of a single LiTi₂O₄ (200nm) film and a single CoFe₂O₄(60nm) film grown on MgAl₂O₄ (1 1 1).
Temperature-dependent resistivity measurement of a CoFe2O4(10 nm)/LiTi2O4(50 nm) bilayer shows metallic behaviour (figure 2). Moreover, the bilayer displays a superconducting transition at $T_C = 11.5$ K, confirming that the bottom layer has kept its metallic-superconducting phase without undergoing any oxidation due to the growth of CoFe2O4. The $T_C$ is in good agreement with previous findings on single LiTi2O4 films [23, 25, 26]. The width of the superconducting transition is less than 0.4 K (figure 2, inset). The Fermi liquid behaviour of the bilayer is confirmed by the variation of resistivity as $T^2$ from 50 to 150 K (blue-dashed line). The residual resistivity $\rho_0$ and the residual resistivity ratio $RRR = \rho_{300K}/\rho_{25K}$ of the films were 460 $\mu\Omega$ cm and 1.5, respectively, in accordance with recent publications [23, 25–27, 36]. At temperatures below 20 K the bilayer exhibits an increase in resistance, characteristic of weak localization in disordered 2D films [37].

The room temperature magnetic hysteresis loops of a CoFe2O4(60 nm)/LiTi2O4(50 nm) bilayer grown on MgAl2O4(1 1 1) substrate are shown in figure 3. The magnetic layer is ferromagnetically easy in the film plane, with a hard direction normal to the film. The in-plane magnetization ($M_s$) at 1 T and the coercive field were 200 emu cm$^{-3}$ (or a magnetic moment of 1.6 $\mu_B$ per formula unit) and 95 mT, respectively. This magnetic moment value is lower than the maximum 3 $\mu_B$, theoretically obtained for bulk CoFe2O4 with an inverse spinel structure [38].

The decreased $M_s$ is consistent with previous reports [28] on CoFe2O4 films grown at low $P_{O_2}$ and low temperature, and was expected due to the conditions required to avoid any oxidation of the underlying LiTi2O4. In a spin filter device, the tunnelling spin currents depend exponentially on the barrier height difference between the two spins. Thus, a lower than expected exchange energy of the FI, due to the lower $M_s$ values, can still produce a high polarisation of the current.

Several other approaches were followed in order to combine LiTi2O4 and CoFe2O4 in a bilayer without detrimentally affect each other during growth: (i) a few capping monolayers of CoFe2O4 were grown at the same reduced $P_{O_2}$ environment of LiTi2O4, in order to not expose the latter to oxygen during the growth of the subsequent monolayers of CoFe2O4 in higher $P_{O_2}$, in order to not expose the latter to oxygen during the growth of the subsequent monolayers of CoFe2O4 in higher $P_{O_2}$, to increase the magnetic moment of latter; (ii) the bilayer was grown entirely in reduced oxygen environment and annealed at different $P_{O_2}$ and at different temperatures, to compensate for the oxygen deficiencies in the CoFe2O4 layer; (iii) a mixture of N2/O2 instead of O2 was used, as suggested by Hassan et al [39], to reduce the chemical potential of the oxygen ions. In all cases, though an increased $M_s$ of the CoFe2O4 layer could be observed, the underlying LiTi2O4 of the bilayers showed insulating behaviour indicating an
grown a symmetric superconducting tunnel junction of the Li$_4$Ti$_5$O$_{12}$ phase.

states at the CoFe$_2$O$_4$ interface. We will begin by assuming fitting parameter section of the side view of the micro-tunnel junction with bottom and top contact leads. (b) Normalised temperature evolution of the Dynes curves could be the possible stoichiometric inhomogeneity density of states due to the proximity effect of a ferromagnetic modified superconductivity on the surface due to a non-stoichiometric surface layer. Another contributing factor to the reduced gap value is the suppression of the order parameter in the electrodes due to the proximity with the CoFe$_2$O$_4$ magnetic barrier; this is also presumably responsible for the large value of $\Gamma$. If we assumed SIN behaviour, our estimate for $2\Delta$ would be doubled to 5 meV that is significantly larger than reported previously and so appears unreasonable.

SIS junctions would normally be expected to show a Josephson supercurrent with a maximum value of $\pi\Delta/2R_j$ where $R_j$ is the junction normal state resistance, but for strongly spin filtering barriers, this is expected to be substantially reduced because the tunnelling of conventional oxidation of the Ti$^{3+}$ ions and the formation of the unwanted Li$_4$Ti$_3$O$_{12}$ phase.

Tunnel junction characterisation

To prove the suitability of LiTi$_2$O$_4$ as an electrode in an almost defect-free all-spinel oxide spin filter junction we have grown a symmetric superconducting tunnel junction of the form LiTi$_2$O$_4$(50 nm)/CoFe$_2$O$_4$(1–3 nm)/LiTi$_2$O$_4$(50 nm). For this purpose, a second layer of LiTi$_2$O$_4$ was grown on top of the CoFe$_2$O$_4$(1–3 nm)/LiTi$_2$O$_4$(50 nm) bilayers. These oxide heterostructures were then patterned into micro-pillars as described earlier (figure 4(a), inset). The dynamic conductance $dI/dV$ spectrum exhibits a characteristic superconducting energy gap structure with a dip around the zero bias and strongly smeared coherence peaks. At temperatures approaching the $T_c$ of LiTi$_2$O$_4$, the gap decreases until it disappears for higher temperatures. The decrease of the conductance observed at voltages above $2\Delta$ is most likely due to flux flow and heating in the electrodes at high current densities ~15 kA cm$^{-2}$. Similar behaviours are common in tunnel junctions based on high $T_c$ superconductors [40]. The broadening of the coherence peaks is an evidence for the smearing of the interfacial density of states due to the proximity effect of a ferromagnetic Mott insulator, which shortens the quasiparticle lifetime [41–43]. Another contributing factor to the smearing of the $dI/dV$ curves could be the possible stoichiometric inhomogeneity between two LiTi$_2$O$_4$ electrodes as a consequence of their different growth conditions.

The form of the $dI/dV$ spectra implies that at least one of the LiTi$_2$O$_4$ electrodes preserves a superconducting density of states at the CoFe$_2$O$_4$ interface. We will begin by assuming that both electrodes are superconducting and then justify this in the light of the available information.

A simplified BCS smeared superconductor-insulator-normal metal (SIN) model was employed to fit the $dI/dV$ raw data and estimate the energy gap $\Delta$. According to this model, $\frac{dI}{dV} \propto \text{Re} \left[ \frac{\Gamma}{(E-E-V-\Gamma)^2-(\Delta^2+\Gamma^2)} \right] \frac{E}{\sqrt{\Gamma}}$, in the limit of low bias voltages and for low temperatures [42]. Here $\Gamma$ is the Dynes parameter accounting for the experimentally observed broadening [41] and for large values of $\Gamma$ in both electrodes this model can also model SIS quasiparticle conductance spectra if $\Delta$ is replaced by $2\Delta$. The fitting values of $\Gamma$ are shown in figure 4(b). In figure 4(c) it is shown the fit to a $dI/dV$ curve collected at 2.5 K with $2\Delta = 2.47$ meV and $\Gamma = 6.9$ meV. The peak height and the gap structure of the raw data are quite accurately reproduced by the fit. The superconducting energy gap width $2\Delta(T)$ was determined from this data. The dependence of $2\Delta$ on the temperature (shown in figure 4(d)) fits well with BCS-type temperature dependence [44], $2\Delta(T) = 2\Delta(0) \text{tanh}(1.74 \sqrt{T_c-T}/T)$ (solid line) confirming a superconducting behaviour. The fitting parameters are $2\Delta(0) = (2.6 \pm 0.1)$ meV, which is lower than the one reported in previous findings [27, 45, 46], and $T_c = (11.0 \pm 0.3)$ K, in accordance with the value measured in our bilayers. Consequently, we find a $2\Delta(0)/k_BT_c$ ratio of 2.8 $\pm$ 0.2, which is less than the typical values ranging between 3 and 4.5 for BCS like superconductors but in agreement with recent scanning tunnelling spectroscopy on LiTi$_2$O$_4$ films [47] suggesting a modified superconductivity on the surface due to a non-stoichiometric surface layer. Another contributing factor to the reduced gap value is the suppression of the order parameter in the LiTi$_2$O$_4$ electrodes due to the proximity with the CoFe$_2$O$_4$ magnetic barrier; this is also presumably responsible for the large value of $\Gamma$. If we assumed SIN behaviour, our estimate for $2\Delta$ would be doubled to 5 meV that is significantly larger than reported previously and so appears unreasonable.

Figure 4. (a) Differential conductance $dI/dV$ versus bias voltage from 1.5 to 10.5 K with 1 K increments and at 11 K in zero field for a LiTi$_2$O$_4$(50 nm)/CoFe$_2$O$_4$(1.5 nm)/LiTi$_2$O$_4$(50 nm) junction. The size of the junction is $3 \times 3 \mu$m$^2$. The inset shows the schematic cross section of the side view of the micro-tunnel junction with bottom and top contact leads. (b) Normalised temperature evolution of the Dynes fitting parameter $\Gamma$. (c) The smeared BCS s-wave model fit to the $dI/dV$ versus bias voltage characteristic at 2.5 K with $2\Delta = 2.4$ meV and $\Gamma = 6.9$ meV. (d) Temperature dependence of normalised energy gap $2\Delta$ and BCS fit. (e) Field dependence of the supercurrent peak appearing at 1.5 K. The error bars represent the s.e. in the fit to the $dI/dV$ data.
singlet Cooper pairs is blocked \[48\]. At the lowest tempera-
tures a zero bias peak appears in low-resistance junctions
\([R_j \sim 0.05 \, \text{k} \Omega]\) while in medium-resistance junctions
\([R_j \sim 0.9 \, \text{k} \Omega]\) this feature is not observed—as might be
expected given the experimental noise. Although this feature
might be related to the flow of a Josephson supercurrent in the
junction, its disappearance at temperatures well below \(T_C\)
is inconsistent with standard behaviour. Similarly, the depend-
ce of the supercurrent peak on an in-plane external applied
field (shown in figure 4(e)) does not show the Fraunhofer-like
periodic suppression of the peak characteristic of Josephson
tunnel junctions. Indeed, the appearance of the zero-bias peak
may also be related to the presence of Andreev bound states
\[49\].

The \(dI/dV\) curves collected at higher biases (figure 5)
reveal an interesting midpoint state between the low bias SIS-
state (i.e. both electrodes are superconducting) and the state in
which the electrodes are metallic (normal state) at high bias. This
conductance midpoint state is related to bias voltages at which one of the LiTi_2O_4 electrodes is superconducting
while the other is metallic. The midpoint state, identified by
the dashed arrow in figure 5, indicates that the electrodes are
in different superconducting states. For high biases the two
electrodes are in their normal state and the conductance of the
junction is equal to that measured at temperatures above \(T_C\)
(12 K). At higher temperatures, lower biases are needed
to turn the electrodes from the superconducting state to the
metallic-normal state. This confirms the SIS-nature of the
junctions, while the presence of two distinct conductance-
states is another validation of a stoichiometric inhomogeneity
between two superconducting LiTi_2O_4 electrodes.

A \(dI/dV\) spectra collected at 1.5 K at different out of plane
applied magnetic fields are shown in figure 6. The closing
of the peak position along with the closing of the gap and the
suppression of the superconducting peak for values approaching the LiTi_2O_4 upper critical field \(H_{c2}\), are clearly
visible. The scaling law follows a field quadratic-depend-
ence \(\Delta(B,T) \sim \Delta_0 - [H/H_{c2}(T)]^2\), as recently reported
in point contact spectra [27]. The fit, shown in the inset of
figure 6, gives an extracted value of \(H_{c2}\) at 2 K of \(\sim 10.8\, \text{T}\),
which is consistent with previous results [45, 46].

Figure 7 shows the temperature dependence of a typical
LiTi_2O_4/CoFe_2O_4/LiTi_2O_4 junction resistance with 1.5 nm
CoFe_2O_4 barrier measured by applying a 0.1 mA current. A
sharp drop in resistance is seen at the LiTi_2O_4 superconducting
transition due to the disappearance of the in-series resistance
of the leads. At higher temperatures the resistance is not
exponentially increasing with decreasing temperature, which
is the behaviour for a semiconducting non-magnetic barrier
\[50\], but is instead continuously dropping with temperature.
The temperature dependence of the resistance of the LiTi_2O_4
downlead of the same junction was measured (inset (b),
figure 7) to verify that the decreasing behaviour of \(R_j\) is attrib-
utable to tunnelling current flowing across the tunnel junction
and not across any series resistances, which would explain the
decreasing behaviour. This is confirmed by difference in the
order of magnitude between the resistance of junction \(\sim 10^1\)
\(\Omega\) and the resistance of the bottom lead \(\sim 10^2\, \Omega\). In addition,
large contributions of non-tunnelling (leakage) conductance
to the dominant tunnel conductance due to shorts between the
two electrodes can be also ruled out since \(R_j\) is non-zero for
temperature below \(T_C\), as opposed to the two LiTi_2O_4 super-
conducting electrodes which show zero resistance.

Moreover, the resistance increases with decreasing temper-
ature below \(T_C\) due to the fact that there are no available states
for tunnelling at the Fermi energy level for measurements
voltages much less than \(\Delta\). In this case the conductance is
dominated by thermal excitation of quasi-particles across the
gap and, as temperature decreases, the number of thermally
excited quasi-particle states decreases exponentially, resulting
in an increase of the sub-gap resistance for decreasing
temperature. These behaviours confirm that the mechanism of
charge transport in the junctions is predominantly tunnelling
in nature and thus, the drop in \(R_j\) with decreasing temperature
observed across the entire temperature range above \(T_C\) may
be a consequence of the exchange splitting of the magnetic tunnel barrier, leading to a temperature dependent reduction of the barrier height of one spin (inset (a), figure 7). The $T_{\text{Curie}}$ of CoFe$_2$O$_4$ is well above room temperature, so the absence of the typical change from semiconducting behaviour to metallicity-like behaviour at $T_{\text{Curie}}$, due to onset of spin filtering, reported in spin filtering devices of this type [8, 12] is expected in our range of measurement.

**Conclusions**

In summary, we demonstrated the successful superconducting tunnel process in an all-spinel SIS tunnel junctions with CoFe$_2$O$_4$ as FI barrier and LiTi$_2$O$_4$ as electrodes grown on MgAl$_2$O$_4$ substrates. The integration of the metallic-superconducting LiTi$_2$O$_4$ in tunnel junctions offers new possibilities in the quest of achieving high efficiency room temperature spin filtering due to lattice match with the spinel Co-ferrite, reducing APBs.

The CoFe$_2$O$_4$/LiTi$_2$O$_4$ holds the potential for all-oxide magnetic tunnel junctions with efficient spin filtering properties at room temperature. An estimation of the polarisation of the current could not be performed by extrapolating the temperature dependence of $R_{\text{L}}$ from the high temperature ($> T_{\text{Curie}}$) regime as $T_{\text{Curie}}$ in this case is well above room temperature. This capability could be investigated by tunnel magnetoresistance-like experiments by replacing the top LiTi$_2$O$_4$ electrode with a spinel ferromagnet (Fe$_3$O$_4$) decoupled from the CoFe$_2$O$_4$ by a thin insulating layer of MgAl$_2$O$_4$, as suggested by promising tunnelling spectroscopy study on junctions with Au electrode [13]. The perfect epitaxy and lattice match between all the layers of such Fe$_3$O$_4$/MgAl$_2$O$_4$/CoFe$_2$O$_4$/LiTi$_2$O$_4$ devices grown on MgAl$_2$O$_4$ substrates, paves the way to high efficiency spin filtering at room temperature.

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**References**

[1] Bibes M, Villegas J E and Barthélémy A 2011 *Adv. Phys.* 60 5
[2] Moodera J S, Santos T S and Nagahama T 2007 *J. Phys.: Condens. Matter* 19 165202
[3] Moodera J S, Kinder L R, Wong T M and Meservey R 1995 *Phys. Rev. Lett.* 74 3273
[4] Moodera J, Hao X, Gibson G and Meservey R 1988 *Phys. Rev. Lett.* 61 637
[5] Moodera J S, Meservey R and Hao X 1993 *Phys. Rev. Lett.* 70 853
[6] Santos T and Moodera J 2004 *Phys. Rev. B* 69 241203
[7] Gajek M, Bibes M, Barthélémy A, Bouzehouane K, Fusil S, Varela M, Fontcuberta J and Fert A 2005 *Phys. Rev. B* 72 20406
[8] Prasad B, Egelmez M, Schoofs F, Fix T, Vickers M E, Zhang W, Jian J, Wang H and Blamire M G 2014 *Nano Lett.* 14 2789
[9] Prasad B, Zhang W, Jian J, Wang H and Blamire M G 2015 *Adv. Mater.* 27 3079
[10] Harada T, Ohkubo I, Lippmaa M, Sakurai Y, Matsumoto Y, Muto S, Konuma H and Oshima M 2012 *Phys. Rev. Lett.* 109 176602
[11] Pal A, Senapati K, Barber Z H and Blamire M G 2013 *Adv. Mater.* 25 5581
[12] Senapati K, Blamire M G and Barber Z H 2011 *Nat. Mater.* 10 849
[13] Chapline M and Wang S 2006 *Phys. Rev. B* 74 144418
[14] Lüders U, Barthélémy A, Bibes M, Bouzehouane K, Fusil S, Jacquet E, Contour J-P, Bobo J-F, Fontcuberta J and Fert A 2006 *Adv. Mater.* 18 1733
[15] Matzen S, Moussy J-B, Miao G X and Moodera J S 2013 *Phys. Rev. B* 87 184422
[16] Ramos A V, Guittet M-J, Moussy J-B, Mattana R, Deranlot C, Petroff F and Gatel C 2007 *Appl. Phys. Lett.* 91 122107
[17] Matzen S, Moussy J-B, Mattana R, Bouzehouane K, Deranlot C and Petroff F 2012 *Appl. Phys. Lett.* 101 42409
[18] Datta R, Loukya B, Li N and Gupta A 2012 *J. Cryst. Growth* 345 44
[19] Ma J X, Mazumdar D, Kim G, Sato H, Bao N Z and Gupta A 2010 *J. Appl. Phys.* 108 063917
[20] Margulies D, Parker F and Rudee M 1997 *Phys. Rev. Lett.* 78 22409
[21] Moussy J-B et al 2004 *Phys. Rev. B* 70 174448
[22] Moussy J-B 2013 *J. Phys. D: Appl. Phys.* 46 i43001
[23] Mesoraca S, Klebeiker J E, Prasad B, MacManus-Driscoll J L and Blamire M G 2016 *J. Cryst. Growth* 454 134
[24] Johnston D, Prakash H, Zachariasen W H and Viswanathan R 1973 Mater. Res. Bull. 8 777
[25] Chopdekar R V, Wong F J, Takamura Y, Arenholz E and Suzuki Y 2009 Physica C 469 1885
[26] Kumatani A, Oh sawa T, Shimizu R, Takagi Y, Shiraki S and Hitosugi T 2012 Appl. Phys. Lett. 101 123103
[27] Jin K et al 2015 Nat. Commun. 6 7183
[28] Zhou J, He H and Nan C-W 2007 Appl. Surf. Sci. 253 7456
[29] Hirayama M, Kim K, Tōjigamori T, Cho W and Kanno R 2011 Dalton Trans. 40 2882
[30] Dumont T, Lippert T, Döbeli M, Grimmer H, Ufheil J, Novák P, Würsig A, Vogt U and Wokaun A 2006 Appl. Surf. Sci. 252 4902
[31] Gallagher W J et al 1997 J. Appl. Phys. 81 3741
[32] Cardoso S, Macedo R J, Ferreira R, Augusto A, Wisniowski P and Freitas P P 2008 J. Appl. Phys. 103 07A905
[33] Leitão D C, Silva A V, Ferreira R, Paz E, Deepak F L and Cardoso S 2014 J. Appl. Phys. 526 17E526
[34] Jeong J and Endoh T 2017 Japan. J. Appl. Phys. 56 04CE09
[35] Gehanno V, Freitas P P, Veloso A, Ferreira J, Almeida B, Sooasa J B, Kling A, Soares J C and da Silva M F 1999 IEEE Trans. Magn. 35 4361
[36] Oshima T, Yokoyama K, Niwa M and Ohomo A 2015 J. Cryst. Growth 419 153
[37] Li T and Sheng P 1996 Phys. Rev. B 53 R13268
[38] Szotek Z, Temmerman W, Ködderitzsch D, Svanæ A, Petit L and Winter H 2006 Phys. Rev. B 74 174431
[39] Hassan R S, Viart N, Ulhaq-Bouillet C, Loison J L, Versini G, Vola J P, Crégut O, Pourroy G, Müller D and Chateigner D 2007 Thin Solid Films 515 2943
[40] Cybart S A, Cho E Y, Wong T J, Wehlin B H, Ma M K, Huynh C and Dynes R C 2015 Nat. Nanotechnol. 10 598
[41] Dynes R C C, Na V, Narayanamurti V and Garno J P 1978 Phys. Rev. Lett. 41 1509
[42] Ozyuzer L, Zasadzinski J F, Kendziora C and Gray K E 2000 Phys. Rev. B 61 3629
[43] Pal A and Blamire M G 2015 Phys. Rev. B 92 180510
[44] Bardeen J, Cooper L and Schrieffer J 1957 Phys. Rev. 108 1175
[45] Tang L, Zou P Y, Shan L, Dong A F, Che G C and Wen H H 2006 Phys. Rev. B 73 184521
[46] Sun C P, Lin J-Y, Mollah S, Ho P L, Yang H D, Hsu F C, Liao Y C and Wu M K 2004 Phys. Rev. B 70 54519
[47] Okada Y, Ando Y, Shimizu R, Minamitani E, Shiraki S, Watanabe S and Hitosugi T 2017 Nat. Commun. 8 15975
[48] Bergeret F S, Verso A and Volkov A F 2012 Phys. Rev. B 86 60506
[49] Greene R H et al 2003 Phys. C Supercond. 387 162
[50] Moodera J S and Mathon G 1999 J. Magn. Magn. Mater. 200 248