Large magnetoresistance in La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films induced by metal masked ion damage technique

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We have developed a simple process to obtain large magnetoresistance (MR) in perovskite manganite thin films by a combination of focused ion beam (FIB) milling and 120 keV H$_2^+$ ion implantation. Metal slits about 70 nm in width were printed by 30 kV focused Ga ion beam nanolithography on a 4 mm track, and the materials in these slits are then irradiated by the accelerated H$_2^+$ ions. Using this method, in a magnetic field of 5 T we can get a MR $>60\%$ over a 230 K temperature scope, with a maximum value of 95% at around 70 K. This technique is very promising in terms of its simplicity and flexibility of fabrication and has potential for high-density integration.

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I. INTRODUCTION

The so-called colossal magnetoresistance (CMR) has been extensively studied recently. Very large resistance changes of about $10^6\%$ have been obtained in applied magnetic fields of several Tesla for a range of different perovskite-like manganites. The MR phenomenon has been divided into intrinsic and extrinsic: whereas intrinsic effects are found in bulks of ferromagnetic materials and are determined by material parameters, extrinsic effects are found only at defect structures, suitable artificial heterostructures and devices. To obtain a large MR in a relatively low magnetic field, many research groups focus on the investigation of extrinsic MR in various magnetic oxides in recent years. Extrinsic MR in ferromagnetic oxides usually falls into three broad classes, namely grain-boundary MR, tunnel junction MR, and domain wall MR. In this article we report a method aimed to enhance the MR in the LCMO thin films by forming nano-constraints through a combination of focused ion beam (FIB) milling and 120 KeV H$_2^+$ ion implantation. The results demonstrate that a maximum MR ratio of 95% (defined as $\Delta R/R_0 = (R_H - R_0)/R_0$, where $R_0$ is the resistance at a magnetic field of H=0 and $R_H$ at H=5T.) and an overall value $>65\%$ can be reached in a 230K temperature range.

II. EXPERIMENT

The films for this study were high quality c-axis oriented 100 nm thick epitaxial La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) grown on (100) LaAlO$_3$ substrates by pulsed laser ablation. A tri-layer mask, consisting of 900 nm S9918 photo resist, 300 nm metal Cr deposited by dc magnetron sputtering and another 900 nm S9918 photo resist, was then coated on the sample. As shown schematically in Fig. 1, tracks with a nominal width of 4 mm were patterned by optical lithography and Ar ion milling at 400 eV and 10 mA on a water-cooled rotating stage. When the figure was transferred from photoresist to the Cr film, we adopted reactive ion etching (RIE) to pattern the track of 4 mm, as shown in Fig. 1. The Cr masking layer was chosen to be sufficiently thick to absorb the implanted protons during the following implantation procedure, but also thin enough that the slit could be cut with sufficient accuracy. To prepare the mask apertures, the patterned chip was mounted on a carrier that was transferred to the FIB system with a Ga source. Using 30 KeV Ga ions, slots of single scan-line width were milled at 10 pA in the Cr film, as can be seen in Fig. 1. Early experimental results showed that Ga ions would be implanted into the slit materials during the milling process, which should be...
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sistance was remarkably decreased. The first and the

local barriers, and concomitantly of large spin angles.

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cient, and therefore shifts the I-M transition point left to

ally reduces the LCMO film, makes the slits oxygen defi-

FIG. 2: Secondary electron image obtained in the FIB of 4

slits approximately 70nm wide cutting into a typical metal

mask.

avoided [11]. For this reason, we chose S9918 photoresist

as a barrier layer to absorb the Ga ion. In order to make

sure the material in the slits is now LCMO, we again

adopted RIE to remove the remaining photoresist in the

slits. The last step, H$_2^+$ irradiation, was then preceded

to create highly localized barriers. This process is shown in

Fig. 3. Fig. 2 shows a secondary electron image obtained in the FIB system, with 4 slits approximately

70 nm wide cutting into a Cr metal mask.

The resistivity and magnetoresistance of the as pre-

pared junction were measured by the four-probe method

in the temperature range 5 K<T<300 K. An MPMS su-

perconducting quantum interference (SQUID) measuring

system was used to generate the uniform magnetic field.

III. RESULTS AND DISCUSSION

The effect of our processing method on the transport

properties in the junction is evidenced in the temperature
dependence of the resistance (in Fig. 3). The original

film (inset of Fig. 3) exhibits a characteristic insulator-

metal (I-M) transition peak at around 230 K, which is

also a signature of its paramagnetic-ferromagnetic tran-

sition. The junction, however, shows three peaks on its

resistance versus temperature curve. The first peak is

consistent with the I-M transition in the LCMO thin film,

and is obviously contributed by the film portions other

than the irradiated slits. The H$_2^+$ implantation intu-

tionally reduces the LCMO film, makes the slits oxygen defi-

cient, and therefore shifts the I-M transition point left to

the second peak position. The origin of the third peak is

still not known. The data fluctuation around this peak

suggests that it may be owe to a kind of metastable state.
We are concerned that it is a result of spin pinning at the
local barriers, and concomitantly of large spin angles.

When a 5T magnetic field was applied, the sample re-

sistance was remarkably decreased. The first and the

third peak clearly right shift to higher temperatures and
the second one is completely suppressed, owe to the re-

duction of spin fluctuations in a magnetic field. With

the field decreasing from 5T to 2T, 0.5T, and 0.1T, the

second peak gradually resumes. However, the low tem-

perature resistance never recovers to its original value

even when the field is totally withdrawn and the sample

is warmed to room temperature to remove any possible

magnetic remanence. The resistance change between the
initial and the after-measurement values is also shown in

the inset, whose apex is coincident with the position of

the third resistance peak. This again suggests that the

low temperature peak is from a metastable state, which

may break down in a high field and thus be irreversible.

The temperature dependence of the MR ratio (defined
as $\Delta R/R_0 = (R_H - R_0)/R_0$) in 5T field is read from Fig.

3 and plotted in Fig. 4. It is impressive that the MR

ratio is above 60% in temperatures below 230K. Three

small bumps appear at temperatures corresponding to

the resistance peaks. A maximum value as large as 95%

is obtained at 70K, near the third resistance peak. An-
other ratio denoted as MR$^*$ is also plotted in the figure,

where the after-measurement resistance is adopted in-

stead of $R_0$. Apparently, MR$^*$ evolves like MR, besides

the slightly reduced value as low temperatures.

To probe the nature of the greatly enhanced MR in the

junction, we recorded the sample resistance in a magnetic
field scanning from -1T to +1T at temperatures 200, 150,

and 75K. The results are shown in Fig. 5. It is noticed

that, at the three temperatures, the junction resistance
all shows an almost linear dependence on the magnetic
field, with no low field shoulders and ignorable hystere-

sises, suggesting an intrinsic behavior. The MR ratio in

1T field is 24% and 39% at 200K and 150K, respectively.

The MR enhancement at 150K is most probably due to

the irradiation induced spin disordering at the slits. The

MR ratio at 75K is only 17% in 1T field, which is some-

\[ R(T) = R_0 + \Delta R T^2 \]
what under-estimated because the zero field resistance cannot recover after measured in a 5T magnetic field. Nevertheless, the value is still substantial as compared with epitaxial thin films. In the case of zero-field-cool, the MR ratio increases to about 20%.

Therefore, the transport measurement results reveal that the device fabricated does not form nanoconstraints or magnetic domain walls in the ion irradiated slits as we had expected. In stead, the characters of the material in the damaged region are changed upon the ion implantation. The width of the slit (70 nm) might be too large to become a geometric constraint for domain walls, or the tunneling barriers. Nevertheless, the large MR ratio obtained in such a broad temperature scope still makes the device potential for eventual technological applications.

IV. CONCLUSIONS

In conclusion, we have developed a metal-masked ion-damage method to improve the MR effect in LCMO thin films. A large MR ratio over 60% was observed in 5T field in a 230 K temperature scope, with a maximum value of 95% at 70K. The linear field dependence of the MR ratio reveals its intrinsic nature. Although the origin of the large MR ratio at low temperatures still has not been clarified, the device demonstrates a very promising technique for practical applications, in terms of its simplicity and flexibility of fabrication and its potential for high-density integration.

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