The influence of Ga\(^+\) irradiation on the transport properties of mesoscopic conducting thin films

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Abstract

We studied the influence of 30 keV Ga\(^+\)-ions—commonly used in focused-ion-beam (FIB) devices—on the transport properties of thin crystalline graphite flakes, and La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) and Co thin films. The changes in electrical resistance were measured in situ during irradiation and also the temperature and magnetic field dependence before and after irradiation. Our results show that the transport properties of these materials strongly change at Ga\(^+\) fluences much below those used for patterning and ion-beam-induced deposition (IBID), seriously limiting the use of FIB when the intrinsic properties of the materials of interest are of importance. We present a method that can be used to protect the sample as well as to produce selectively irradiation-induced changes.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last years a focused-ion beam (FIB) of Ga\(^+\) ions for etching \[1\] has attracted the attention of the community as an alternative and flexible method to produce micro- and nanostructures of materials, especially where the use of conventional methods appears to be limited. This FIB technique has been successfully used for nanostructuring different materials like magnetic and superconducting \[2–4\] or, more recently, to study the conduction behavior in metallic constrictions \[5\]. One of the advantages of this technique is its versatility; the use of any resist appears, a priori, unnecessary. Nowadays, FIB devices are also used for deposition of metallic or insulating materials with the help of the same Ga\(^+\) ions. These ions induce a decomposition of a chemical metal precursor over the surface in question, a technique called ion-beam-induced or-assisted deposition (IBID, IBAD) \[6–8\]. The main advantage of IBID/EBID is the deposition of the desired patterns of a material without the need of a mask or a pre-structured pattern using optical or e-beam lithography (EBL). Also the possibility to modify only parts of the patterns in electronic devices within nanometer dimensions is another of the advantages of FIB.

The modification of different properties of different materials has been studied in the past, such as, for example, in magnetic La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) thin films \[9\] or Co/Pt multilayers \[10\]. However, a fundamental problem of FIB was less discussed in the literature, namely the modification of the sample’s near-surface region and, to a certain extent, also its interior and their influence on the transport properties by the use of Ga\(^+\) ions of energies up to 30 keV and fluences below 10\(^{12}\) cm\(^{-2}\) in the usual devices. We note that, before cutting or depositing material, the use of FIB requires the precise alignment of the Ga beam and this is done by taking a picture of the region in question and irradiating it with the same Ga\(^+\) ions. Depending on the surface properties of the material in question, in general Ga\(^+\) fluences \(\gtrsim 10^{11}\) cm\(^{-2}\) are used. As we demonstrate below, these Ga\(^+\) fluences necessary for the first alignment may already seriously affect the intrinsic properties of the material of interest and can lead to the wrong interpretations of the effects that a reduction of the sample geometry may produce.

The influence of Ga irradiation during the FIB preparation processes has not yet been quantitatively studied, neither in situ nor after irradiation for fluences below 10\(^{12}\) cm\(^{-2}\).
La0 process and pre-characterized with electron backscattering a crystalline graphite flake prepared by a rubbing and ultrasonic stages. In the first stage we have done for beam alignment. The experiments were realized in two stages. In the first stage we have done \textit{in situ} measurements of the electrical resistance during irradiation and in the second stage its resistance was measured as a function of $T$ and magnetic field $B$ dependence after irradiation of three different thin film materials to show the influence of the Ga irradiation used in FIB devices and at fluences as low as the ones used for beam alignment. The experiments were realized in two stages. In the first stage we have done \textit{in situ} measurements of the electrical resistance during irradiation and in the second stage its resistance was measured as a function of $T$ and $B$ to compare with the corresponding virgin states. Using graphite as a test material because its electrical resistance is extremely sensitive to lattice defects [11], we provide in this work a possible solution that can be used to strongly reduce the effects due to Ga$^+$ irradiation on different materials.

2. Experimental details

We have used the FIB capabilities of an FEI NanoLab XT 200 Dual Beam microscope (DBM). The acceleration voltage was fixed in all our experiments to 30 kV. The ion current and the area to be irradiated were changed in order to obtain different Ga$^+$ fluences, see table 1. The selected samples were a crystalline graphite flake prepared by a rubbing and ultrasonic process and pre-characterized with electron backscattering diffraction (EBSD) and Raman scattering [12, 11], a La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) thin film prepared by plasma laser deposition (PLD) and microstructured by EBL and a wet etching process [13], and thermally evaporated Co thin films (#1 and #2) previously structured by EBL, see figures 1(a)–(c) and table 1.

In particular, when materials are selected to investigate their transport properties while their size is being reduced, care should be taken since the electrical transport can be sensitive to lattice defects as well as to the Ga contamination produced. The aim of this paper is to report on the changes in the transport properties while their size is being reduced, care should be taken since the electrical transport can be sensitive to lattice defects [11], we provide in this work a possible solution that can be used to strongly reduce the effects due to Ga$^+$ irradiation on different materials.

Low-noise four-wire resistance measurements (two for the input current and two for the voltage measurement, important to eliminate contributions of the lead resistance) have been performed with the AC technique (Linear Research LR-700 Bridge with an eight-channel LR-720 multiplexer) with ppm resolution and in some cases also with the DC technique (Keithley 2182 with a 2001 Nanovoltmeter and Keithley 6221 current source).

The Au/Pt lead contacts used for all samples were prepared by the EBL process using an e-beam resist PMMA 950 K of ~200 nm thickness. The lithography process was done with the Raith ELPHY Plus system included in our microscope. The Au/Pt deposition of the contact electrodes was done by evaporation in a high-vacuum chamber with a nominal thickness of 25 and 9 nm, respectively. The \textit{in situ} resistance measurements performed before and during the irradiation of the sample were done using a self-made sample holder fixed inside the microscope chamber. The temperature and magnetic field dependence measurements were performed using a commercial cryostat with a temperature stability of 0.1 mK at 100 K. The magnetic field generated by a superconducting solenoid was always applied normal to the sample and input current.

To avoid or reduce irradiation effects we protected the graphite sample with a negative electron beam resist (AR-N 7500) of thickness 300 nm. In order to test the effectiveness of the resist film to avoid contamination during irradiation, part of the graphite flake was covered with the above-mentioned resist in an additional process after the Au/Pt leads were deposited on the sample, see figure 1(a). This resin protects the graphite sample in the region of the three upper electrodes, allowing us to compare the change in voltage in the unprotected, protected and intermediate regions.

Table 1. Samples used, their dimensions (total length × width × thickness) and the Ga$^+$ fluence irradiated on the samples. The fluence number in brackets refers to the total fluence after the second irradiation. The corresponding data of Co sample #2 is given in the table. Co sample #1 had a thickness of 57 nm. Other dimensions can be taken from figure 1(c).

| Sample          | Graphite | L$_{0.7}$Ca$_{0.3}$MnO$_3$ | Co#2 |
|-----------------|----------|---------------------------|------|
| Dimensions ($\mu$m) | 11 × 2 × 0.015 | 52 × 7.3 × 0.035 | 18 × 0.9 × 0.022 |
| Fluence ($10^{11}$ cm$^{-2}$) | 5 (10) | $\geq 2.2$ | $\geq 2.2$ |

Figure 1. Scanning electron microscope images of: (a) the graphite flake (dashed line denotes its borders) with the six Au/Pt contacts. (b) The LCMO film with the two inner voltage electrodes and one of the input current electrodes. (c) Co microwire #1 with electrodes at different positions. The irradiation has been made on the whole region and the electrical resistance was measured between the third and second electrodes from the right.
Figure 2. Resistance as a function of time before, during and after Ga$^+$ irradiation inside the FIB chamber for the samples (a) crystalline graphite flake (first irradiation with a fluence of $5 \times 10^{11}$ cm$^{-2}$), (b) LCMO film and (c) Co film #1. For these two samples the fluences used are written in the figures. All these measurements were done in situ and at room temperature.

The advantages of this resist is that it allows us to do patterning by EBL in the desired shape, it is sufficiently robust in the temperature range used and it is a very bad electrical conductor. The penetration depth of the Ga$^+$ ions in this resist as well as in the samples and the distribution of the density of vacancies as a function of sample depth were estimated taking into account their density and using Monte Carlo simulations given by the stopping range of ions in matter (SRIM) [14, 15] taking into account the energy of the Ga$^+$ ions, see figure 3.

3. Results and discussion

3.1. In situ transport measurements

A detailed study of the electrical resistance of the above-mentioned materials was realized in situ during the Ga$^+$ ion irradiation in the microscope chamber. In the case of the graphite sample we measured simultaneously the resistance of the covered and uncovered parts before, during and after irradiation. Figure 2 shows the changes observed in this sample during and after the first irradiation of fluence $5 \times 10^{11}$ cm$^{-2}$. This fluence produces nominally $10^3$ ppm vacancy concentration inside the sample whereas the Ga concentration implanted is less than 1 ppm, see figure 3. The disorder produced by the irradiation increases the resistance of the uncovered part of this sample by a factor $>4$.

The resistance of the covered part remains unchanged within $10^{-4}$ relative change, indicating that the 300 nm thick resist was enough to stop the Ga$^+$ ions as expected since, according to the SRIM calculations, the maximal penetration of the Ga$^+$ ions in the resist should be $\approx 75$ nm. Immediately after irradiation the resistance of the uncovered part starts to decay exponentially with two characteristic relaxation times, as has also been observed after proton irradiation at room temperature [11]. This time relaxation is observed for all samples just after the irradiation finishes. This decay is related to local thermal relaxation processes and to the diffusion of carbon interstitials and vacancies [16, 17].

Figure 3. (a) Qualitative distribution of implanted Ga ions as a function of penetration depth into the sample for the three studied materials. (b) Similarly for the vacancy density but taking into account fixed fluences. The curves were obtained using the stopping range of ions in matter SRIM or HIS [14, 15], taking into account the energy of the Ga$^+$ ions and the material densities.

Qualitatively speaking, similar resistance changes during the irradiation process are also observed in the other two samples, see figures 2(b) and (c). In the case of the LCMO
sample the maximal penetration of the ions is $\sim 45$ nm, see figure 3(a). Because the thickness of this sample is 35 nm, part of the Ga$^+$ ions are expected to be implanted and the rest to go through the sample generating a considerable amount of defects, as can be seen in the calculated curves, see figure 3(b). In the case of the Co wire #1 the maximal ion penetration is $\sim 30$ nm < $57$ nm thickness, see figure 3. Therefore the produced defects plus Ga implantation are responsible for the relatively small increase in the electrical resistance, see figure 2(c). To study the influence on the transport properties mainly due to the defects produced by the Ga$^+$ irradiation, a second Co #2 sample with less thickness has been studied and its results are discussed below.

The effect of the Ga irradiation on sample volume expansion (thickness swelling) as well as milling (thickness reduction) depends on the ion fluence, ion energy and target material. As an example we refer to the work done in [9] where such studies were done on La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films. According to this work and taking into account our used fluences, any thickness increase as well as any milling are completely negligible and do not affect the changes measured in the resistance.

3.2. Temperature and magnetic field dependence before and after irradiation

3.2.1. Graphite. The special lattice structure of graphite and the weak coupling between graphene layers make graphite a quasi-2D semimetal, whose carrier density depends strongly on the lattice defects like vacancies and/or impurities. In a recent work it was demonstrated that the electrical resistance of thin graphite crystals of micrometer size changes after inducing less than 1 ppm vacancy concentration by ion irradiation [11]. This makes graphite a extraordinary sensor for testing the efficiency of the resin cover as well as to show the dramatic changes produced by a relatively weak Ga$^+$ ion irradiation.

Figure 4 shows the temperature dependence of the graphite sample in its three states, as prepared and after the two irradiations. The temperature dependence in the as-prepared state has a semiconducting behavior above 50 K and metallic below. The semiconducting behavior is mainly due to the increase in carrier concentration with temperature because most of the carriers are thermally activated and the Fermi energy increases linearly with temperature [11]. The metallic behavior below 50 K is not intrinsic to graphite but comes from internal interfaces between crystalline regions parallel to the graphene layers but of slightly different orientations [12]. The mentioned interfaces originate during the pyrolysis process$^1$.

\[ \text{Normalized resistance as a function of temperature for the graphite.}
\]

\[ \text{Normalized resistance as a function of temperature for the graphite.}
\]

\[ R(T)/R(T=250K) \]

\[ \begin{align*}
R(250K): & \\
(1) & 22 \Omega \\
(2) & 76.5 \Omega \\
(3) & 162.2 \Omega
\end{align*} \]

\[ \text{Temperature T(K)} \]

\[ 0 \quad 50 \quad 100 \quad 150 \quad 200 \quad 250 \]

\[ R(T)/R(T=250K) \]

\[ \text{Normalized resistance as a function of temperature for the graphite.}
\]

The first irradiation increased the resistance in all the temperature range without changing strongly the relative change with temperature, see figure 4. The metallic part was shifted to below 25 K and its $T$ dependence gets weaker, suggesting that the irradiation also affected the properties of the internal interface(s). After the second irradiation the metallic region vanishes completely and the resistance decreases rather linearly with $T$, see figure 4. We note that the absolute value of the resistance is fairly proportional to the fluence used. Between the virgin state and first irradiation we have an increase in the resistance of a factor of 3.5. Doubling the fluence we expect an increase by a factor $\sim 7$ of the resistance of the as-received state, a factor in agreement with the experimental observation.

As shown in [11] the increase in resistance is due to the decrease in the mean free path that overwhelms the increase in the carrier density that these irradiations produce inside the graphite structure. This behavior is related to the different weights the carrier density $n$ and the mean free path $l$ have in the 2D resistivity, i.e. $R \propto 1/(n^2l)$, in contrast to the 3D resistivity equation $R \propto 1/(nl^2)$. Note also that the second irradiation produces already a vacancy density that implies a vacancy distance of less than 2 nm in the graphene plane. At distances smaller than $\sim 3$ nm we do not expect a large increase in the carrier density with further irradiation [11].

Figure 5 shows the magnetoresistance (MR) versus applied field at different constant temperatures for the graphite

\[ \text{Magnetoresistance (MR) versus applied field at different constant temperatures for the graphite.}
\]

or $b$ directions, i.e. parallel to the graphene planes [24, 25, 12]. It appears plausible that structural defective regions, generated during the growth process and influenced by the release of gases, prevent a larger increase of the thickness of the crystalline regions, producing these planar interfaces.

\[ \text{Magnetoresistance (MR) versus applied field at different constant temperatures for the graphite.}
\]
Figure 5. Magnetoresistance as a function of the field applied normal to the graphene planes for the sample in its virgin state (a), and after the first (b) and second (c) irradiation.

Figure 6. First derivative of the resistance on field versus inverse field for the first (continuous line) and second (dotted line) irradiation. The data have been multiplied by a factor in order to show both derivatives on the same y-axis scale.

Figure 7. Magnetoresistance of the upper covered part of the graphite flake, see figure 1(a), at $T = 4$ K and in the virgin state (continuous line) and after the second Ga$^+$ irradiation ($\otimes$).

Sample in the virgin (a), first (b) and second (c) irradiated state. The MR in the virgin state agrees with previous reports [12]. Note that the MR shows a quasi-linear field behavior at low temperatures. Also anomalous is the systematic increase of the MR below 100 K. This is related to the decrease in resistance with decreasing temperature, see figure 4. The MR reaches a value of 16 at 8 T and 2 K. After the first irradiation the MR decreased by a factor 16 and remains practically temperature-independent. After the second irradiation the MR decreased further by a factor of six and shows a similar temperature independence. The data reveal that the Shubnikov–de Haas (SdH) oscillations increase their amplitude and start to be measurable at lower fields after the first irradiation [11]. This behavior is related to the increase in the carrier density due to the creation of defects, whereas the decrease in the MR is due to the decrease in the mean free path.

Note that after the second irradiation the SdH oscillations do not change qualitatively (their absolute amplitude changes due to the large change of the MR), see figure 6. After the second irradiation we observe the first low-field oscillation at a similar field and a similar oscillation period in a reciprocal field as after the first irradiation, see figure 6. These results indicate that no further change in the carrier density has been produced for a vacancy distance less than 2 nm. Taking into account that 3 nm is of the order of the range of modification of the electronic structure produced by, for example, a single vacancy [18], then a saturation of the carrier density is reached, decreasing the vacancy distance below $\sim 3$ nm but keeping the graphene structure. As expected, the covered part of the sample...
Figure 8. (a) Temperature dependence of the normalized resistance of the LCMO thin film before and after irradiation. The inset shows the same data but on a double logarithmic scale. (b) The MR versus applied field for the as-prepared state.

Figure 9. (a) The MR of the LCMO film after irradiation. Compare these results with those in figure 8(b) and note the induced changes in the MR by the irradiation. (b) Magnetoresistance as a function of the field at 75 K before and after irradiation in a reduced field range to show the clear increase in coercivity. This increase is observed at all temperatures in the ferromagnetic state.

does not show any change after the first or second irradiation, as can be seen in figure 7.

3.2.2. LaCaMnO film. The manganite sample undergoes a paramagnetic insulator-to-ferromagnetic metal transition, leading to a sharp peak in the resistance near its Curie temperature as shown in figure 8(a). For our sample this peak is observed at $T_c = 106$ K. Interestingly, after irradiation the temperature dependence does change only in the ferromagnetic state of the sample, which shows now a $T_c = 95$ K, see
The measured MR of this sample in the as-prepared state agrees with the published literature and shows hysteretic behavior in the ferromagnetic state whereas no hysteresis is shown in the paramagnetic state above $T_c$, see figure 8(b).

The influence of ion irradiation on the magnetic and transport properties of manganites were studied in the past but mainly at much higher ion energies, see, e.g., [19–22, 9]. In general at fluences above $10^{12}$ cm$^{-2}$ the ion irradiation reduces the metal–insulator transition temperature and the magnetic hysteresis gets broader, reflecting the increase of the pinning of the domain walls by the induced defects. A similar behavior is observed in our sample, see figure 9(a). Figure 9(b) shows in detail the MR between $-2$ and $2$ T at 75 K. The irradiation induces an increase in the coercivity $H_c$ from 0.1 to 0.42 T after irradiation, defined at the maxima of the MR, as well as in the overall hysteresis width.

These results indicate that care should be taken when changes in the transport properties of ferromagnetic oxides are observed after microstructuring the samples with FIB. The observed results after patterning might not be due to the change of the sample dimension but to the structural changes induced by the Ga$^+$ irradiation.

### 3.2.3. Co film

Figure 10 shows a SEM picture of Co sample #2 with the four electrodes for the resistance measurement. The resistance as a function of temperature and magnetic field before and after a Ga$^+$ irradiation is shown in figures 11(a) and (b). Due to the smaller thickness of this sample the irradiation at 30 kV produces mainly defects instead of doping since the Ga$^+$ ions stop beyond the sample thickness, i.e. inside the substrate. The influence of the induced defects in the Co sample can be clearly recognized by the increase in the absolute value of the resistance. For example, at 275 K the resistance of Co sample #2 increases from 36 to 175 $\Omega$, flattening the temperature dependence, see figure 11(a). The MR shown in figure 11(b) indicates a clear change in the hysteresis, indicating a change in pinning of the domain walls. These results are qualitatively similar to those obtained for the manganite shown above, see figure 9.

## 4. Conclusion

In conclusion our studies indicate clearly that care should be taken with the change of the intrinsic properties of the materials when FIB devices are used for patterning, cutting or...
just for depositing other materials for contacts, for example. Our work demonstrates that already the usual Ga\textsuperscript{+} fluences needed for a precise alignment of the Ga\textsuperscript{+} beam before really using it induce relevant changes in the transport properties of the three different materials studied here. Using a thin crystalline graphite flake we were able to demonstrate also that covering the sample with a sufficiently thick resist film one can avoid the irradiation damage completely. This indicates that, in principle, one can use this technique to protect certain parts and produce defined changes in other parts of the sample of interest. This method might be used to induce changes in the hysteretic properties of ferromagnetic micro- and nanostructures or in the electronic density in graphite or multigraphene in specific parts of the sample, for example.

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References

[1] Matsui S, Kojima Y, Ichiai Y and Honda T 1991 J. Vac. Sci. Technol. B 9 2622–32
[2] Gierak J 2005 Microelectron. Eng. 78/79 266–78
[3] Tseng A A 2005 Small 10 924–39
[4] de la Pierre M, Cagliero S, Agostino A, Gazzadi G and Truccato M 2009 Supercond. Sci. Technol. 22 045011
[5] Fernández-Pacheco A, De Teresa J M, Córdoba R and Ibarra M R 2008 Nanotechnology 19 415302
[6] Melnga ilis J 1987 J. Vac. Sci. Technol. B 5 469
[7] Matsui S and Ochiai Y 1996 Nanotechnology 7 247
[8] Langford R M, Petford-Long A K, Rommeswinkle M and Eagelkamp S 2002 Mater. Sci. Technol. 18 743
[9] Pallecchi I, Pellegrino L, Bellingeri E, Siri A S, Marré D and Gazzadi G C 2008 J. Magn. Magn. Mater. 320 1945–51
[10] Hyndman R, Warin P, Gierak J, Ferre J, Chapman J N, Jamet J P, Mathet V and Chappert C 2001 J. Appl. Phys. 90 3843–9
[11] Arndt A, Spoddig D, Esquinazi P, Barzola-Quíquia J, Dusari S and Butz T 2000 Phys. Rev. B 60 195402
[12] Barzola-Quíquia J, Yao J-L, Rüdiger P, Schindler K and Esquinazi P 2008 Phys. Status Solidi a 205 2924–33
[13] Bridoux G, Barzola-Quíquia J, Bern F, Böhmann W, Esquinazi P and Ziese M 2009 German patent office application 10 2009 045 114.5
[14] Ziegler J F 1977–1985 The Stopping and Range of Ions in Matter (New York: Pergamon)
[15] Ziegler J F, Biersack J P and Ziegler M D 2008 SRIM—the Stopping and Range of Ions in Matter SRIM Co. see also the simulation software IIS available at http://www.ele.uva.es/jesman/iis.html, which has some advantages in comparison with the usual SRIM simulation
[16] Niwase K 1995 Irradiation-induced amorphization of graphite Phys. Rev. B 52 15785–98
[17] Lee G-D, Wang C Z, Yoon E, Hwang N-M, Kim D-Y and Ho K M 2005 Phys. Rev. Lett. 95 205501
[18] Ruffieux R, Gröning O, Schwaller P, Schlaphbach L and Gröning P 2000 Phys. Rev. Lett. 84 4910–4
[19] Stroud R M, Browning V M, Byers J M, Chrisey D B, Fuller-Mora W W, Grabowski K S, Horwitz J S, Kim J, Knies D L and Osofsky M S 1997 MRS Symp. vol 154
[20] Wolfman J, Hervieu M and Simon Ch 2001 Nucl. Instrum. Methods Phys. Res. B 179 176–85
[21] Chattopadhyay S, Pal S, Sarkar A, Kumar R and Chaudhuri B K 2005 Nucl. Instrum. Methods Phys. Res. B 230 274–8
[22] Ramesh Babu M, Han X F, Mandal P, Kumar R, Asokan K and Jayavel R 2009 Mater. Chem. Phys. 117 113–6
[23] Hishiyama Y, Yasuda S, Yoshida A and Inagaki M 1988 J. Mater. Sci. 23 3272
[24] Inagaki M 2000 New Carbons: Control of Structure and Functions (Amsterdam: Elsevier)
[25] García N, Esquinazi P, Barzola-Quíquia J, Ming B and Spoddig D 2008 Phys. Rev. B 78 035413