NiCu–based superconducting devices: fabrication and characterization

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Abstract. The critical Josephson current ($I_c$) in superconducting/ferromagnetic (S/F) multilayer-based junctions can be controlled by changing the relative directions of the magnetization in the F-layers. Recent experimental works [1,2] show that an enhancement of $I_c$ is achieved in S/F weak links when the alternating F-layers are antiparallel aligned. We present preliminary experimental results concerning the dependence of $I_c$ on the relative orientation of the ferromagnetic layers in S/F/Al/F/S tunnel junctions where the F-layers are obtained by changing the relative composition of NiCu alloys. The multilayers were grown by electron beam deposition, and processed by Focused Ion Beam lithography. The magnetic state of the devices was directly determined by measuring the current perpendicular to plane (CPP) magnetoresistance (MR) at high bias. $I_c$ was found to be larger when the F-layers are antiparallel aligned. The maximum change of $I_c$ corresponds to the maximum change of MR. The application of a magnetic field induces a transition in the shape of the current-voltage curve that seems to suggest Coulomb blockade effect.

1. Introduction
Spin-valve Josephson junctions have gained attention in the last years because of the possibility of actively controlling both the amplitude and the sign of the Josephson current [3,4]. Recent experimental works [1,2] show that, in Josephson weak links, the critical Josephson current ($I_c$) is substantially larger when the adjacent ferromagnetic (F) layers are antiparallel aligned compared to the case of parallel orientation. Both the works are concerned with submicron scale devices. This is because devices on nanometer scale give some advantages, among which the negligibility of the direct suppression of $I_c$ by the external applied magnetic field in the range of field of interest. In ultrasmall spin-valve Josephson junctions, if the spin-valve is made of weak ferromagnets, e.g. Copper-Nickel (Cu$_x$Ni$_{1-x}$) or Palladium-Nickel (Pa$_x$Ni$_{1-x}$) alloys, $I_c$ could be large enough to produce spin torque. This would give the possibility of controlling the magnetic state of the device, and hence the amplitude and sign of the Josephson current, by making a setting current passing through the junction itself, instead of by an external applied magnetic field.

We present preliminary results on S/F/Al/F/S Josephson junctions where the superconducting (S) electrodes are Niobium (Nb) and the insulator barrier is Aluminum oxide ($\text{Al}_2\text{O}_3$). The structure
sandwiched between the two thick Nb electrodes is a magnetic tunnel junction (MTJ) in which the ferromagnetic layers are Cu$_{x}$Ni$_{1-x}$ with different composition but of the same thickness. The compositions were chosen so that the F-layers reversed at different applied magnetic fields. The junctions were fabricated on a submicron scale by a three-dimensional focused ion beam (FIB) etching technique. As will be discussed, a cleaning of the perimeter of the tunnel barrier with very low beam current was used in order to remove metallic shorts created by resputtering. The behavior of the Josephson critical current on the mutual orientation of the F-layers is discussed. Moreover, the coexistence of a Coulomb blockade effect with the Josephson tunnel effect is considered as a possible explanation of the observed transition in the shape of the current-voltage $I(V)$ curve when a magnetic field is applied in the plane of the junctions.

2. Experiment

The devices were fabricated by growing the whole multilayers without breaking vacuum and making all the patterning afterwards by a three-dimensional FIB etching technique. Nb/Cu$_{0.37}$Ni$_{0.63}$/Al-Al$_{2}$O$_{3}$/Cu$_{0.47}$Ni$_{0.53}$/Nb multilayers were grown on oxidized Si (100) substrates by electron beam deposition. The base pressure in the chamber was always better than $P_b = 4 \times 10^{-8}$ Pa. The Nb was deposited at a rate of 1.5 nm s$^{-1}$ for a total thickness of $t_{Nb} = 250$ nm for both the superconducting electrodes. The CuNi layers were grown by evaporating Cu and Ni at the same time from two different crucibles. The evaporation rates were $r_{Cu} = 0.04$ nm s$^{-1}$ and $r_{Ni} = 0.06$ nm s$^{-1}$ for the Cu$_{0.37}$Ni$_{0.63}$ whereas $r_{Cu} = 0.05$ nm s$^{-1}$ and $r_{Ni} = 0.05$ nm s$^{-1}$ were used for growing Cu$_{0.47}$Ni$_{0.53}$. The crucibles were shielded one from the other in order to avoid cross contamination. The two facing ferromagnetic layers were always of the same thickness $t_F = t_F = t_F$. Multilayers with different $t_F$ were grown. The exact compositions of the alloys were previously checked on thick films by energy dispersive x-ray spectrometry. In order to exclude any significant formation of Ni clusters in the alloys, we measured the Curie temperature ($T_{Curie}$) of the films by measuring the electrical resistivity as a function of the temperature. The measured $T_{Curie}$ were ~200 K and ~50 K for Cu$_{0.37}$Ni$_{0.63}$ and Cu$_{0.47}$Ni$_{0.53}$, respectively. The values are in agreement with those reported in the literature [1,5] for the same composition of the alloys. The Al$_2$O$_3$ tunnel barrier was obtained by thermal oxidation at room temperature of a 5 nm thick Al film evaporated at a rate of $r_{Al} = 0.09$ nm s$^{-1}$ and oxidized in pure oxygen atmosphere of $P_{O_2} = 1 \times 10^5$ Pa for a time of 30 minutes. All the rates of deposition were controlled by a feedback system using quartz crystal oscillators as monitors.

We report preliminary measures on devices fabricated from a multilayer with $t_F = 6$ nm. This value is quite smaller than the pair-decay length $\xi_p$ in Nb/Ni$_{1-x}$Cu$_x$ multilayers reported in the literature for similar compositions of the alloys [6,7].

The multilayers were first patterned with standard photolithography and wet chemical etching into a pattern with 20 μm long and 4 μm wide tracks with the associated connections and contact pads. The chemical solution used for the etching was composed by one part of 40% aqueous diluted hydrofluoric acid (HF) and two part of 65% aqueous dilute nitric acid (HNO$_3$). The samples were then processed in a FEI Dual Beam FIB/SEM Quanta 200 3D with Gallium (Ga) ion source. The tracks were narrowed to less than 1 μm from an angle of $\theta = 0$ with a beam current of 100 pA. A typical box of $4 \times 2$ μm$^2$ was used for the milling. The milling time was calibrated by using the specimen current measurement reported in Fig. 1. The sidewalls of the narrowed tracks were then cleaned with a beam current of 10 pA. This makes the sidewalls more vertical due to the smaller spot size and removes excessive Ga implantation. As will be discussed later, a second cleaning will be made at the end of the process to remove shorts on the barrier due to resputtering. The sample was then tilted by 85° and the isolation cuts were made with a beam current of 10 pA. The milling time was calibrated by monitoring the specimen current, which experiences a sharp jump when the track is completely milled through. The process as described so far is similar to that previously used to produce Josephson weak links [1,2,8] and spin-valve devices [9]. It is believed not to be suitable to produce Josephson tunnel junctions and magnetic tunnel junctions because of the shorting veils created by resputtering that form on the sidewalls. A post-anodization process has revealed to be successful in removing the shorting veils [10]. The process relies on a very fine control of the anodization dynamics and introduces a further uncertainty on the dimensions of the devices, particularly in the case of very small (lateral size < 200
nm) junctions. This could be one of the reasons of the large changing in resistance from sample to sample reported in Ref.10. We here demonstrate that producing hysteretic Josephson junctions is possible by simply cleaning the sidewalls with a very low beam current. We have provided our machine with a beam aperture of 1 pA. The alignment of such a small aperture is strongly sensitive to the sample position and much less stable than the others. By accessing to the maintenance program, the alignment procedure was performed for this aperture always before the post-cleaning. A cleaning of the side cuts was first performed close to the barrier from 85° and then the sample was tilted back to 0° where the cleaning was performed on the lateral sides. When the cleaning at 0° takes place, the previously cleaned side cuts are shielded from resputtering by the upper electrode. A typical final device is shown in Fig. 2.

Transport measurements were carried out in a liquid He dip probe. The magnetic field was always applied in the plane of the tunnel barrier by using a Copper coil.

![Specimen current versus milling time for a 1.5 × 1.5 μm² box milled from 0° using a 30 pA beam current.](image)

**Fig. 1:** Specimen current versus milling time for a 1.5 × 1.5 μm² box milled from 0° using a 30 pA beam current.

![FIB image of a final device from 65°. Current flow is indicated by the arrows.](image)

**Fig. 2:** FIB image of a final device from 65°. Current flow is indicated by the arrows.
3. Results and discussion

The junctions were characterized at $T = 4.2$ K by measuring the current-voltage $I(V)$ characteristic and the modulation of the Josephson critical current as a function of the applied magnetic field $I_c(H)$. The magnetic state of the spin-valve tunnel barrier during the sweeping of the magnetic field was determined by measuring the magnetoresistance (MR) at high bias as a function of the applied field.

Fig. 3 shows a typical $I(V)$ curve and the corresponding numerical conductance $dI/dV(V)$. The $I(V)$ curve is hysteretic and displays two different measurable critical currents, $I_c$ and $I_r$. $I_c$ is the maximum current that can be carried before the jump into the high voltage regime. $I_r$, the retrapping critical current, is the current at which the system returns to the zero voltage state. The numerical conductance has been calculated after suppressing the critical currents. As can be seen, the subgap voltage $V_g$ is around 1.5 mV. This reduction of the energy gap, due to proximity effect at the S/F interfaces, is consistent with that reported in other studies [11] on S/F/I/S junctions with composition of the CuNi alloy similar to our weaker one.

![Graph showing typical I(V) curve and corresponding numerical dI/dV(V).](image1)

**Fig. 3:** Typical $I(V)$ curve measured at $T = 4.2$ K and the corresponding numerical $dI/dV(V)$.  

The $I(V)$ characteristic is typical of a resistively shunted Josephson junction with a quality factor $Q = 4I_c/\pi R = 2$ (at $T = 4.2$ K). Although we cannot completely exclude so far that this low quality factor is due to shorts on the sidewalls that persist in spite of the accurate post-cleaning, there are at least three experimental observations that suggest that pinholes or localized single particle states in the tunnel barrier can be present. The Josephson current density is about 500 A/cm$^2$, which is quite larger than expected for our oxidation parameters. There is a low modulation of the $I_c$ by the field $H$ (see Fig. 4). The maximum changing in tunneling MR, shown in Fig. 4, is only 0.07 %, which is rather smaller than expected. These experimental results are all consistent with the presence of highly conducting channels for electron transport in the barrier.

![Graph showing dependence of Ic and MR on magnetic field H.](image2)

**Fig. 4:** Dependence of (black) Josephson critical current $I_c$ and (red) magnetoresistance MR at $T = 4.2$ K on magnetic field $H$ for a junction of area 400 $\times$ 400 nm$^2$. Field sweep direction is indicated by the arrows.
If the transition in the shape of the $I$-$V$ curve (see Fig. 5) that we observe when applying a magnetic field is due to standard Coulomb blockade effect, a precise estimation of the intrinsic capacitance of the junctions can be made. For example, for the junction whose $I(V)$ is reported in Fig. 5, with a field of 20 mT applied, a knee is present at $V_b = 0.5$ mV. The measured $V_b$ must correspond to $e/2C$ that yields $C = 0.16$ fF. The intrinsic capacitance must be also given by $C = \varepsilon_\varepsilon / d$ with $A$ area of the junction and $d$ thickness of the tunnel barrier. The junction area, obtained by FIB imaging is $\sim 0.15 \mu m^2$. Using a typical value for $Al_2O_3$ of the dielectric constant $\varepsilon_r \sim 10$ [12], the estimated barrier thickness is of the order of tens of nanometers which is impossible for our junctions, given the high Josephson current density. The mismatch must be due to a significant lower effective area of the device, which is unlikely to be caused by Ga diffusion or shorting veils on the sidewalls. Another way to see it is considering the very small value of the measured normal resistance ($R_n$) of the junctions. Considering, for example, the junction of Fig. 5, the normal resistance (evaluated at a voltage $V >> 2 \Delta$) is $R = 10 \Omega$. This value for such a small tunnel junction definitely indicates the presence of other conduction channels in the barrier. The question is whether the shorting takes place on the sidewalls or into the barrier. If thin Nb veils were the reason of the short, the respattered Nb would be highly polluted with Ga, Cu and even ferromagnetic Ni. This makes very unlikely that the shorting veils are superconducting at $T = 4.2$ K. According with the size of the devices and the used oxidation parameters, the intrinsic resistance ($R_i$) of the junctions must be in the range of $1 - 100$ kΩ. This is also consistent with the condition $R >> R_i = h/(2e)^2 \approx 6 k\Omega$ for the Coulomb blockade to set in, where $R_i$ is the so-called quantum resistance. Given the value of the measured $R_i$, we can assume a shorting parallel resistance value of 10 Ω. If the shorting took place on the sidewalls, even assuming a strongly underestimated resistivity of thin Nb in normal state at 4.2 K of $\sim 1 \mu \Omega cm$ [13,14] and a shorting length of the barrier thickness, a resistance of 10 Ω would require a thickness of the veils greater than the lateral dimension of the junctions. This leads once again to the conclusion that superconducting shorts must be present into the barrier.

![Fig. 5: $I(V)$ curve measured at $T = 4.2$ K in a magnetic field of 20 mT. From the knee, an intrinsic capacitance of 0.16 fF is estimated for this junction.](image)

The magnetic pattern $I_c(H)$ in Fig. 4 has a hysteretic behavior that is clearly correlated with the MR measured at a current bias of 2.5 mA ($V > V_c$). Increasing $H$ from the negative lowest field value, for positive values of $H$, as the soft $F$-layer reverses its magnetization, the MR rises and so does $I_c$. The maximum value of $I_c$ corresponds to the maximum changing in MR. After the relative orientation of the $F$-layers magnetization has reached its maximum, the MR starts decreasing and so, then again, does $I_c$. The reduction of MR due to the reversing of the hard $F$-layer is rapidly overwhelmed by the direct action of the field on the superconducting films that tends to increase the resistance of the whole structure. When lowering $H$ from the positive upper field value, the spin-valve barrier remains in the parallel state until the negative coercive field of the soft $F$-layer is reached and the reversing of its
magnetization starts taking place. The enhancement of the Josephson critical current in our tunnel junctions extends the results reported in Refs. 1 and 2 dealing with Josephson weak links. According to the theoretical model proposed in Ref 4, a systematic investigation of devices with different F-layers thickness and composition should lead to the realization of a controllable non-volatile \(\pi\)-junction.

Finally, let us discuss the transition in the shape of the I-V curve in the presence of a magnetic field. The kind of transition we here report is rather common [15,16] in ultrasmall Josephson junctions when a regime of very small Josephson energy \((E_c << E_J)\) is established, although is usually observed at very low temperatures and large magnetic fields. It is usually attributed to the coexistence of a Coulomb blockade effect with the Josephson tunnelling. When the condition for the Coulomb blockade to be observed are satisfied \((E_c > k_BT, R_i > R_q)\), if the Josephson coupling is weakened by a magnetic field, the charging energy dominates on the Josephson energy and the aspects of the Coulomb blockade come out. Assuming a minimum value of \(R_i = R_q\), an upper limit of the Josephson coupling energy can be estimated for our junctions from the measured value of the energy gap \((E_J = h\Delta/8e^2R_i)\) as \(E_c < 1\) K, when no external field is applied. Assuming the value of the intrinsic capacitance previously estimated, the charging energy is \(E_c = e^2/2C = 5.8\) K which is smaller but comparable with the Josephson energy. A relatively small magnetic field further reduces the Josephson coupling, and hence \(E_c\). On the other hand, the switching towards parallel orientation of the F-layers in the barrier is known to facilitate the reduction of the Josephson coupling, which can lead to the regime of very small Josephson coupling energy with relatively small applied magnetic fields. Once the typical Coulomb knee sets in, the value of \(V_c\) was found to be insensitive to magnetic field and temperature (above 4.2 K). It is finally worth noticing that, given the very low value of the intrinsic capacitance, the condition \(E_c > k_BT\) for the Coulomb blockade to be observed is satisfied even at \(T = 4.2\) K, whereas lower temperatures are usually requested. Such a low value of the intrinsic capacitance suggests the presence of quantum traps in the barrier, capacitively coupled with the junction electrodes. Repeated filling of single-particle states is a rather generic phenomenon [17]. It has been observed in systems where, either by accident or by specific design, quantum dots exist between two electrodes.

4. Conclusions
We have fabricated spin-valve Josephson tunnel junctions by using a three-dimensional Focused Ion Beam etching process and demonstrated that, despite the common knowledge, good quality tunnel junctions can be made by FIB without any other post-processing. The devices show an enhancement of the Josephson critical current when the sandwiched magnetic tunnel barrier is in antiparallel state compared to the case of parallel orientation. A systematic investigation of such a structure with different F-layers thickness and composition will be the next step forward the realization of a controllable non-volatile \(\pi\)-junction. Moreover, when the spin-valve barrier is switched towards the parallel state, the Josephson coupling is rapidly weakened and the system show Coulomb blockade of the supercurrent.

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