Ferromagnet–superconductor nanocontacts grown by focused electron/ion beam techniques for current-in-plane Andreev Reflection measurements

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\textit{A B S T R A C T}

Superconductor-ferromagnetic in-plane nanocontacts have been created with focused-electron/ion-beam-induced deposition techniques for studies of Andreev Reflection. The final resistance of the nanocontact is tuned during the growth by in situ resistance measurements. The results show that Co nanodeposits grown with focused electron beam have large spin polarization (\(\sim 35\%\)), making this nanomaterial of great potential for use in Spin Electronics applications. The experiments have also allowed the determination of the superconducting gap of the W-based nanodeposits grown with focused ion beam.

\textbf{1. Introduction}

The quality and functionality of materials grown by focused electron/ion beam techniques are of primary importance in a vast range of applications such as photomask repair, scanning probe sensors, circuit editing, nanophotonics, micro- and nano-electronics, etc.\cite{1}. These techniques rely on the dissociation of precursor gas molecules by the focused beam, giving rise to a nanomaterial deposited on a targeted place with controllable thickness and lateral size down to a few nanometers\cite{2}. One promising gas precursor is Co\textsubscript{2}(CO)\textsubscript{8}, which produces nanodeposits by focused electron beam exhibiting sizable magnetic properties\cite{3,4}, with potential applications in magnetic storage, sensing and logics. On the other hand, the combination of focused Ga ion beam and the W(CO)\textsubscript{6} gas precursor results in superconducting nanodeposits with \(T_\text{C}\) higher than 5 K\cite{5}. This superconducting nanodeposit follows the standard Bardeen–Cooper–Schrieffer (BCS) theory and its vortex lattice can be nicely observed by Scanning Tunnelling Spectroscopy\cite{6}. The relatively large \(T_\text{C}\) obtained in these W-based nanodeposits is thought to stem from its amorphous nature as crystalline W displays \(T_\text{C}\) of only a few mK\cite{5,6}. In the present work, we investigate the combined use of Co-based magnetic nanodeposits and W-based superconducting nanodeposits to create superconductor–magnetic-metal nanocontacts to determine the spin polarization of the Co electrons by suppression of the Andreev Reflection. The value and temperature dependence of the superconducting gap have also been extracted from the results.

The Andreev Reflection (AR) is a physical phenomenon occurring at the interface between a metal and a superconductor. Briefly, an electron injected from the metal into the superconductor requires to recruit another electron with opposite spin in order to create a Cooper pair, producing a reflected hole back in the metal with the spin direction opposite to that of the initial electron. Thus, the conductance is expected to double across the interface with respect to the conductance measured when the superconductivity is suppressed: by temperature increase, application of magnetic field or the use of high bias voltage. However, when the metal is magnetic, the AR process is limited by the unequal amount of spin-up and spin-down electrons (spin polarization) in the metal. In that case, the conductance lowers below the maximum “double value” and eventually can vanish if the magnetic material is half metal, i.e. with only one possible spin direction at the Fermi level. Interestingly, it has been shown that the spin polarization of a magnetic material can be extracted from measurements of the conductance in contacts between the magnetic material and a superconductor through the study of the AR\cite{7,8}. So far, the methods described in the literature to

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perform these measurements generally rely on geometries with current-perpendicular-to-plane, the most accepted ones being either pressing a superconducting point on top of the metal [7,9] or growing a superconducting and a metallic film, each on one side of a thin membrane with a hole connecting both [8,10]. Here, we report a reproducible method to create nanocontacts for current-in-plane AR measurements via the use of superconducting W-based nanodeposits grown by focused-ion-beam-induced deposition (FIBID) and in situ resistance measurements during nanocontact growth. Previously, planar heterocounters between a ferromagnet and a superconductor have been grown with optical lithography, showing contact size of several microns [11], thus not being comparable to the present study, where nanometric sizes are reached.

2. Experimental details

The types of nanocontacts studied so far for AR studies, with current-perpendicular-to-plane (CPP), and the present current-in-plane (CIP) ones, are sketched in Fig. 1. In Fig. 1(a) we represent a superconducting point pressed onto a metallic film (CPP geometry) in contrast with the schematic diagram shown in Fig. 1(b), where the metallic and superconducting materials are deposited on the same substrate and make contact at one point, allowing us to perform AR measurements in the CIP geometry. The nanocontacts are created between a superconducting W nanodeposit and a magnetic Co nanodeposit under high vacuum conditions (∼10⁻⁶ mbar) using a commercial dual beam equipment that integrates a focused electron column and a focused Ga column forming 52°. Using suitable parameters of electron beam energy, beam current and dwell time, the Co nanodeposits are grown with high purity (∼95%) as previously demonstrated [4,12]. Similarly, the ion beam energy and beam current are chosen to produce superconducting micro- and nanowires as previously investigated [13]. The main advantage of this method is that the two electrodes forming the contact are grown under high vacuum, minimizing oxidation during the contact growth. The in situ monitoring of the resistance by means of four electrical microprobes while the nanocontact is being formed lets us tune very precisely the final room-temperature resistance of the nanocontacts. The experimental setup to measure the resistance, whilst FEBID and FIBID growth is performed, has been previously used in our group in Pt-based nanodeposits [14]. To enable transport measurements, four external metallic pads of 5 µm in width are previously micropatterned on the insulating substrate with standard optical lithography techniques. These pads are connected to the nanocontact by four FIBID-Pt nanodeposits of 10 µm in length, connected in such a way (as can be seen in Fig. 1(c)) that the voltage drop measured is composed of the voltage drop across the nanocontact and the voltage drop across a portion of the superconducting electrode. This second term vanishes below the critical temperature of the superconductor. All the steps followed were described in the creation of the nanocontacts and the corresponding Scanning Electron Microscopy (SEM) images are shown in the Supplementary Information that can be found online at doi:10.1016/j.ssc.2010.10.028. Briefly, the Pt nanodeposits are first grown and the W electrode afterwards. The Co electrode is grown in the last step and is never irradiated by the Ga ions, which warrants its high-quality magnetic and transport properties.

3. Results and discussion

To illustrate the present method in which CIP nanocontacts are fabricated, we will show the results obtained on two Co-W nanocontacts, with low-temperature resistance of the order of 160 Ω and 320 Ω, respectively. The SEM image of the first of these nanocontacts is shown in Fig. 1(c). The nanocontact resistance measured inside the Dual Beam chamber was ∼10% lower, which indicates very good resistance stability with time and probably the resistance changes due to the formation of a very thin oxidation layer at the upper part of the contact after exposure to ambient conditions. This value of resistance is a factor of 100 lower than the inverse of the quantum of conductance, thus being far from the description of conductance within the full-quantum regime. We have grown several of these Co–W nanocontacts (∼20), the best samples for the investigation of the AR were obtained for resistances in the range 100–500 Ω. For resistance values higher than ∼500 Ω, the nanocontact diameter starts to be very small, thus having a strong tendency to oxidation when taken out of the process chamber for the transport measurements. For resistance values below ∼100 Ω, the thermal regime of transport is expected to start to play some role and the characteristics of such a point contact cannot be distinguished from heating effects because the energy dissipation in the nanocontact region heats the contact above the bath temperature.

In order to explore the AR effects on the transport across the Co–W interface, we have carried out two types of electrical transport measurements using a commercial physical property measurement system (PPMS) equipment. The resistance of the Co–W nanocontacts has been measured under several current values as a function of temperature. This type of experiment permits to track the Tc of the superconductor, the partial suppression of the AR, and the range of currents allowing the AR to occur. In Fig. 2 one can see the temperature dependence of the resistance for the two nanocontacts as they are cooled below the critical temperature of the superconductor. It is obtained that Tc ≈ 5.1 K for I = 20 nA, ≈ 4.9 K for I = 4 µA, and ≈ 4.5 K for I = 10 µA; this type of dependence being expected due to critical current issues. The maximum current used, 10 µA, corresponds in the nanocontacts to a voltage drop of 1.65 mV and 3.25 mV, respectively, being higher than the superconductor gap (≈0.7 meV) [6]. Therefore, the resistance is roughly constant in the temperature range 1–4 K because the AR does not take place and the electrons injected from the Co electrode are transferred into the quasiparticle density of states of the superconducting electrode. On the other hand, I = 20 nA corresponds to a voltage drop of 3.2 and 6.4 µV, much lower than the superconductor gap, which brings about the appearance of AR in the form of a strong resistance increase below 4 K. The measurement with I = 4 µA corresponds to a voltage drop below but close to the superconductor gap value, the AR being observed only partially. The increase of resistance measured below Tc when using low currents suggests the existence of AR as well as a spin imbalance in the ferromagnet, that does not favour the formation of Cooper pairs in the superconductor. As was pointed out by De Jong and...
Beenakker [15], the AR probability is limited by the minority carriers in the metal because all the spin-up incident electrons cannot be Andreev reflected, since the density of states for spin-down electrons is smaller than that for spin-up electrons. This results in an increase in the resistance if the voltage drop across the nanocontact is lower than the superconducting gap.

The current versus voltage characteristics have been measured at fixed temperatures, from where the differential conductance as a function of voltage, $G(V) = dI/dV$, can be extracted. From these results it is possible to obtain quantitative information on the superconductor gap and the ferromagnet spin polarization. We analyze the differential conductance as a function of the bias voltage using the model proposed by Blonder, Tinkham and Klapwijk (BTK) [16] for a contact between a normal metal and a superconductor, but extended to include the spin polarization $P$ of the metal. Using the Bogoliubov–de Gennes formalism, BTK calculated the scattering probabilities at a normal metal–superconductor interface introducing a delta function formality, the Fermi distribution. For a contact between a ferromagnet and the superconductor, it is necessary to extend this model bearing in mind that the polarization $P$ of the metal is not zero in that case. The simplest way to include the effects of $P$ is to divide the current into two parts, an un-polarized part, $I_u$, and a completely polarized part, $I_p$.

$$I(V) = 2eSNV_F\int_{-\infty}^{\infty} [f(E-V,T)-f(E,T)][1+A-B]dE$$  \hspace{1cm} (1)

with $S$ the effective cross-sectional area of the contact, $N$ the one-spin density of states at the Fermi energy and $V_F$ the Fermi velocity, $A$ and $B$ are the probabilities for an incident electron with energy $E$ for AR and normal reflection, respectively, and $f(E)$ is the Fermi distribution. For a contact between a ferromagnet and a superconductor, it is necessary to extend this model bearing in mind that the polarization $P$ of the metal is not zero in that case. The simplest way to include the effects of $P$ is to divide the current into two parts, an unpolarized part, $I_u$, and a completely polarized part, $I_p$.

$$I = (1-P)I_u + PI_p$$  \hspace{1cm} (2)

Following Strijkers et al. [9], the bias voltage dependence of the differential conductance can be obtained by calculation of $I_u$ and $I_p$ by numerically solving (1) with the proper set of probabilities $A_u$, $B_u$, $A_p$ and $B_p$ and then calculating the differential conductance $G$ as a function of the bias voltage $V$ at a temperature $T$ by differentiating (1) as a function of the bias voltage.

Fig. 3 displays the differential conductance results $G(V)$ for the Co–W nanocontacts below the critical temperature of the superconducting W nanodeposit, where the conductance values have been normalized to the value of the conductance of the contact in the normal state subtracting the drop at $T_C$. The solid lines are the best fits obtained by using the model described above with the AR and normal reflection probabilities computed in the diffusive regime [17] and letting $Z$, $P$, the spectral broadening and the superconducting gap behave as free parameters. We have assumed the diffusive regime of transport because the mean free path of the Co deposit we have used as magnetic electrode is 1.1 nm. As a consequence, in order to have ballistic nanocontacts the contact size should be smaller than that value, the current density being higher than $1.1 \times 10^8$ A/cm$^2$. It seems unreasonable that the nanocontact could withstand this value of current density without destroying the junction and the diffusive regime is consequently assumed. Taking into account the fits obtained for all the temperatures measured (not all displayed in Fig. 3 for clarity), the values of $Z$ and $P$ are $P = 0.356 \pm 0.006$ and $Z = 0.07 \pm 0.01$ for the first contact, both values being independent of temperature within the error of the least-squares fitting procedure as is shown in the inset of Fig. 3(a). This finding confirms that both free parameters, $Z$ and $P$, are intrinsic parameters of the specific magnetic metal–superconductor nanocontact studied [18]. Also, the spectral broadening is found to be zero for this nanocontact at all the temperatures studied. For the second contact, it is found that $P = 0.356 \pm 0.004$ and $Z = 0.080 \pm 0.005$, these two parameters are also found to be independent of temperature as it can be observed in the inset of Fig. 3(b). To fit the conductance curves of this second nanocontact we need to include, unlike for the first nanocontact for which it is not necessary, a spectral broadening ($\omega/k_B = 0.8$ K) that takes into account all broadening mechanisms, such as thermal effects and interface scattering, indicating that for this nanocontact the interface scattering plays a role as can be observed in Fig. 2(b) because the normal resistance depends slightly on current. One of the reasons why we know that the conduction is metallic instead of tunnelling is that the conductance curves become sharper as temperature decreases unlike the tunnelling ones which become flatter.
Fig. 4. (Color online): $\chi^2$ versus $P_{\text{trial}}$ analysis for the two samples studied at 2.5 K (sample a in Fig. 4a) and sample b in Fig. 4(b). The well-defined minimum observed, at $P_{\text{trial}} \sim 0.38$ for sample a and at $P_{\text{trial}} \sim 0.35$ for sample b, ensures that the spin polarization can be accurately extracted from the fits.

Fig. 5. (Color online): The dots and squares correspond to the superconductor gap values (normalized to the low-temperature value of 0.7 meV) obtained from fits of the differential conductance to the extended BTK model. The line is the temperature dependence of the gap predicted by the BCS theory of s-wave superconductivity.

In order to ensure that the spin polarization can be unambiguously extracted from the fits, we study the convergence and uniqueness of the fits following the analysis protocol proposed by Bugoslavsky et al. [19] that guarantees an accurate interpretation of the data. The fitting process consists in using an optimization algorithm ($\chi^2$) with the target function being the normalized sum of the squared deviations between the fitted data and the trial function that is computed in the diffusive regime of the generalized BTK model. After fixing the value of the polarization, we run the optimization in ($Z$, spectral broadening, superconducting gap) and obtain the value of the target function at the minimum. The result of the application of this procedure is shown in Fig. 4, where we have used as an example the conductance curve measured at 2.5 K for the first nanocontact. The presence of a well-defined minimum corresponding to $P$ in the range between 0.35 and 0.39 confirms the value of the spin polarization obtained in the fits of the conductance curves.

The high quality of the fits allows a detailed analysis of the temperature dependence of the superconducting gap of the FIBID-W nanodeposit. Whereas $P$ and $Z$ remain constant with temperature, the superconducting gap value extracted from the fits is expected to show strong temperature dependence and eventually vanish at $T_c$. As can be seen in Fig. 5, the superconducting gap value for both contacts follows the standard BCS dependence using the zero-temperature value of 0.7 meV and critical temperature about 5 K. A very similar value and temperature dependence of this gap has been observed by Scanning Tunnelling Spectroscopy (STM) in the previous work [6]. Very similar gap values are obtained from fits in all the nanocontacts studied, which is in good agreement with the good stability and homogeneity of the superconducting gap of this material in ambient conditions as observed previously [6].

We would like to emphasize that in the fits of our nanocontacts the electrode resistance was considered but found to be negligible. This gives much more reliability to the fits and indeed is an indication of good contacts. Besides, in some of our nanocontacts we have found the spectral broadening factor to be zero, unlike normally required with other growth techniques, thus avoiding another factor introducing uncertainty. The confirmation of the quality of our fits is that we obtain a superconducting gap value similar to that one determined with STM measurements. Other techniques for Andreev Reflection measurements very rarely produce such good agreement of the superconducting gap.

These results stress the relevance of two novel materials created with focused electron/ion beam techniques. FEBID-Co has been recently found to exhibit potential applications as a magnetic material [3,4] and the present work reveals that it shows full functionality also for applications in Spintronics. Its large spin polarization ($P \sim 0.35$), comparable to Co thin films grown with sputtering or evaporation techniques [18], is very promising for spin injection in semiconductor materials, for integration as an electrode in magnetic tunnel junctions, for studies of ballistic anisotropic magnetoresistance, etc. The present results also indicate that FEBID-W is, from the point of view of its transport properties, a stable and homogeneous superconductor showing good BCS behaviour at the nanoscale. These features are required for AR studies as the one shown here. This superconducting material is potentially usable for AR nanocontacts in combination not only with FEBID/FIBID materials but also with materials grown with standard techniques such as sputtering or evaporation.

4. Conclusions

In summary, we have presented an innovative method to create ferromagnetic-superconductor nanocontacts by using focused electron/ion beams and in situ control of the nanocontact resistance during growth. This method has been applied to the measurement of current-in-plane Andreev Reflection phenomena between a ferromagnetic FEBID-Co nanodeposit and a superconducting FIBID-W nanodeposit. The conductance measurements in these nanocontacts have produced clean results, showing evidence for the effect of the spin imbalance of the ferromagnet in the AR. Below the $T_c$ of the superconductor, the bias voltage dependence of the differential conductance can be nicely fitted using the BTK model including spin-polarization effects. The spin polarization of the FEBID-Co nanodeposit obtained from fittings is about 35%, which confirms that the FEBID-Co nanodeposit exhibits suitable properties for its implementation in Spintronics and other magnetoelectronic devices down to nanometric size. The obtained value of the superconducting gap of the W nanodeposits found at the contact region implies that W nanodeposits are very promising for applications in Andreev Reflection studies as well as mesoscopic superconductivity.

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