Magnetotransport properties of iron microwires fabricated by focused electron beam induced autocatalytic growth

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Abstract

We have prepared iron microwires in a combination of focused electron beam induced deposition and autocatalytic growth from the iron pentacarbonyl, Fe(CO)$_5$, precursor gas under ultra-high vacuum conditions. The electrical transport properties of the microwires were investigated and it was found that the temperature dependence of the longitudinal resistivity ($\rho_{xx}$) shows a typical metallic behaviour with a room temperature value of about 88 $\mu\Omega$ cm. In order to investigate the magnetotransport properties we have measured the isothermal Hall-resistivity in the range between 4.2 and 260 K. From these measurements, positive values for the ordinary and the anomalous Hall coefficients were derived. The relation between anomalous Hall resistivity ($\rho_{AN}$) and longitudinal resistivity is quadratic, $\rho_{AN} \sim \rho_{xx}^2$, revealing an intrinsic origin of the anomalous Hall effect. Finally, at low temperature in the transversal geometry a negative magnetoresistance of about 0.2% was measured.

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

1. Introduction

The ability to control matter down to the nanometre scale is basic for the development of new artificial materials and devices in nanotechnology. Focused electron beam induced deposition (FEBID) is an emerging direct writing technique used to fabricate samples down to the nanometre scale [1–3]. Within this technique the fabrication of the samples takes place using the adsorbed molecules of a precursor gas injected in a scanning electron microscope (SEM): by interaction with the electron beam of the SEM the adsorbed molecules dissociate into a volatile component, eventually pumped away and into a non-volatile one, which constitutes the sample, also called deposit. By rastering with the electron beam over the area of interest, structures with the desired shape can be written. The availability of a large number of precursors [1, 2] enables the fabrication of structures with variable chemical composition. The spectrum of target materials ranges from insulators to semiconductors, to metals, to superconductors [1]. This is combined with the excellent lateral resolution intrinsic to the FEBID process and thus allows for the fabrication of artificial and tunable solid state model systems [4]. Magnetic materials mainly prepared from Co$_2$(CO)$_8$ and Fe(CO)$_5$ are of particular relevance in this regard [5–7]. Magnetic nanostructures have been fabricated and proposed as high resolution magnetic tips [8], domain wall based memory devices [9] and magnetic sensors [10, 11].

Despite the growing interest for magnetic materials fabricated by FEBID, only very few studies have been performed to investigate their electrical [5, 12] and magnetotransport properties [10, 11, 15]. This is due to the difficulty of obtaining pure materials, which are often required for applications. Recently, much effort has been devoted to improving the metal content of FEBID materials [16], which often consists of metal clusters embedded in a carbonaceous matrix [5, 8, 17]. One strategy to obtain higher metal content deposits is to optimize the deposition parameters [5, 6, 12–15]. Furthermore, various purification techniques can be used, as recently reviewed by
Botman et al [16]. These include the deposition on hot substrates [18], post-growth annealing [19] also combined with the dosage of a reactive gas [20], post-growth electron irradiation [21] and the deposition in mixed gas atmosphere [22]. Such techniques have been applied for FEBID fabrication of iron-based nanocomposites prepared from Fe(CO)5 (post deposition heating) and Fe2(CO)9 (additional dosage of water during deposition), and yielded metal contents as high as 70% and 75% [12, 17], respectively. A further reduction of the contamination level in deposits from Fe(CO)5 has been achieved by performing FEBID under ultra-high vacuum (UHV) conditions [23]. With this approach the level of carbon and oxygen contaminations is considerably reduced, leading to deposits with a metal content significantly higher than 90% [23]. Working under UHV also allows for a novel two-step protocol to generate clean iron structures, namely focused electron beam induced surface activation (FEBISA) [24]. In an exemplary study, a SiOx sample is in a first processing step locally activated by the irradiation with a focused electron beam. In a second step the corresponding activated patterns are exposed to the precursor Fe(CO)5, which is then catalytically decomposed at the electron irradiated positions resulting in pure iron deposits. These iron deposits continue to grow autocatalytically as long as the precursor is supplied. Remarkably, this process proceeds already at room temperature in UHV. The process is even more effective, if the first step is a true FEBID step, i.e. if the precursor gas is already present during irradiation with electrons. Herein, we report the electrical and the magnetotransport properties of iron microstructures grown using this latter approach.

2. Experimental details

We have fabricated iron microwires in a two-chamber UHV system (Omicron Multiscan Lab) with a base pressure below 2 × 10−10 mbar. The chamber houses a UHV-compatible SEM with a resolution better than 3 nm at a beam current of 400 pA and acceleration voltage of 15 kV. Composition analysis can be performed in situ by local Auger electron spectroscopy (AES) with a resolution better than 10 nm employing a hemispherical electron energy analyser. As a precursor we used iron pentacarbonyl with a purity of 99.5% from the Sigma-Aldrich company. The dosage of the precursor gas was performed through a dosing nozzle with an inner diameter of 3 mm, positioned approximately 12 mm away from the sample surface leading to an estimated local pressure at the surface of 9 × 10−6 mbar, which corresponds to an enhancement by a factor of 30 as compared with the background pressure.

The transport measurements were performed several days after the sample preparation, with the samples stored under ambient conditions for some days. The measurements were performed in a variable-temperature insert mounted in a 4He cryostat equipped with a 9T superconducting solenoid. The temperature ranged between 1.8 and 265 K. A current of 10 μA, for a resulting current density of about 1.25 × 108 A m−2, was applied to the sample using a Keithley Sourcemeter 2400. In order to measure the voltage during the four-probe resistance and the Hall measurements we employed an Agilent 34420A nanovoltmeter.

3. Results

3.1. Fabrication of the microwires

In figure 1(a) (double-cross shaped) iron microwire structure generated by FEBID and successive autocatalytic growth is depicted. This iron microwire was prepared at room temperature on a Si(p-doped)/SiOx(300 nm) substrate; the electron beam current was 400 pA at an energy of 15 keV and the accumulated line dose was 1.9 μC cm−1. During electron irradiation, the background pressure of Fe(CO)5 was 3 × 10−7 mbar. After irradiation with electrons, the pressure was kept at the same level for additional 210 min to allow for continued autocatalytic growth at the deposited iron nuclei.

The width of the iron lines is roughly 4 μm, which is expected from the simulated exit area of backscattered electrons on SiO2. The length of the vertical and the horizontal irradiated lines was 45 μm (i.e. significantly longer than required) in order to bridge the gaps between the contact spots and to ensure a sufficient electrical contact in all cases. The original path of the electron beam can be recognized as narrow dark lines visible on the electrodes (indicated in figure 1 by an arrow at the lower right gold contact). These narrow lines originate from the conventional FEBID process on the gold contact. A comparison with the much wider microlines on the SiO2 substrate shows that the autocatalytic growth is much less efficient on the Au contact. This is either due to the much
The behaviour is that of a metal. Below 12 K the resistivity slightly increases, see the inset.

The sensitivity to the nature of the local substrate is also evident when inspecting the gap between the Au contact and the granular Fe wire, as depicted in the zoomed out figure 1. Local Auger measurements, as can be compared in [20], reveal the presence of chromium in the region of the gap stemming from the buffer layer, effectively inhibiting the growth of a sufficiently thick Fe wire via autocatalytic effects in this region.

### 3.2. Magnetotransport measurements

In figure 2 we plot the temperature dependence of the longitudinal resistivity for a typical microwire. The behaviour is that of a metal with a resistivity of 84 $\mu$Ω cm at 260 K, about a factor 8 higher than the value for pure bulk iron. An increase in the resistivity by reducing the thickness is expected from the surface scattering theory of Fuchs–Sondheimer [25]. The theory predicts for a 30 nm thick sample like our wire, a resistivity of approximately 40 $\mu$Ω cm at room temperature.

The difference between this value and the one obtained in our measurement can be explained with the presence of further scattering sources such as defects, grain boundaries or the presence of carbon and oxygen mainly at the surface of the iron crystallites. At low temperature, see the inset in figure 2, the resistivity shows a minimum; a similar effect was also observed in epitaxially grown Fe films [26–28] and was explained in terms of weak electron-localization and/or electron-interaction effects [28].

In figure 3 we display the result of a Hall resistivity measurement performed at 12 K. The Hall resistivity, $\rho_{xy}$, is given by the sum of the ordinary and the anomalous Hall effects, $\rho_{xy} = \rho_{OR} + \rho_{AN}$, with $\rho_{OR} = R_0 B$ and $\rho_{AN} = R_s \mu_0 M$, where $B$ is the magnetic induction, $M$ the magnetization of the wire, $R_0$ and $R_s$ the ordinary and the anomalous Hall coefficients, respectively. The demagnetizing factor of the microwires used in our investigations is $N = 0.9$ [29]. Therefore, the Hall resistivity becomes $\rho_{xy} = R_0 \mu_0 H + R_s \mu_0 M$, $H$ being the applied magnetic field, and the Hall coefficients can be extracted directly from the plot of figure 3. For the ordinary Hall coefficient we find $R_0 = 7.0 \times 10^{13} \mu$Ω cm T$^{-1}$, which can be compared with the bulk value of polycrystalline iron films, $R_0 = 2.3 \times 10^{13} \mu$Ω cm T$^{-1}$ [30], and to that of epitaxially grown thin films, $R_0 = 5 \times 10^{13} \mu$Ω cm T$^{-1}$ [28], measured at room temperature. From figure 3 we extract the value of the saturation magnetization to be $M_s = 1.47$ T, which is smaller than 2.1 T of bulk Fe. The trend is similar to the one measured in sputtered polycrystalline Fe thin films where the saturation magnetization decreases with the thickness [31].

In the inset of figure 3 we show the magnetoresistance measured for a magnetic field normal to the surface of the microwire. The magnetoresistance is negative and decreases with increasing magnetic field because the scattering probability decreases as more magnetic moments align to the magnetic field. For magnetic fields higher than the saturation field, the magnetoresistance varies as $H^2$. By increasing or decreasing the magnetic field from zero towards saturation, the magnetoresistance first slightly increases reaching a maximum at around 0.2 T and then it drops at about 0.5 T. This feature generates a small hysteresis, which shows the presence of two metastable states involved during the magnetization process.

In figure 4a we report the results of the Hall resistivity measurements performed between 4.2 and 260 K. From the analysis of the isothermal we find that, both, the ordinary and the anomalous Hall coefficients are positive in the temperature range explored.
Figure 4. (a) Hall resistivity versus applied magnetic field at various temperatures. (b) Anomalous Hall resistivity, \( \rho_{AN} \), versus longitudinal resistivity, \( \rho_{xx} \). The red line is the quadratic fit to the data: \( \rho_{AN} \sim \rho_{xx}^2 \). (c) \( \rho_{AN} \) versus temperature. (d) Ordinary Hall coefficient \( R_0 \) versus temperature. (e) Anomalous Hall conductivity \( \sigma_{xy} \) versus temperature.

range investigated (see figures 4(d) and (c)). The ordinary Hall coefficient of our microwires is quite temperature independent, see figure 4(d). Note that we attribute the deviations at 159, 206 and 260 K to the difficulty of keeping the temperature constant during the measurement which complicated the appropriate subtraction of spurious longitudinal contributions in the Hall voltage. The temperature independence of \( R_0 \) is also consistent with the data of [30]. The anomalous Hall resistivity increases with the square of the longitudinal resistivity, \( \rho_{AN} \propto \rho_{xx}^2 \) (figure 4(b)), which excludes skew scattering as mechanism as a possible reason for the anomalous Hall effect. In figure 4(e) we plot the temperature dependence of the anomalous Hall conductivity, defined as \( \sigma_{yx} \simeq \rho_{xy}/\rho_{xx}^2 \). The values of the conductivity ranges from 119 to 158 \( \Omega^{-1} \) cm\(^{-1} \); for a comparison with the literature see section 4.

4. Discussion

One major problem of deposits prepared by FEBID is the formation of an unwanted additional deposit around the chosen deposition area. The lateral size of this co-deposit (or halo), whose existence has been reported for samples grown from a variety of precursors [1, 5, 10, 32], can reach some micrometres depending on the material and on the electron beam parameters [10]. The halo is due to backscattered electrons (BSEs) and the secondary electrons (SEs) generated from them [1, 2, 10, 32]. The presence of the halo is detrimental because it can affect the magnetic, the electrical and the magnetotransport measurements performed on the deposits [10, 33, 34]. The influence on the magnetic properties depends strongly on the precursor used. For example, it has been reported that nanowires grown from the \( \text{Co}_2(\text{CO})_8 \) precursor gas have a quite extended co-deposit area [9, 10], with only the central part of the sample being ferromagnetic, indicating an inhomogeneous chemical composition [9]. With the FEBID-based approach used here, the efficient autocatalytic growth after initial electron irradiation leads to the formation of an Fe layer with quite uniform thickness in the directly irradiated region plus in the region where a sufficient number of BSEs exit the surface again. This is due to the fact that the majority of precursor molecules impinging on the surface decompose autocatalytically in the close vicinity of their impact point. As a result, the autocatalytic growth of clean iron proceeds in the whole area usually affected by the proximity effects. In this way the generation of chemically homogeneous iron microwires is realized.

The deposited iron microwires display metallic and ferromagnetic behaviour. At room temperature the resistivity is about 88 \( \mu \Omega \) cm, which is the lowest, to our knowledge, measured for iron deposits from Fe(\text{CO})\(_5 \) [6, 16]. Furthermore, this resistivity is of the same order of magnitude of the one measured for cobalt nanowires [15], which is
the lowest for FEBID deposits from carbonyl precursors in general. This is remarkable since the structures were exposed to ambient conditions for some days and are expected to be partly oxidized. For a comparison with samples prepared by IBID, which are often used because of their highly conduction behaviour, note that tungsten deposits from W(CO)₆ have a typical resistivity of ρ = 200 μΩ cm. Finally, it has to be mentioned that comparable resistivity values to the one obtained in this work can be obtained using carbon free precursors gases [16, 35].

In general, the results of the Hall resistivity measurements and the magnetoresistance measurements performed in our work are in agreement with the investigations on iron thin films reported in the literature. In particular, we find that the anomalous resistivity has a quadratic dependence with the longitudinal resistivity. This dependence rules out skew scattering as the mechanism at the origin of the AHE (linearity), but not the side jump effect (quadratic). It remains to be understood if the effect is intrinsic (due to the band structure) or extrinsic (side jump). To answer this question we have to consider the anomalous Hall conductivity (σₓᵧ ≈ ρₓᵧ/ρₓₓ²). According to a recent unified theory valid for multiband ferromagnetic metals with dilute impurities, there exists a crossover between the intrinsic to the extrinsic anomalous Hall effect as a function of the longitudinal conductivity and the anomalous conductivity [36]. In the limit of highly conductive metals the anomalous conductivity is proportional to the longitudinal conductivity (σₓᵧ ∝ σₓₓ). In this region the AHE is extrinsic and its origin is the skew scattering effect. The intrinsic-to-extrinsic crossover takes place for lower conductivities (σₓₓ = 10⁵−10⁶ Ω⁻¹ cm⁻¹), where the anomalous conductivity is constant with typical values of σₓᵧ = 10⁵−10⁶ Ω⁻¹ cm⁻¹ [26, 37]. The values present in the literature for iron whiskers (10³2 Ω⁻¹ cm⁻¹) [38] and 1 μm iron thin films (1000 Ω⁻¹ cm⁻¹) [37] belong to this region (moderately dirty metals). Finally, for σₓₓ < 10⁴ Ω⁻¹ cm⁻¹ (dirty metals) σₓᵧ ∝ σₓₓ¹/₂, which is found in the hopping transport regime [37]. The anomalous conductivity in our experiment is between 119 and 159 Ω⁻¹ cm⁻¹, see figure 4(e). Correspondingly the longitudinal conductivity is in between 1.65 × 10⁴ and 1.21 × 10⁵ Ω⁻¹ cm⁻¹. With respect to [26, 36] our samples behave like moderately dirty metals where the anomalous effect is intrinsic. It is interesting to note that the values of the conductivity measured in our experiment are in the same range as those reported recently for 2.0−2.5 nm thick Fe thin film epitaxially grown on MgO (0 0 1) [26].

5. Conclusions

We have prepared microwires using a novel fabrication technique, which mainly relies on the autocatalytic growth of clean iron structures from Fe(CO)₅. We have investigated the electrical- and magnetotransport properties of the microwires by means of Hall resistivity and magnetoresistance measurements. It turns out that the microwires are metallic with a resistivity of about 88 μΩ cm, which is among the lowest reported for samples prepared by FEBID from carbonyl precursors. The magnetotransport behaviour of the microwires are comparable to those of iron thin films reported in the literature. In particular, we find that the magnetization saturation is Mₛ = 1.47 T and the ordinary and anomalous Hall coefficients are positive in the temperature range investigated. The anomalous Hall resistivity scales quadratically with the longitudinal resistivity, which points to an intrinsic origin of the anomalous Hall effect. This conclusion is supported by the analysis of a recent unified theory for multiband ferromagnetic metals.

Finally, it should be mentioned that with the FEBID-based approach used here the fabrication of pure iron line structures with line widths well below 100 nm is possible [24]. Therefore, it appears feasible to improve the linewidth of the iron structures to the nanoscale, which is required in spintronic and magnetorecording technology, and which might make focused electron beam induced processing the technique of choice to prepare sub-100 nm periodic nanostructures used to study dipolar coupling effects [39].

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