Review of magnetic nanostructures grown by Focused Electron Beam Induced Deposition (FEBID)

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Abstract:

We review the current status of the use of focused electron beam induced deposition (FEBID) for the growth of magnetic nanostructures. This technique relies on the local dissociation of a precursor gas by means of an electron beam. The most promising results have been obtained using the Co₂(CO)₈ precursor, where the Co content in the grown nanodeposited material can be tailored up to more than 95%. Functional behaviour of these Co nanodeposits has been observed in applications such as arrays of magnetic dots for information storage and catalytic growth, magnetic tips for scanning probe microscopes, nano-Hall sensors for bead detection, nano-actuated magnetomechanical systems and
nanowires for domain-wall manipulation. The review also covers interesting results observed in Fe-based and alloyed nanodeposits. Advantages and disadvantages of FEBID for the growth of magnetic nanostructures are discussed in the article as well as possible future directions in this field.

**Keywords:** nanomagnetism, beam induced deposition, FEBID, magnetic nanostructures, nanolithography

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6. Summary and outlook
1. Introduction

1.1 Magnetic nanostructures

The field of nanomagnetism is nowadays one of the most active topics in condensed-matter and materials-science research, offering many opportunities (1). Successful applications of magnetic nanostructures have been found for instance in high-density information storage and magnetic sensing (2). One of the key events in this development was the discovery of giant magnetoresistance in magnetic nanostructures (3, 4), awarded with the Nobel prize in Physics in 2007 (5, 6), which opened the field of Spintronics. The magnetoresistance effect is applied for the sensitive detection of small stray fields produced by tiny magnetic information bits or magnetic beads and in non-volatile magnetic memories (7).

Another relevant application of magnetic nanostructures has been proposed, though not yet realized, based on the manipulation of domain walls in magnetic nanowires. Thus, the racetrack memory proposed by Parkin et al. (8) and the magnetic logic proposed by Allwood et al. (9) are promising applications based on the fast movement (in the scale of the nanosecond) of magnetic domain walls triggered by magnetic fields or current pulses. Intense research is developed at present aiming to produce domain-wall manipulation by spin-torque effects via injection of a spin-polarized current (10). Furthermore, this spin-torque mechanism can bring about the magnetization precession in certain conditions, producing the emission of radio-frequency waves with application as RF oscillators in telecommunication devices (11).

Another emergent field is that of magnetic biosensing, where magnetic nanoparticles tag biorecognition events and are detected by magnetic sensors such as giant or tunnel magnetoresistance sensors (12) or planar Hall sensors (13). From the detected signal, it is possible to obtain a quantitative determination of the concentration of a targeted analyte.
(virus, hormone, enzyme, DNA strand, etc.) (14). Also in life-sciences applications, arrays of highly-sensitive magnetic sensors are being developed for detection of the heart and brain activity (15).

Most working devices in the field of magnetic nanostructures rely for their creation on a top-down approach. This implies the use of thin-film growth techniques and/or micro- and nano-lithography techniques (16, 17). The methods of choice should address crucial aspects such as resolution, roughness, shape, materials involved, cost, etc. For the growth of magnetic films by physical techniques, sputtering is usually preferred, even though thermal or electron-beam evaporation, molecular beam epitaxy and pulsed laser deposition are also frequently used (18). With respect to the lithography techniques used, optical lithography is normally preferred down to the micron scale and electron-beam lithography below the micron scale (17). Optical lithography relies on UV-sensitive light resists and is indeed able to reach resolution better than 22 nm in the state-of-the-art steppers used in the Semiconductor industry, but their huge cost impedes the use at the laboratory level. Electron beam lithography relies on electron-sensitive resists spun onto the sample and submitted to electron beam irradiation inside a Scanning Electron Microscope (SEM). Ion milling or lift-off processes permit to define nanostructures in the range of 100 nm and in some favourable cases down to 10 nm. However, some of the involved steps are critical and the final sample features can be far from ideal and affect the device functionality (19). In order to circumvent the use of resists and multiple-step lithography processes, direct patterning by focused-ion-beam is not rare, but this technique can strongly modify the magnetic properties of the materials, restricting its use (20). Nanoimprinting (and related techniques) has the potential to produce high throughput, thus being recommended for industrial applications, but the mold has to be grown with another lithography technique.
It is in this context that Focused Electron Beam Induced Deposition (FEBID) of magnetic materials is becoming a promising route for the direct growth of magnetic nanostructures in a single step. As will be developed along the next sections, this technique does not involve the use of resists, etching or lift-off processes, whereas maintaining the high lateral resolution down to the nanometric scale and being able to grow materials with appropriate magnetic properties.

1.2 FEBID technique

FEBID can be considered a beam-assisted Chemical Vapour Deposition (CVD) technique. But, in this case, the energy required to dissociate the precursor molecules is not thermally provided, as occurs in CVD, but by electron beam irradiation, whilst the substrate is generally maintained at room temperature. The precursor molecules are delivered onto the substrate surface by means of a nearby gas-injection system and the focused beam is scanned on the substrate, creating a deposit with the same shape of the beam scanning. Figure 1 illustrates this process.

![Figure 1](image-url)

**Figure 1.** Sketch of Focused Electron Beam Induced Deposition (FEBID). This is an electron-assisted chemical growth technique giving rise to high-resolution patterning in a single step. The precursor molecules are locally dissociated by a Scanning Electron Microscope.
A few review articles (21-24) and books (25) on the FEBID technique are available and the reader is referred to such references for deeper understanding of this technique. An important aspect to consider is that the energy of the bonds in the precursor molecules is in the range of a few eV, implying that their dissociation is generally governed by the secondary electrons produced in the substrate and the growing structure (26-28). This phenomenon is important for the understanding of the achievable lateral resolution and the appearance of a thin halo grown around the main deposit, as will be shown in the following sections of this review.

We note that, prior to the present review article, other publications have partially addressed the specific topic of magnetic deposits with a relative broad perspective (29, 30). However, such publications are not comprehensive review articles of the topic. Here, we aim to include references to all published work so far on the topic of magnetic deposits by FEBID technique.

1.3 Gas precursors for magnetic nanodeposits

The precursors used so far for magnetic nanodeposits by FEBID are collected in Table I together with all the references that have reported their experimental use. The number of these precursors is limited to a few but the number of references has strongly increased during last years. It should be mentioned that practical issues limit the availability of precursors for FEBID, as recently discussed by J. J. L. Mulders (31). For the sake of completeness, we include in Table I references where these magnetic precursors were also used for Focused Ion Beam Induced Deposition (FIBID), as well as for the growth of magnetic alloys with two precursors simultaneously injected. In the case of cobalt, Co$_2$(CO)$_8$ is by far the precursor gas commonly used (29, 30, 32-93). The advantage of this precursor is its low spontaneous dissociation temperature, around 100°C (94). This indicates
relative low bonding energies in this molecule, which is favorable for its dissociation by 
electron irradiation in order to attain high metallic content. In fact, in 2002 the growth of Co 
tips on AFM cantilevers by FEBID using that precursor was reported and magnetic imaging 
of a hard disk was realized (34-36). The reported Co content reached 80% (34, 41), and that 
large value was mainly ascribed to heating effects when using high beam current. Recent 
studies enlarged the expectations of this precursor, as 95% Co content was reported when 
the growth was performed under high electron beam current and using a field-emission 
electron gun (42). Heating effects were definitely found to be important for the degree of 
precursor dissociation (46, 57), although other effects are competing (45, 60) making 
difficult to disentangle the role of all contributing effects. The good news is that using low 
electron beam currents it is also possible to obtain deposits at room temperature with Co 
content greater than 90% (60). Another cobalt-based precursor, Co(CO)$_3$NO, has been 
studied experimentally (34, 57, 95-100) but does not seem advantageous with respect to 
Co$_2$(CO)$_8$ regarding the achievable Co content.

In the case of Fe-based nanodeposits, several carbonyl-based precursors have been 
used such as Fe(CO)$_5$, Fe$_3$(CO)$_{12}$, Fe$_2$(CO)$_9$ and Fe(C$_5$H$_5$)$_2$. In 1987, Kunz and Mayer 
reported the growth of 150 nm-wide iron wires by FEBID using the Fe(CO)$_5$ precursor (101, 
102). The composition of the nanodeposits was not shown in that work. The spontaneous 
thermal decomposition of Fe(CO)$_5$ on Si was found at 250 °C, and strong catalytic effects 
were reported in that work. Only in 2004, Fe deposits by FEBID were again reported by 
Shimojo et al., who described the formation of alpha-Fe and some carbides using the 
Fe(CO)$_5$ precursor and performing an annealing process (103). Since that moment, literature 
on Fe-based nanostructures is more abundant and, for example, Zhang et al. reported the 
growth of alpha-Fe nanocrystals on carbon grids (104). In 2005, Bruk et al. reported the use 
of Fe$_3$(CO)$_{12}$ (105), whereas in 2006 Takeguchi et al. reported the use of Fe(C$_5$H$_5$)$_2$ (106)
and Lavrijsen et al. reported the use of Fe$_2$(CO)$_9$ in 2011 (107). Working under high-vacuum conditions, standard for SEM chambers, the Fe content using all the available Fe precursors seems limited to about 80% before annealing or purification processes (108) although the use of ultra-high-vacuum conditions has allowed Luckasczyk et al. to grow Fe nanostructures on Si substrates using the Fe(CO)$_5$ precursor with Fe content above 95% (109).

Recently, a heteronuclear precursor, HFeCo$_3$(CO)$_{12}$, has been used with total Fe plus Co content around 80% (110). For Ni deposition, Ni(C$_5$H$_4$CH$_3$)$_2$ and Ni(PF$_3$)$_4$ have been used for the growth of Ni-based deposits whereas Ni(CO)$_4$ has been discarded for its toxicity (111, 112).
Table I: References reporting magnetic-based nano-deposits grown by FEBID, classified by the precursor used and the year of publication. A few existing examples where the growth was carried out by FIBID have been included as well, and marked with an asterisk.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>References</th>
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<tbody>
<tr>
<td>Co₂(CO)₈</td>
<td>2002: (32)<em>, (33)</em>, (34), (35), (36); 2003: (37)<em>; 2004: (38)</em>, (39); 2005: (113)<em>, (40), (41); 2007: (114)</em>; 2009: (42), (43), (44); 2010: (45), (46), (115), (47), (48); 2011: (49), (50), (51), (52), (53), (54), (55), (56), (57), (58), (59), (60); 2012: (61), (62), (63), (64), (65), (93); 2013: (66), (67), (68), (69), (70), (71), (72), (73), (74)*; 2014: (75), (76), (29), (77), (78), (79), (80), (81), (82), (83); 2015: (84), (85), (86), (87), (88), (89), (90); 2016: (91), (92)</td>
</tr>
<tr>
<td>Co(CO)₅NO</td>
<td>2002: (34); 2009: (100); 2011: (95), (96), (57); 2013: (98), (97); 2014: (99)</td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>1987: (101), (102); 2004: (103); 2005: (116), (117), (118), (119), (120), (121); 2006: (122), (106), (123), (104), (124), (125), (126); 2007: (127), (128), (129); 2008: (130), (109); 2009: (131); 2011: (132), (133); 2013: (134), (135); 2014: (136), (137), (138), (139); 2015: (140)</td>
</tr>
<tr>
<td>Fe₃(CO)₁₂</td>
<td>2005: (105)</td>
</tr>
<tr>
<td>Fe(C₅H₅)₂</td>
<td>2005: (113)<em>; 2006: (123); 2007: (141)</em></td>
</tr>
<tr>
<td>Fe₃(CO)₉</td>
<td>2011: (107); 2012: (142); 2014: (143); 2015: (144)</td>
</tr>
<tr>
<td>HFeCo₃(CO)₁₂</td>
<td>2015: (110)</td>
</tr>
<tr>
<td>Ni(C₅H₅CH₃)₂</td>
<td>2007: (111); 2016: (112)</td>
</tr>
<tr>
<td>Ni(PF₃)₄</td>
<td>2007: (111)</td>
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2. Cobalt nanostructures by FEBID

2.1 Composition and microstructure

The main parameters determining the Co content in Co₂(CO)₈ will be discussed hereafter. The first reports, dating back to 2002, already stressed the influence of the electron beam current in the Co content (34). The use of high beam currents (µA range) permitted to reach Co contents up to 80%, but killing the lateral resolution due to the corresponding micrometric beam diameter (41). Substrate heating up to 58°C at 3 µA beam current was put
forward to explain such dependence. The microstructure of the deposits was observed to be composed of small (few nm) polycrystalline Co grains immersed in a carbonaceous matrix (34, 41). Fernández-Pacheco et al. found that Co content up to 95% was feasible using a field-emission electron gun, as shown in figure 2(a). At a low beam current of 0.1 nA, the Co content was found to be 80% but rose to 95% when the beam current became greater than 1 nA (42). Beam currents in the nA range impose limitations in lateral resolution. Reaching resolutions below 100 nm is in general not possible with such current values. However, by means of a heater, Córdoba et al. showed that it is possible to obtain high Co content (above 90%) if the substrate is heated above 100 °C even for beam currents as low as 44 pA, as shown in figure 2(b) (46). Substrate heating was expected to favor precursor dissociation, as later confirmed by Mulders et al. (57). This is in good agreement with the expected low dissociation energy of bonds in the Co$_2$(CO)$_8$ molecule, which is thermally decomposed around that temperature (46, 57, 94).
Figure 2. (a) Atomic percentage of Co, C and O as a function of the electron-beam current in Co nanodeposits grown at 10 kV using Co$_2$(CO)$_8$ as the precursor gas. Reprinted with permission from A Fernández-Pacheco et al 2009 J. Phys. D: Appl. Phys. 42 055005. Copyright (2009). DOI: 10.1088/0022-3727/42/5/055005; deteresa@unizar.es. (b) Atomic percentage of Co and C as a function of the substrate temperature in Co nanopillars grown at 30 keV, 44 pA and 5 keV, 25 pA. Reprinted from Microelectronic Engineering, 87, R. Córdoba et al., High-purity cobalt nanostructures grown by focused-electron-beam-induced deposition at low current, 1550–1553, Copyright (2010), with permission from Elsevier. rocorcas@unizar.es.
Despite the importance of thermal effects, there are other relevant growth parameters in FEBID impacting the final metal content of the deposits. For example, Bernau et al. found that residual hydrocarbon molecules in the chamber can contribute to the deposit composition but can be controlled by variations in the electron dwell time (45). As an example, figure 3 shows experiments in which the use of short dwell time gives rise to significant hydrocarbon decomposition compared to carbonyl decomposition, leading to only 20% Co content in the deposit. However, there is lack of enough hydrocarbon replenishment when the dwell time is long, which increases the Co content three times (45).

![Figure 3](image_url)  
**Figure 3.** Atomic percentage of Co, C and O versus dwell time $t_d$ (25 keV, 1 nA, 10 ms refresh time) in Co-C deposits grown in the presence of two adsorbates $[\text{Co}_2(\text{CO})_8]$ and hydrocarbon. *Reprinted from L. Bernau et al., Angewandte Chemie, 49, 8880–8884, Copyright (2010), with permission from WILEY. Ivo.Utke@empa.ch*

Additionally, Serrano-Ramón et al. have shown that, besides the dwell time, the precursor flux is a tuning parameter of the metal content (60). As shown in figure 4, there is an optimum precursor flux that maximizes the Co content. The explanation is that at low precursor gas flux (precursor-limited regime) there is a significant amount of chamber
residual molecules that are decomposed compared to the number of Co molecules. Some atoms of such residual molecules become incorporated in the deposit. At high precursor flux, the amount of Co molecules outcomes the residual ones, and the probability of having more Co in the deposit increases. However, in this electron-limited regime, some bonds of the Co molecule cannot be dissociated, leading to C and O atoms in the deposit with origin in the Co$_2$(CO)$_8$ molecule itself. Thus, an optimum value of the precursor flux, at the crossover between the precursor-limited and electron-limited regimes is found. In that situation, even for low beam currents such as 21 pA (allowing lateral resolution of 30 nm) Co content greater than 90% is found (60). Similarly, Wachter et al. have reported the advantage of Co growth at the crossover between the precursor-limited and electron-limited regimes (82). Summarizing, thermal effects are not necessary to achieve high Co content as thought in the first studies, which makes possible to obtain simultaneously high Co content and lateral resolution.

![Figure 4. Atomic percentage of Co, C and O as a function of the Co$_2$(CO)$_8$ precursor flux in nanodeposits grown at 3 kV and 21 pA. An SEM image of the typical cobalt squares grown](image)
is shown in the inset. The relative change of precursor flux is here defined by the expression: Precursor flux (%) = 100 x (P_{process} - P_{base})/P_{base}. Reprinted with permission from ACS Nano, 2011, 5 (10), pp 7781–7787. Copyright (2011) American Chemical. deteresa@unizar.es.

In case that as-grown deposits present low Co content, it is possible to apply a post-growth purification process to enhance the metal content. Begun et al. have investigated several treatments to find that the most effective one is the combination of 300ºC, H₂ exposure and electron irradiation, which produces virtually-pure Co deposits from the surface down to a depth of 20 nm (84).

Regarding the microstructure of the Co deposits, detailed Transmission Electron Microscopy (TEM) studies on low-Co-content and high-Co-content deposits have shown their polycrystalline nature (50). The difference between both types of deposits is that low-Co-content ones present isolated 2-3 nm Co grains immersed in a carbonaceous matrix, whereas high-Co-content ones present a compact metal structure with 5-7 nm Co grains. Electron diffraction indicates that the crystallographic structure of such grains is a mixture of hexagonal-close-packed (hcp) and face-centered-cubic (fcc) ones (50). Gazzadi and Frabboni have recently shown that the application of large electrical current through Co nanowires produces structural changes, modifying the relative amount of hcp and fcc grains (86).

As mentioned before, Co(CO)₃NO precursor molecule has also been studied as an alternative to Co₂(CO)₈ for Co deposition. Lau et al. found that high-current deposition from this precursor results in autocatalytic growth due to temperature rise (34). Gazzadi et al. (95, 96) as well as Mulders et al. (57) found that this precursor produces deposits with around 50% Co content. Gazzadi et al. performed annealing procedures up to 400ºC finding that
despite the Co relative percentage does not vary significantly, there is a change of the Co crystalline structure and grain size (86, 95).

Additionally, growth of Co nanostructures exploiting autocatalytic effects has been observed on specific surfaces using Co$_2$(CO)$_8$ (62, 63) and Co(CO)$_3$NO (99).

### 2.2 Magnetic and electrical properties

The magnetic and electrical functionality of Co nanostructures grown by FEBID will depend to a great extent on their composition and microstructure. In the previous section, we have noted that these can vary significantly amongst different growth conditions. As a summary, the set of results with Co$_2$(CO)$_8$ as precursor indicates that deposits with high Co content (>90%) show metallic and ferromagnetic behavior, whereas deposits with low Co content (<80%) show semiconducting and paramagnetic/super-paramagnetic behavior. Regarding electrical properties, Lau et al. found electrical resistivity values equal to 159 µΩcm in those deposits with highest Co content (of ≈80%), which is 25 times greater than pure Co (34). Fernández-Pacheco et al. found significantly lower resistivity values, of 40 µΩcm at 300K, and 27 µΩcm at 2 K, in deposits with 95% Co (42). Figure 5 shows some of these results, including the temperature dependence of resistivity for this type of high-Co-content deposits (figure 5(a)) and the Hall effect (figure 5(b)), where two contributions, the anomalous Hall effect (proportional to the magnetization) and the ordinary Hall effect (linear with the magnetic field and depending on the number of carriers) are observed. Similar results have been observed in purified Co deposits, with metal content approaching 100% and resistivity value of 15 µΩcm at low temperature (84). On the other hand, Co content below 80% in general gives rise to semiconducting behavior (42) and absence of clear separation of the ordinary and anomalous Hall effects (48).
Figure 5. (a) Resistivity-vs-temperature measurement for the wire shown in the inset, grown by FEBID, showing metallic behaviour. (b) Hall effect for this wire, measured at 300 K and 2 K. The indicated saturation field makes possible to obtain the saturation magnetization of the material. Reproduced with permission from "Magnetotransport properties of high-quality cobalt nanowires grown by focused-electron-beam-induced deposition", by A. Fernández-Pacheco, et al, Journal of Physics D: Applied Physics 42, 055005 (2009). IOP Publishing Ltd.

Regarding the magnetic switching behavior of Co structures by FEBID, deposits with metal content above 90% display conventional ferromagnetic behavior. Given that these deposits are polycrystalline with a small (5-7 nm) grain size, the magnetocrystalline anisotropy is averaged to zero and shape anisotropy governs the magnetization reversal. This was demonstrated by Fernández-Pacheco et al. on Co wires with the same length and thickness but varying width by means of Magneto-optical Kerr Effect (MOKE) measurements. As shown in Figure 6, the coercive field becomes larger as the width decreases due to the increasing shape anisotropy (44). As a consequence, the coercive field is easily tunable through modification of the dimensions of the Co nanostructures, as later also observed by Nikulina et al. (64).
Figure 6. (a-d) MOKE hysteresis loops for Cobalt FEBID rectangles of different aspect ratios: AR = 1 (a), 2 (b), 12 (c), 26 (d). (e) Coercivity of the rectangles as a function of its width, for two thicknesses, showing a 1/width dependence. Reproduced with permission from "Magnetization reversal in individual cobalt micro- and nanowires grown by focused-electron-beam-induced-deposition", by A Fernández-Pacheco et al, Nanotechnology 20 (47), 475704 (2009). IOP Publishing Ltd.
The same type of high-content Co nanowires gives very good contrast in Magnetic Force Microscopy (MFM) measurements (54, 55), which allows the microscopic investigation of the magnetic state of these Co nanostructures. As Figure 7 shows, the magnetic remanent state in these Co wires depends on the aspect ratio for fixed length, as expected when shape anisotropy dominates. For narrow wires (width smaller than 400 nm), a mono-domain magnetic state occurs whereas magnetic domain walls are noticed in wider nanostructures (55).

Figure 7. (a) Topography and (b) MFM image of an array of Co wires with varying width. Notice how the domain configuration is a function of the aspect ratio of the nanostructures (c) Wires domain configuration distribution as a function of their dimensions. Reproduced with permission from M. Jaafar et al., Nanos. Res. Lett. 6, 407 (2011). Springer.
Electron holography and Lorentz microscopy inside a TEM have been carried out in order to investigate the magnetic state of Co nanowires grown by FEBID on Si₃N₄ membranes (70, 71). The observed magnetic states are in good agreement with the performed micro-magnetic simulations in standard polycrystalline Co nanowires (71).

On the other hand, low-Co-content deposits display super-paramagnetic behavior, in good agreement with their microstructure, formed by small isolated grains within a non-magnetic carbonaceous matrix, which, incidentally, is useful for the fabrication of Hall sensors with large sensitivity as shown by Gabureac et al. (48).

The work by Gazzadi et al. indicates that Co deposits grown with the Co(CO)₃NO precursor are very resistive (6000 µΩcm), but an annealing procedure at 400 ºC gives rise to Co nanowires with low resistivity at room temperature, 60 µΩcm, and metallic behavior as a function of temperature (96).

### 2.3 High-resolution and densely-packed cobalt nanostructures

As introduced in section 2.1, it was soon understood that although the use of high beam current (µA range) could produce Co deposits with high metal content, the lateral resolution was in that case compromised (34) due to the increasing electron beam size with increasing beam current. This effect adds to the production of secondary electrons beyond the impact point, due to the interaction of the primary electron beam with the growing deposit as well as with the substrate, which further limits the lateral resolution (26, 145). The first approach to improve the lateral resolution is consequently the growth under low electron beam currents, in the pA range, with beam diameters of only a few nm. As discussed in 2.1, for the Co₂(CO)₈ precursor, there are appropriate combinations of precursor flux and dwell time that permit the growth of Co nanostructures with high Co content (≈90%) and lateral resolution. In Figure 8, the best lateral resolution obtained by Serrano-Ramón et al. (≈30
nm) is observed (60). In that figure, some nanowires and Hall crosses are displayed, which correspond to the optimum growth conditions for concomitant high Co content and lateral resolution.

Figure 8. (a) SEM image of a cobalt nanowire with dimensions of 3 μm in length, 29 nm in width, and 30 nm in thickness grown at 3 kV, 21 pA (image taken at tilting angle of 52). A zoom-in image is shown in the inset. (b) SEM image of a cobalt nanostructure (L-shape) with dimensions of 3 μm in length for the horizontal part and 1 μm in length for the perpendicular part, 40 nm in width, and 30 nm in thickness, grown at 3 kV, 21 pA. (c) SEM image of a Co Hall sensor based on four independent 75 nm wide Co lines and a central 150 nm-wide square as active area. (d) SEM image of a cobalt Hall cross with a width less than 30 nm. Reprinted with permission from ACS Nano, 2011, 5 (10), pp 7781–7787. Copyright (2011) American Chemical. deteresa@unizar.es.

A very good lateral resolution has been reached even on non-conventional substrates such as flexible and transparent polycarbonate ones (87). As can be noticed in Figure 9, sub-100 nm Co nanowires, with high Co content and metallic behavior, have been grown on this
non-conductive substrate, opening new avenues for applications of this material in flexible electronics or magnetic sensing (87).

![SEM images of Co nanowires](image)

**Figure 9.** (a, b) Scanning electron micrographs of Co nanowires grown by FEBID on flexible and transparent polycarbonate substrates. (c) Picture of a polycarbonate substrate patterned by means of optical lithography to allow electrical measurements. (d) Current vs voltage characteristic of a Co nanowire grown by FEBID on polycarbonate. *Reproduced with permission from P. Peinado et al.*, *ACS Nano*, 2015, 9(6), 6139-6146. Copyright (2015) American Chemical Society.

An important issue in the area of nano-magnetism is the feasibility to integrate many nanostructures in a small space. This is for example the case for magnetic memories and logic applications. On the one hand, the FEBID technique is known to have a potential lateral resolution of a few nanometers in isolated structures (146). On the other hand, there
are practical limitations to attain such resolution in densely-packed structures, mainly dictated by the proximity effect present in FEBID. A small halo around the main deposit exists in FEBID deposits due to precursor dissociation by secondary electrons reaching far distances beyond the primary impact point (26). The thickness of this halo (in the range of 10% of the thickness of the main deposit) rapidly falls with distance, and is in general not a problem for the functionality of isolated deposits. In the case of Co nanostructures, it has been shown that such halo structure in the vicinity of the main deposit at most modifies the magnetic coercive field (44). However, in densely-packed structures, a deposit grows in between the main structures that can be considerably thick, in the range of 50% of the thickness of the main deposit, as shown in Figure 10 (76). The route followed by De Teresa and Córdoba to fabricate arrays of densely-packed Co nanowires has been to grow in first place thickness-modulated deposits by fine control of the beam pitch (76). The pitch was as small as 30 nm. Figure 10 illustrates the case of 40 nm pitch. One can notice in that figure a crest-valley periodic structure in agreement with such small beam pitch value. A subsequent soft Ar⁺ plasma post-processing decreases the deposit thickness quite homogeneously along the full deposit, which finally leads to a set of isolated Co nanowires separated by distance corresponding to the pitch value. With that approach it has been possible to fabricate isolated nanowires every 40 nm.
(a) Top-down image of an array of Co nanowires grown by FEBID with a pitch (center-to-center distance) of 40 nm (b) Cross-sectional SEM image of that array. Cross-sectional TEM image of the same array before (c) and after 240 s of Ar⁺ milling (d).


It is worth mentioning that Co nanowires have been grown by FIBID using a helium ion microscope (74). Although the lowest electrical resistivity reported in those nanowires (64 $\mu\Omega$cm) is higher than in some Co FEBID nanowires (see section 2.2), the lateral resolution of isolated nanowires is very good, down to 10 nm.

2.4 Ion irradiation effects

Nikulina et al. have found that a significant amount of material is deposited in between Co pillar structures (caused by halo effects), which totally modifies the magnetic coupling between them as well as their magnetization reversal mechanism (68). These authors have
used a 1kV Xe\textsuperscript{+} beam post-processing to get rid of such unwanted halo deposit, which minimizes the magnetic coupling amongst the pillars, separated around 200 nm as displayed in Figure 11.

![Figure 11](image.png)

**Figure 11.** Out-of-plane MOKE hysteresis loops and schematic sketches of possible magnetization reversal states for 2-dimensional arrays of FEBID cobalt nanopillars: as-deposited structures, having the pillars connected with the cobalt halo (a), (b) and Xe ion exposed with a dose of 120 mC/cm\textsuperscript{2} (c), (d). The inset in (c) shows the optical image of the sample, and the dotted square defines the region of interest used for measuring the MOKE loops. *Reprinted with permission from E. Nikulina, O. Idigoras, J. M. Porro, P. Vavassori, A. Chuvilin and A. Berger “Origin and control of magnetic exchange coupling in between focused electron beam deposited cobalt nanostructures”, Appl. Phys. Lett. 103, 123112 (2013). Copyright 2013, AIP Publishing LLC.*

Serrano-Ramón et al. have performed 30 kV Ga\textsuperscript{+} irradiation on 2D Co nanowires, finding some important consequences (72, 73). Up to irradiation doses of 3\times10\textsuperscript{16} ions/cm\textsuperscript{2}, the coercive field for magnetization reversal increases due to two main effects (72). The first effect is a decrease in the magnetic volume of the parasitic halo around the nanowire, which
leads to the disappearance of nucleation centers of domains. The second effect is the formation of a 20 nm outer shell with Co crystals about twice the size of those forming the core of the nanowire, causing a net increase of the local magnetocrystalline anisotropy. By studying the behavior of both, nucleation and propagation fields of domain walls, it is concluded that this type of global irradiation improves the overall magnetic behavior of the nanowires significantly after irradiation doses in the range of $1 \times 10^{16}$ ions/cm$^2$. As expected, high irradiation doses (> $4 \times 10^{16}$ ions/cm$^2$) deteriorate the nanowires structurally and magnetically (72).

### 2.5 Three-dimensional Co nanostructures

One of the distinct features of FEBID is its capability to grow 3D structures. So far, most of the work has been focused on the growth of out-of-plane Co nanowires (30, 34, 36, 66, 68, 81, 88, 90). The angle formed by the nanowire with the substrate can be controlled through the tilting angle of the substrate with respect to the electron beam direction (66). Co nanowires with shape of nano-spirals can be fabricated by scanning the beam in circular form (30, 66). Some images of 3D Co nanowires grown by FEBID are displayed in Figure 12. The magnetization reversal mechanism of such 3D nanowires has been characterized by means of MOKE measurements (66). Also, recent electron tomography-holography measurements of a 3D Co nanowire grown on a special sample holder have allowed the study of the spatially-resolved 3D magnetic state of the nanowire (90). Suspended 3D Co nanowires have been investigated by Vavassori et al. for application in remote magnetomechanical nanoactuation (92).
Figure 12. (a-f) SEM images of Cobalt 3D nanostructures grown by FEBID, including nano-spirals (a,b) and nanowires grown at different angles (c-f). (g,h) MOKE experiments in 3D nanowires on nanowires forming a 45° angle with the substrate. Reprinted with permission from A. Fernández-Pacheco et al, Three dimensional magnetic nanowires grown by focused electron-beam induced deposition. Sci. Rep. 3, 1492 (2013). NPG.

FEBID is more adequate than other lithography techniques for cantilever functionalization given the difficulty of using photo- or electron-beam- resists on cantilevers. This was already realized on the pioneer work by Utke et al. to fabricate Co nanowires at the apex of cantilevers for Magnetic Force Microscopy (MFM) (36). More recently, magnetic Co deposits have been grown on soft cantilevers suitable for Ferromagnetic Resonance Force Microscopy (FMRFM) experiments (61, 79). In particular, the spherical geometry is the most suitable for that application given that it minimizes the magnetic hysteresis of the tip. In Figure 13, we show examples of nano-spheres grown by
Sangiao, Casado and De Teresa in Zaragoza. The diameter of such nano-spheres ranges from 100 nm to 500 nm and their magnetic moment has been characterized by Mofakhami and De Loubens in CEA-Saclay to find that nano-spheres with diameter above 150 nm display magnetization values close to that of bulk Co, 1370 emu/cm$^3$ (unpublished).

3. Fe nanostructures by FEBID

3.1 Composition and microstructure

The group of Furuya et al. investigated Fe deposits grown by FEBID using the Fe(CO)$_5$ precursor along the period 2004 to 2007. They found that as-grown deposits consisted of a Fe:C nanocomposite with amorphous crystal structure which transformed into crystalline $\alpha$-
Fe and Fe-carbides phases after annealing processes at 600ºC, (103), (117), (118). Also, using mixtures of H$_2$O and Fe(CO)$_5$ precursors, these authors achieved the growth of crystalline Fe$_3$O$_4$ at room temperature (122). Additionally, by using mixtures of Fe(C$_3$H$_5$)$_2$ and Fe(CO)$_5$ precursors, the Fe content was controlled in the range 70%-30% (123). Furthermore, electron-beam-post-irradiation of Fe structures grown by FEBID was found to produce the formation of $\alpha$-Fe nanocrystals (104). In certain growth conditions (high precursor flux and long irradiation times), it was possible to observe the formation of $\alpha$-Fe nanocrystals at room temperature (124). The same effect of Fe-nanocrystal formation was later observed by Rodríguez et al. using the Fe$_2$(CO)$_9$ precursor under growth conditions of high precursor flux and large beam current (144). Lavrijsen et al. used a mixture of H$_2$O and Fe$_2$(CO)$_9$ precursors to produce amorphous Fe deposits at room temperature, with varying Fe content in the range 50-80% (107). The growth of 3D nanopillars using the Fe(CO)$_5$ precursor was found to be quite complex by Hochleitner et al. due to strong thermal effects (130). The nanopillars and the planar Fe deposits that show an amorphous or nanocrystalline structure, also present a 3-to-5-nm oxidized layer at the surface (134), (143), (144), (138). The best reported Fe content (80-85%) in FEBID deposits grown in high-vacuum conditions at room temperature without annealing have been obtained by Gavagnin et al. using the Fe(CO)$_5$ precursor (134) and by Rodríguez et al. using the Fe$_2$(CO)$_9$ precursor (144).

3.2 Magnetic and electrical properties

Using the Fe$_3$(CO)$_{12}$ precursor, Bruk et al. found that Fe deposits showed electrical resistivity values in the range $10^4$-$10^9$ $\mu$Ωcm (105). Lavrijsen et al. used a mixture of H$_2$O and Fe$_2$(CO)$_9$ precursors, giving rise to deposits with resistivity values in the range $10^2$-$10^7$ $\mu$Ωcm (107) (142), to be compared with the value for pure Fe, of 10 $\mu$Ωcm. A clear correlation is observed between the Fe content and the resistivity, as shown in Figure 14.
Measurements of resistivity as a function of temperature indicate that the residual resistivity value ($\rho_{300K}/\rho_{2K}$) approaches 1 for deposits with 70% Fe whereas it decreases to 0.05 for deposits with 56% Fe, a signature of semiconducting behavior (142). A giant value of the anomalous Hall effect was found in these samples, ascribed to the large contribution of skew scattering (142).

**Figure 14.** Room-temperature resistivity versus Fe content for Fe wires. The line is a guide to the eye. *Reprinted with permission from R Lavrijsen et al 2011 Nanotechnology 22 025302. Copyright (2011), IOP. DOI: 10.1088/0957-4484/22/2/025302; deteresa@unizar.es.*

In the following, we will describe the magnetic properties of Fe-based nanostructures grown by FEBID. Takeguchi et al. reported in as-grown and annealed nanorods the use of electron holography to infer magnetic induction values of 0.61 T and 0.45 T respectively (117). These are significant values, corresponding unequivocally to ferromagnetic response, but far from the bulk value of $\alpha$-Fe, equal to 2.2 T. In samples fabricated from mixtures of
Fe(C₅H₅)₂ and Fe(CO)₅ precursors, where the Fe content was controlled in the range 70%-30%, electron holography measurements gave magnetic induction values from 0.8 T down to 0.2 T (123). Lavrijsen et al. performed Kerr effect and magnetoresistance measurements demonstrating the ferromagnetic character of the Fe deposits grown with the mixture of H₂O and Fe₂(CO)₉ precursors (107) (142). From Hall-effect measurements on those samples, the authors estimated saturation magnetization values scaling with the deposit Fe content. Thus, the sample with 70% of Fe showed roughly 70% of Fe bulk saturation magnetization (107) (142). Using the Fe₂(CO)₉ precursor, Franken et al. grew Fe pillars by FEBID on top of perpendicular magnetic domain-wall conduits which were able to pin moving domain walls through the stray field created by the pillar (143).

Gavagnin et al. fabricated small nano-magnets using the Fe(CO)₅ precursor for application in nano-magnet logic, which were characterized by means of MFM measurements. They found that for fixed length and width, the coercive field was different for three different thicknesses. The same authors investigated by MFM the remanent magnetic state of Fe deposits with different geometrical forms (136). As shown in Figure 15, good correspondence is found with the expected magnetic state when shape anisotropy is the main anisotropy source in such nanomagnets.

Rodriguez et al. have fabricated Fe nanowires (Fe content above 80%) using the Fe$_2$(CO)$_9$ precursor (144). These nanowires present lengths of 4.5 µm and varying thickness (10 to 45 nm) and width (50 to 500 nm). A summary of the MOKE results in these samples is shown in Figure 16, where it can be noticed that the coercive field decreases with increasing width and thickness. Thus, the coercive field can be easily tuned by adjusting the dimensions of the nanowire. Micromagnetic simulations indicate that such dependence can be explained by magnetization reversal taking place via non-coherent magnetization rotation. The characteristic bell-shape of the deposits and the surface oxidation are also
found to be relevant parameters in the exact value of the coercive field for each nanowire (144).

Figure 16. MOKE hysteresis loop of an Fe nanowire with 10 nm thickness (a) and 35 nm thickness (b). Dependence of the coercive field with width at fixed thickness of 25 nm (c) and with thickness at fixed width of 250 nm (d). Reproduced with permission from Rodriguez LA, Deen L, Cordoba R, Magen C, Snoeck E, Koopmans B, et al. “Influence of the shape and surface oxidation in the magnetization reversal of thin iron nanowires grown by focused electron beam induced deposition” Beilstein Journal of Nanotechnology 6, 1319-1331 (2015).

3.3 Fe deposits in ultra-high-vacuum conditions

The group of H. Marbach et al. has investigated Fe deposition in UHV conditions using the Fe(CO)₅ precursor. In 2008, Lukasczyk et al. reported the growth of Fe nanostructures with
95% of Fe content, which was attributed to the ultra-clean conditions of the chamber and the Si substrate surface (109). By working on perfectly-clean and less-clean Rh (110) surfaces, Lukasczyk et al. have revealed the importance of the surface to produce catalytic-driven precursor decomposition (131). The catalytic growth-rate enhancement under certain growth conditions using the Fe(CO)\textsubscript{5} precursor had already been observed by Kunz and Meyer (101). Walz et al. have found that electron irradiation of SiO\textsubscript{2} surfaces prior to gas dosing produces active SiO sites that decompose the Fe(CO)\textsubscript{5} molecules without the need of electron-beam direct dissociation (147). After nucleation of the first Fe clusters, nanocrystal formation proceeds via auto-catalytic decomposition of the Fe(CO)\textsubscript{5} precursor. This procedure has been coined Electron Beam Induced Surface Activation (EBISA) and the topic has been recently reviewed by H. Marbach (148). As displayed in Figure 17, Fe micro-wires prepared by EBISA show electrical resistivity of 88 μΩcm at room temperature (132), still far from the bulk Fe value (10 μΩcm) but lower than the value of 186 μΩcm displayed by micro-wires with 70% Fe content grown in high-vacuum conditions and studied by Córdoba et al. (142). From Hall resistivity measurements in the same EBISA samples, Porrati et al. (132) estimated a saturation magnetization of 1.47 T, which is similar to the value found by Córdoba et al. (142). The tendency of Fe deposits to surface oxidation can be avoided by the growth of a protective capping layer, as carried out by Schimer et al. with a second titanium-oxide deposit (133). Fe deposits grown by EBISA have permitted fundamental studies related to the proximity effect (149) (150). In fact, using TiO\textsubscript{2} substrates and the EBISA technique, Vollnhals et al. have fabricated Fe nanowires of width about 20 nm (151).
Figure 17. Temperature dependence of the longitudinal resistivity $\rho_{xx}$ of Fe microwires grown by EBISA technique, showing that the behaviour is that of a metal. Below 12 K the resistivity slightly increases, see the inset. Reproduced with permission from F. Porrati, R. Sachser, M-M. Walz, F. Vollnhals, H-P. Steinrück, H. Marbach and M. Huth, “Magnetotransport properties of iron microwires fabricated by focused electron beam induced autocatalytic growth”, J. Phys. D: Appl. Phys. 44, 425001, (2011).

4. Ni and alloyed nanostructures

4.1 Ni nanostructures

Perentes et al. investigated the growth of Ni nanostructures using the Ni(PF$_3$)$_4$ and Ni(C$_5$H$_4$CH$_3$)$_2$ precursors (111). The maximum Ni content obtained was 40% and 10% respectively. The minimum electrical resistivity achieved was respectively $10^3 \mu\Omega$cm and $10^6 \mu\Omega$cm, much larger than that of pure Ni, 6.9 $\mu\Omega$cm. These authors also tried simultaneous injection of molecular flows of oxygen and hydrogen with the Ni precursors, without improvement of the Ni content (111). More recently, Córdoba et al. have extended
the research on Ni deposits using Ni(C_5H_4CH_3)_2 (112). The as-grown deposits display a maximum Ni content of 18% by FEBID and 22% by FIBID. A post-treatment process has been performed at room temperature, consisting of electron beam irradiation under oxygen flux, which gives rise to carbon removal and the appearance of the cubic NiO species in polycrystalline form (with 5 nm grain size). The as-grown FEBID Ni deposits show an electrical resistivity value at room temperature of \(\approx 10^7 \, \mu\Omega \text{cm} \), whereas the FIBID one of \(\approx 10^5 \, \mu\Omega \text{cm} \). Both deposits display semiconducting behavior as a function of temperature. The post-processed Ni deposits, with NiO stoichiometry, have very large resistivity values, \(\approx 10^9 \, \mu\Omega \text{cm} \). Such NiO deposits exhibit potential resistive-switching and exchange-bias phenomena (112). It is also worth mentioning that, Ni(CO)_4 has never been used for FEBID due to the high toxicity of the Ni radical (31).

4.2 Co and Fe alloys

The main route to achieve the growth of Co and Fe alloys by FEBID has consisted of the simultaneous use of two precursors during growth plus subsequent annealing procedures. Following this route, Che et al. synthesized L1_0 Fe-Pt alloy nanorods at 600 °C that showed high magnetic induction values (\(\approx 1.5 \, \text{T} \)) as measured by electron holography (121). The same group used later a modified sequence of deposition and annealing procedures to achieve various Fe-Pt alloys (125). Porrati et al. obtained L1_0 Co-Pt alloys by using two simultaneous precursors plus a room-temperature post-electron-irradiation process (65). Interestingly, Dobrovolskiy et al. have carried out controlled post-processing with mesoscale lateral resolution, which permits to tune the coercive field locally (85). The same group has also fabricated Co-Si alloys by simultaneously injecting two precursors which relative flux can be controlled, producing alloys with tunable Co/Si content and corresponding modulation in the electrical resistivity (69). Shawrav et al. have grown in a similar way Fe-
Au nanoalloys (139). In general, this route is able to produce nano-crystalline alloys at room temperature but with a substantial amount of residual species, typically carbon.

Another strategy followed by Tanaka et al. was to synthesize iron silicide arrays of nano-rods or nano-triangles by using Fe(CO)\(_5\) precursor, Si(111) substrates, high substrate temperature and electron deposition in a TEM (152). Nano-rods as long as 100 nm and 10 nm in width were grown in this way (153). When the same authors used Si(110) substrates, beta-FeSi\(_2\) islands were formed instead (126).

On the other hand, Pérez-Roldán et al. have grown nano-pillars by FEBID using simultaneously Co\(_2\)(CO)\(_8\) and Si(OC\(_2\)H\(_5\))\(_4\) precursors, finding that the growth of Co occurs at the outer part of the pillar (88). This forms a kind of Co magnetic tube filled with non-magnetic silicon oxide. The ferromagnetic properties are thus exclusively localized at the outer part of the structure as revealed by electron holography. Compositionally-inhomogeneous deposits at the nanoscale had been previously observed in FIBID deposits using two precursors, W(CO)\(_6\) and C\(_{10}\)H\(_8\) (154). Precursor competition with relevant kinetical processes upon certain growth conditions is the underlying reason for that intriguing behavior, which could be of general occurrence in co-deposition.

Recently, Porrati et al. have used a single bimetallic precursor, HFeCo\(_3\)(CO)\(_{12}\), to directly grow an alloy (110). The composition of the deposits is roughly Co:Fe:C:O= 60%:20%:10%:10%. The lowest room-temperature resistivity found is 43 \(\mu\)\Omega\(\cdot\)cm and the maximum magnetic induction is estimated to be \(\approx\)1.6 T. TEM measurements indicate that the deposits consist of a bcc Co-Fe phase mixed with a FeCo\(_2\)O\(_4\) spinel oxide phase with nanograins about 5 nm.

It is pertinent to mention that some magnetic alloys grown by FIBID have been reported. Thus, Xu et al. grew FePt and CoPt micro-particles using two precursors simultaneously and performing an annealing process at 600\(^\circ\)C to crystallize the particles.
(113). Pogoryelov and Suzuki used three precursors simultaneously to grow FeCoPt ternary-alloy micro-particles which showed different magnetic properties before and after annealing at 600ºC (141).

5. Applications of magnetic nanostructures by FEBID

In the following subsections, the most important applications reported so far for magnetic nanostructures grown by FEBID will be described.

5.1 Magnetic dots for magnetic storage and catalytic growth

Dots grown by FEBID can have very small dimensions, in the nanometer range, as already demonstrated using Pt precursor (155). However, the requirements of current magnetic-recording technology are very stringent (2, 156). For example, the magnetic anisotropy of the recording units should be large enough to retain the information for long periods of time. The present limitations in the chemistry of precursors and the difficulties in tailoring the crystal structure make quite improbable the use of magnetic dots grown by FEBID for this application. Nevertheless, the potential of beam-induced deposition for growing magnetic dots with small periodicity has been demonstrated (32) (33) (37) (38) (116) (120) and an interesting application of this type of structures in catalysis has been demonstrated by Ervin and Nichols (100). These authors used Co deposits grown with different doses to catalyze the growth of carbon nanotubes (CNTs). They found that at low doses no growth of CNTs occurred, whereas at intermediate and high doses single-wall and multi-wall CNTs were grown respectively. These differences were ascribed to the Co nanoparticle size variation (100).
5.2 Growth of MFM and FMRFM tips

For applications in high-resolution Atomic Force Microscopy, carbon-based tips grown by FEBID have been proposed (157). The high aspect ratio of the apex achievable in such tips made them to be coined *supertips*. For the study of magnetic samples, MFM tips are usually fabricated by evaporating a magnetic layer on an AFM cantilever (158). This implies that the magnetic interaction between tip and sample is somehow delocalized, which can lead to a loss of sensitivity and lateral resolution. Utke et al. challenged the growth of Co *supertips* for MFM studies (35) (36). As shown in Figure 18, the advantage of FEBID is the precise growth of the magnetic tip at the apex of a cantilever with controlled tip dimensions. Such tips were used to image the magnetic bits of a hard disk, reaching magnetic imaging resolution of 40 nm (36). Subsequent work by Belova et al. has improved the resolution of Co magnetic tips down to 10 nm (61). On the other hand, Gavagnin et al. have grown Fe tips using FEBID for MFM where the importance of the tilt angle of the magnetic tip with respect to the scanned sample has been revealed (138).
Figure 18. Scanning electron micrographs of typical FEB deposits. A high-aspect-ratio magnetic tip on top of a pyramidal Si tip is shown in (a). Deposition parameters are 133 pA at 25 kV during 2 min. The tip apex diameter is 72 nm, the shank diameter 160 nm, and the tip length is 1.7 mm. Magnetic cap coatings (b) are deposited at 100 pA, 25 kV, and 5 s resulting in 50 nm of apex diameter. (c) MFM resolution of several FEB deposits measured under ambient conditions with the lift-retrace tapping mode. The magnetic resolution corresponds to the smallest resolved magnetic transition. The resolution error is assumed as one half of the difference of the smallest resolved transition and the adjacent nonresolved transition. The dashed interpolated line has a slope of 0.8. Reprinted with permission from [I. Utke et al., Applied Physics Letters 80, 4792 (2002)]. Copyright [2002], AIP Publishing LLC.
Another interesting application of magnetic deposits by FEBID in the field of scanning microscopies has been recently unveiled. As introduced in section 2.5, FMRFM experiments are based on magnetic resonance force microscopy, where the magnetic resonance of a magnetic sample is sensitively detected through the magnetic force exerted on a cantilever equipped with a small magnetic tip (159). A soft cantilever is commonly used with a magnetic nanosphere glued at the apex (160). The spatial resolution of the technique is directly linked to the size of the nanosphere. Gluing a sub-micron particle to the apex of a cantilever tip is a painstaking work that can be substituted by directly growing it by FEBID. Using FEBID Co nanoparticles, very successful FMRFM experiments have been performed so far (161) (162) (163) (164) (165) (166).

5.3 Nano-Hall sensors for bead detection

In a Hall sensor, the voltage output changes as a function of magnetic field due to the Hall effect, which generates a transverse voltage perpendicular to the passing current. The voltage output is governed by the properties of the material and the existing external magnetic field. In general, the Hall sensor is based on either a semiconductor material with a linear response as a function of the external magnetic field due to the ordinary Hall effect or a magnetic material with an additional contribution due to the anomalous Hall effect (167). Hall sensors with high spatial resolution are interesting in diverse applications: in biosensing for the detection of biological moieties conjugated to magnetic nanoparticles (13), in scanning Hall microscopy (168), in nano-magnetometry (169), in magnetic logic applications (170), etc. Boero et al. reported that sub-micrometric Co Hall sensors can be grown by FEBID with good sensitivity (40). Further work demonstrated the great potential of such Co Hall sensors, with minimum magnetic flux detectable in the range of $10^{-6}\Phi_0$, where $\Phi_0$ is the quantum of flux (48) (60). This value is very competitive compared to other
nanoscale Hall sensors and was achieved by carefully tuning the composition and dimensions of the Co-based FEBID deposit. An experiment with controlled approximation of a magnetic bead to the Co-based Hall sensor was performed by Gabureac et al. (67). By performing the experiment in a SEM chamber, the Hall sensor output is monitored at the same time that the bead is controllably approached to the device. On the other hand, Córdoba et al. have fabricated Hall structures based on Fe deposits grown by FEBID (142). These authors have found a giant anomalous Hall effect in these structures due to their high resistivity, which gives rise to large skew-scattering phenomena.

5.4 Nanowires in 2D and 3D for domain-wall manipulation

The concept of domain-wall conduit was introduced in 2002 by Cowburn et al. to illustrate the unperturbed propagation of magnetic domain walls inside a magnetic material (171). Such behavior implies that the magnetic field required to displace a domain wall within the nanowire (the propagation field) is lower than the magnetic field required to create new domain walls (the nucleation field). This effect can be applied for applications in magnetic logic (9) as well as in racetrack memories (8). Fernández-Pacheco et al. demonstrated that 2D Co nanowires grown by FEBID sustain unperturbed propagation of domain walls (43). Figure 19 illustrates such behavior. L-shaped nanowires were grown in order to measure the nucleation and propagation fields of domain walls in this material. The results indicated that, in the range of nanowire dimensions studied, the propagation field is lower than the nucleation field. The most appropriate dimensions for optimized domain-wall conduit behavior were later determined by Rodríguez et al. using Lorentz microscopy (71). These authors concluded that such dimensions were related to the crossover between the formation of transverse and vortex domain walls.
Figure 19. (a,b) MOKE hysteresis loops (black and red) and field sequences used (green) in L-shaped nanowires grown by FEBID, showing a lower switching field for propagation (a) than for nucleation (b). (c) Nucleation and propagation field as a function of width, proving a good domain wall conduit for the wires. Reprinted with permission from Fernández-Pacheco et al. Domain wall conduit behavior in cobalt nanowires grown by focused electron beam induced deposition. Applied Physics Letters. 2009;94(19):192509. Copyright 2009 AIP Publishing LLC.

Additionally, Serrano-Ramón et al. found that an improvement in the domain-wall-conduit behavior of 2D Co nanowires grown by FEBID was achievable by high-voltage global Ga⁺ irradiation (72), as mentioned in section 2.4. This was linked to the structural and micro-structural changes produced by the highly-energetic irradiation. Moreover, local Ga⁺ irradiation was found to pin domain walls efficiently at well-localized areas, as directly observed by means of scanning transmission x-ray microscopy (73).
The domain-wall-conduit behavior has not been proved in FEBID Fe nanowires so far. Micromagnetic simulations performed by Rodríguez et al. in 2D nanowires indicate that the magnetization reversal is quite complex and not via simple transverse or vortex wall nucleation and propagation (144). The domain-wall-conduit behavior in 3D magnetic nanowires grown by FEBID is still an open question too, although Fernández-Pacheco et al. suggested that it could be the case in 3D Co nanowires (66).

Another application has been demonstrated by Franken et al., who have used Fe nanopillars grown by FEBID on top of perpendicular domain-wall conduits to pin domain walls in a controllable way (143). The positive or negative stray field produced by the Fe nanopillars on the magnetic domain-wall conduit is used to stop or let pass the corresponding domain wall under the pillar.

5.5 Spintronics and nanomagnetism
Spintronics relies on the spin degree of freedom of the electron to build electronic devices (172) (173). Spintronics is currently at the basis of many types of memories and sensing schemes (5) (7) (8) (174). One of the most successful devices is a magnetic tunnel junction, consisting of two magnetic layers separated by an insulating layer. The current proceeds via spin-polarized tunneling and gives rise to large magnetoresistance ratios beyond 500% at room temperature (175). This has been achieved through complex engineering of the thickness, composition and crystallographic structure of all the layers forming the magnetoresistive stack. Constanzi et al. have challenged the growth of magnetic tunnel junctions using Co electrodes and SiO$_2$ barrier, all grown by FEBID (75). Unfortunately, the obtained 0.5% magnetoresistive ratio, comparable to the anisotropic magnetoresistance value of Co, 0.8% (42), is three orders of magnitude below the state of the art, and has little chances of applicability without further development. One of the potential issues in the
grown device is the quality and nature of the barrier, which is known to play a central role in magnetic tunnel junctions (176). It is worth mentioning that Sangiao et al. have measured a high spin polarization (40%) for Co grown by FEBID in Andreev reflection measurements (59). This value is close to that measured for Co grown by sputtering (177). This means that, in principle, Co grown by FEBID can be used efficiently in spintronic devices as an active element. It is also worth mentioning the work by Fernández-Pacheco et al. regarding the fabrication of Co nanoconstrictions grown by FEBID in a single step (93). The good correlation between the magnetoresistive behavior of such nanoconstrictions and their magnetic state probed by scanning transmission x-ray microscopy is indicative of the good functionality of this material down to the nanoscale (93).

Other routes have been followed by the group of M. Huth to apply FEBID materials in the field of Spintronics and Nanomagnetism. Pohlit et al. have grown artificial square spin ice structures based on Co nanowires grown by FEBID (89) (91). Artificial spin ice structures, characterized by geometrical frustration, are being studied for their exotic physical behavior and are potential candidates for memory devices (178). The results by Pohlit et al. point towards magnetization reversal statistically following different paths most likely driven by thermal perturbations (89). The differences between the magnetic behavior of isolated Co nanoislands grown by FEBID and the cluster formed by several interacting Co nanoislands have been highlighted by the same authors (91). On the other hand, Porrati et al. have fabricated Co nanopillars embedded in a Pt-C nano-granular matrix to achieve magnetoresistive effects (81). All the constituents of the device have been grown by FEBID. The value of the magnetoresistive effect measured at 4 K is low, below 6%. Besides, Lara et al. have fabricated circular Co disks by FEBID, designing holes by FIB in order to investigate their magnetization reversal through metastable states with half antivortices (80). The device is shown in Figure 20. The pinning landscape provided by the
holes guide the magnetization reversal. The authors argue that the finding is relevant for the development of multi-hole spintronic and magnetic memory devices.

![Image of optical and SEM images of Co dots deposited by FEBID between gold contacts.]

**Figure 20.** The top left panel shows an optical image of the high frequency probe and the gold contacts to which it is attached. The other three panels show SEM images of the Co dots deposited by FEBID between the gold contacts. Three cases are shown: without nanoholes, with two nanoholes, and with three nanoholes. *Reprinted with permission from A. Lara et al., Applied Physics Letters 105, 182402 (2014). Copyright [2014], AIP Publishing LLC.*

The recent use of 3D Co nanowires for magnetomechanical actuation is another promising route of work. The authors foresee applications in fields such as nanobiomechanics, nano-optics and nano-transport (93).

### 5.5 Nano-magnetic logic

Highly-integrated nanomagnets with dipolar coupling have been proposed for application in logic computing, the field being coined nanomagnet logic (179). Different logic gates have
been demonstrated using materials such as Permalloy or Co/Pt films grown by sputtering (180). Gavagnin et al. have used 2D Fe nanomagnets grown by FEBID to build demonstrative logic gates (134). As an example of this, a NAND/NOR logic gate is shown in Figure 21. The same group later showed the capability of FEBID to fabricate 3D logic gates using again Fe deposits (138).

![Figure 21](image.png)

**Figure 21.** Topography (top) and phase shift (bottom) MFM images of the NAND/NOR gates fabricated by the merging of NWs. The phase shift images evidence the magnetic reversal of the gates by applying an external magnetic field in opposite directions (arrows directions), whereas the inlays in panel a, show the magnetic dipole orientations where blue and yellow represent north and south poles, respectively. *Reprinted with permission from M. Gavagnin, H. D. Wanzenboeck, D. Belic and E. Bertagnolli, “Synthesis of individually tuned nanomagnets for nanomagnet logic by direct write focused electron beam induced deposition”, ACS Nano, 7, 777-784, (2013). Copyright 2012 American Chemical Society.*
5.5 Combination of magnetic deposits with superconductors

The group in Zaragoza demonstrated for the first time functional devices combining magnetic nanostructures grown by FEBID and superconducting nanostructures grown by FIBID (59) (58). The device, shown in Figure 22, consists of a nanocontact between the magnetic Co FEBID deposit and the superconductive W FIBID deposit. Such nanocontacts have allowed the extraction of important material parameters such as the spin polarization of the magnetic material and the superconducting gap (59). The value of the superconducting gap extracted from these experiments is in agreement with direct scanning tunneling microscopy experiments, which stresses the capability of preparing clean nanocontacts by FEBID/FIBID techniques with a single (or very few) conduction channel (181). Subsequent experiments in nanocontacts with worse definition or cleanliness gave rise to multi-channel transport (83). In fact, the experiments are difficult and, for example, the growth order is critical. If the FIBID superconducting deposit is grown after the magnetic one, the use of ions can degrade the magnetic properties of the nanocontact (182).
Figure 22. (a) Artificially coloured scanning electron micrograph of a Co-W nanocontact created for current-in-plane Andreev Reflection measurements. (b) Temperature dependence of the normalized differential conductance of a Co-W nanocontact as a function of the applied voltage. Solid lines are fits to the extended BTK model. Reprinted from Solid State Communications vol. 151, S. Sangiao et al., Ferromagnet-superconductor nanocontacts grown by focused electron/ion beam techniques for current-in-plane Andreev Reflection measurements, 37-41, Copyright (2011), with permission from Elsevier.

In another application followed by the group of M. Huth, arrays of Co stripes have been grown by FEBID on superconductive Nb films to create uniaxial pinning potentials for
the movement of the vortex lattice (115) (47). Transport measurements in the superconductor confirm the expectation of an anisotropic behavior induced by the uniaxial pinning (47) as well as steps ascribed to matching effects between the Co line periodicity and the vortex lattice periodicity (51).

6. Summary and outlook

In the previous sections, the state-of-the-art usage of FEBID for the growth of magnetic nanostructures has been described. As a brief summary, since 2009 there is a revived interest in the growth of magnetic nanostructures by FEBID. In the following, our view on the expected evolution of the topic will be given. We focus on the main aspects involved in the topic, first on the growth, later on the applications themselves:

Regarding the growth, these are our views:

-New precursors for magnetic deposits: As shown in Table 1, the available precursors for growth of magnetic materials by FEBID are scarce. Recently, Porrati et al. introduced a heteronuclear precursor containing Fe and Co atoms (110). The total amount of metal content (Fe+Co) in the grown deposits was 80%. New developments in precursor chemistry for the growth of alloyed magnetic materials are expected. In particular, the incorporation of rare-earth atoms in such precursors could be advantageous in certain applications in magnetism. In general, one of the limitations in the use of FEBID compared to other growth techniques such as sputtering is the lack of fine control in the final composition of the grown material.

-New strategies for purification of deposits: Although a high metal content (above 80%) can be currently achieved in magnetic deposits grown at room temperature using Co-based and Fe-based carbonyl precursors, in some applications metal values close to 100% may be necessary. This is why purification methods such as those recently developed for
magnetic materials are desired (84). In fact, such strategies should be easy to implement for broad dissemination.

-Growth of alloys by co-deposition: As described in section 4, very little work has been performed towards the growth of alloys by co-deposition. In some cases, the achievement of the searched crystallographic phase calls for high-temperature annealing processes. New magnetic alloys are expected to be grown by FEBID in the coming years to enlarge its applicability.

-Multi-layer deposition: For some magnetic devices like magnetic tunnel junctions, a stack of several materials should be grown. FEBID is well-suited for sequential deposition of materials and one can expect new strategies in this direction. The combination of magnetic materials with other functional materials (superconductive, optically-active, insulating, etc.) seems attractive to explore beyond the few existing examples discussed in section 5.

-Combination of FEBID with other growth or lithography techniques: FEBID technique has been combined with Atomic Layer Deposition (ALD) for the growth of pure Pt nanostructures (183) (184) (185). Finding compatible FEBID-ALD processes for the growth of pure magnetic nanostructures would be an exciting new route. FEBID has been combined with FEBIE (Focused Electron Beam Induced Etching) to create CoF$_3$ material (77), which is known to be an antiferromagnetic material. This could potentially give rise to Co/CoF$_3$ exchange-biased bilayers, with application in magnetic sensing.

-Use of FIBID: The composition and lateral resolution of Co deposits obtained by Wu et al. using the Helium Ion Microscope (HIM) are very promising (74). Although, in general, the use of ions on magnetic materials degrades their properties, in this case, the exhibited properties are of high quality. Further work using the HIM (or other ion sources) for the growth of magnetic materials would be fantastic.
- **Use of multi-electron-beam deposition:** Another limitation of FEBID, the low growth rate, could be overcome by the use of multi-electron-beam deposition (186). Although such technology is still under development, its application for the fast growth of magnetic arrays would be welcome.

- **FEBID on liquid environment:** Some work exists on the use of liquid-phase electron-beam-induced deposition for Pt, Cu and Ag (187) (188). In this case, the precursor is adsorbed on the substrate in liquid phase and a focused electron beam from an environmental SEM allows precursor decomposition into pure nanostructures. This strategy has not been used for the growth of magnetic materials yet.

- **Catalytic growth:** As described in section 5.1, the growth of CNTs on Co dots grown by FEBID has been achieved, underlining the potential of the technique for catalytic growth (100). On the other hand, various experiments have been developed regarding catalytic effects in FEBID itself (131). Further investigations in those directions can be envisaged, with importance in the fields of surface science and self-assembly.

- **Use of non-standard substrates:** One of the advantages of FEBID is the freedom in the choice of substrate. The work by Peinado et al. has demonstrated that FEBID can be achieved on unconventional substrates such as flexible and transparent polycarbonate ones (87). Given that some applications such as stretchable magnetoelectronics are very promising (186), further work regarding the growth of magnetic nanostructures on unconventional substrates is expected.

Regarding applications, these are our views:

- **Magnetic storage:** The present magnetic storage density, beyond 1Tbit/inch², and the stringent requirements of the hard disk components make difficult the change towards new magnetic storage strategies (189). However, the use of concepts for 3D magnetic storage is in vogue given the potentially-high storage density achievable (8, 190). As FEBID
is well-suited for 3D growth, the development of 3D magnetic nanowires by FEBID (66) could be interesting in contexts like the racetrack memory (8). Given that 2D Co nanowires grown by FEBID display domain-wall conduit (43), 3D Co nanowires could also exhibit such a property.

-Domain-wall and logic: The use of magnetic domain walls for 2D logic concepts was introduced a few years ago using Permalloy nanostructures (9). Magnetic materials grown by FEBID, displaying domain-wall conduit (43), are appropriate for this application. On the other hand, Permalloy and Co/Pt nanomagnets have been also used for the development of nanomagnet logic concepts (180). 2D and 3D logic gates grown by FEBID have been demonstrated (134) (138), but the present throughput is too low for cost-effective device production. One should also consider that, despite domain-wall and nanomagnet logic concepts are beautiful, the great improvements achieved in Si-based logic makes improbable the use of magnetic domain walls in next-generation logic devices.

-Scanning Probe Microscopy (SPM) tips: The difficulties to functionalize SPM tips with standard growth and lithography techniques make FEBID a competitive technique in this application. Although some proof-of-concept examples have been shown for MFM, as described in section 5.2, real applications are almost inexistent. However, we foresee strong potential for topics such as quantitative MFM or high-resolution MFM. The results achieved so far in FMRFM using Co deposits grown by Belova et al. indicate that FEBID is indeed very useful in this application (163).

-Magnetic prototyping: FEBID produces nanopatterned magnets with high resolution and shapes, and on non-standard substrates, which can be very difficult or impossible to obtain with other growth and lithography techniques. This is very useful for magnetic prototyping so that new magnetic states can be investigated with advanced local magnetic characterization techniques (90).
- **Vortex lattice pinning:** Physical phenomena in superconductors is very rich and with important technological implications. One of the holy grails in this field is the improvement of the critical current by means of hampering the motion of the vortex lattice in type-II superconductors. The use of magnetic nanostructures grown by FEBID for vortex pinning is a clean and effective process that permits the study of important effects related to vortex physics (51). Further studies in this direction will improve the understanding of the phenomena for adequate design of the vortex-pinning landscape in high-T_c superconductors used in real applications.

- **Remote magnetomechanical actuation:** Nano-actuators normally use electrical contacts to convert electrical stimuli into mechanical motion. However, remote operation of nano-actuators by magnetic fields, avoiding the need of electrical contacts, has been recently demonstrated (93). The nano-actuators have been fabricated using Co nanowires grown by FEBID. This will surely inspire new devices based on this strategy.

Summarizing, the FEBID technique finds various applications in the fields of nanomagnetism and spintronics, mainly on some specific situations where this technique has competitive advantages with respect to the use of standard thin-film growth plus nanolithography. We foresee that FEBID will become better known in the coming years and will be used on the same foot as other growth and lithography techniques.

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