Functional nickel-based deposits synthesized by focused beam induced processing

Citation for published version (APA):

Cordoba Castillo, R. M., Barcones, B., Roelfsema, E., Verheijen, M. A., Mulders, J. J. L., Trompenaars, P. H. F., & Koopmans, B. (2016). Functional nickel-based deposits synthesized by focused beam induced processing. *Nanotechnology*, 27(6), 1-11. [065303]. <https://doi.org/10.1088/0957-4484/27/6/065303>

Document license:
TAVERNE

DOI:
[10.1088/0957-4484/27/6/065303](https://doi.org/10.1088/0957-4484/27/6/065303)

Document status and date:
Published: 13/01/2016

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Functional nickel-based deposits synthesized by focused beam induced processing

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 Nanotechnology 27 065303

(<http://iopscience.iop.org/0957-4484/27/6/065303>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 131.155.151.92

This content was downloaded on 26/05/2016 at 08:47

Please note that [terms and conditions apply](#).

Functional nickel-based deposits synthesized by focused beam induced processing

R Córdoba¹, B Barcones^{1,2}, E Roelfsema¹, M A Verheijen¹, J J L Mulders³, P H F Trompenaars³ and B Koopmans¹

¹ Department of Applied Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

² NanoLab@TU/e, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

³ FEI Electron Optics, 5651GG Eindhoven, The Netherlands

E-mail: rosa.cordoba.castillo@gmail.com

Received 17 September 2015, revised 25 November 2015

Accepted for publication 1 December 2015

Published 13 January 2016

Abstract

Functional nanostructures fabricated by focused electron/ion beam induced processing (FEBIP/FIBIP) open a promising route for applications in nanoelectronics. Such developments rely on the exploration of new advanced materials. We report here the successful fabrication of nickel-based deposits by FEBIP/FIBIP using bis(methyl cyclopentadienyl)nickel as a precursor. In particular, binary compounds such as nickel oxide (NiO) are synthesized by using an *in situ* two-step process at room temperature. By this method, as-grown Ni deposits transform into homogeneous NiO deposits using focused electron beam irradiation under O₂ flux. This procedure is effective in producing highly pure NiO deposits with resistivity of 2000 Ωcm and a polycrystalline structure with face-centred cubic lattice and grains of 5 nm. We demonstrate that systems based on NiO deposits displaying resistance switching and an exchange-bias effect could be grown by FEBIP using optimized parameters. Our results provide a breakthrough towards using these techniques for the fabrication of functional nanodevices.

Online supplementary data available from stacks.iop.org/NANO/27/065303/mmedia

Keywords: focused electron beam induced deposition (FEBID), focused ion beam induced deposition (FIBID), electron beam irradiation, nickel and nickel oxide wires, electrical properties, resistance switching, exchange-bias effect

(Some figures may appear in colour only in the online journal)

1. Introduction

Focused electron/ion beam induced deposition (FEBID/FIBID) are direct write techniques based on the dissociation of precursor molecules adsorbed on a substrate surface where the focused electron beam (FEB) or focused ion beam (FIB) is scanned over them. By the FEB/FIB induced process, the molecules are partially decomposed into a volatile part and a non-volatile part. The latter is attached to the substrate surface forming a specific deposit [1, 2].

FEBID and FIBID are single step processes, versatile regarding the explored materials and have full control on dimensions and shape at the nanoscale. Thus, advanced functional nanostructures with diverse electronic and magnetic properties can be fabricated [3–11]. Together with their unique ability for the fabrication of real 3D nanostructures [12, 13], these nanofabrication methods could have potential applications in nanoelectronics and nanomagnetism [14–17].

The main drawback of deposits grown by FEBID/FIBID is their low purity which could impair their functionality. The

low metallic content in these deposits is caused by the incomplete precursor molecule dissociation and the lack of volatile products resulting from this process. The most used precursors are based on carbon, for example the standard metal-organic compounds, like $(\text{CH}_3)_3\text{Pt}(\text{CpCH}_3)$ and $(\text{CH}_3)_3\text{PtCp}$ leading to deposits mainly composed of carbon with a metal content that ranges from 15 at.% Pt to 46 at.% Pt. Their typical resistivities range from $2 \times 10^4 \mu\Omega\text{cm}$ to $1.8 \times 10^8 \mu\Omega\text{cm}$ for Pt FEBID [7, 18, 19] and from $61.5 \mu\Omega\text{cm}$ to $10^8 \mu\Omega\text{cm}$ for Pt FIBID [6, 7, 20–23]. Higher purities can be obtained by carbon-free precursors like $\text{Pt}(\text{PF}_3)_4$, which results in FEBID deposits with a metallic content ranging from 58 at.% Pt to 81 at.% Pt and lower resistivities, from $30 \mu\Omega\text{cm}$ to $650 \mu\Omega\text{cm}$ [24]. However, the best results in FEBID in terms of purity are reported using starting materials based on carbonyl compounds, like $\text{Co}(\text{CO})_8$ and $\text{Fe}_2(\text{CO})_9$. Thus, highly pure FEBID deposits with metallic content above of 95 at.% Co and above 80 at.% Fe have been grown, achieving resistivities of $40 \mu\Omega\text{cm}$ [25] and $100 \mu\Omega\text{cm}$ [10], respectively.

In this study, suitable Ni precursor candidates in terms of purity of the deposits have been discarded either for their high toxicity ($\text{Ni}(\text{CO})_4$) or synthesis feasibility. Thus, for the synthesis of nickel-based deposits we used a nickel-carbon-based precursor, the bismethylcyclopentadienyl-nickel $(\text{MeCp})_2\text{Ni}$. The deposited material is usually composed of 10 at.% Ni and has resistivities of $1 \Omega\text{cm}$ [26]. However, it is possible to decrease the carbon content increasing the purity of deposits with *in situ* and *ex situ* treatments summarized in the review article by Botman *et al* [27]. Besides that, *in situ* purification strategies such as heating the substrate during deposition [28], FEB irradiation under oxygen flux with [29–31] or without annealing [32–34], and pulsed laser irradiation [35, 36], have been reported in recent years. On the other hand, diverse *ex situ* purification methods have also been explored recently [19, 37–43]. Some of these studies prove the fabrication of pure materials such as platinum and gold by focused electron beam induced processing (FEBIP) [32, 34, 39]. Furthermore, for broadening the application fields of focused beam induced processing, alloys and binary systems using two precursor materials have also been reported [44–49].

In the present paper, we explore further steps in this research area. First, we study as-grown Ni deposits fabricated by FEBID and FIBID techniques. Secondly, we report for the first time a procedure to synthesize binary oxide (nickel oxide, NiO) FEBIP deposits at room temperature. The fabrication method of the latter consists of two sequential *in situ* steps: (1) Ni FEBID and (2) FEB irradiation under O_2 flux. Since nickel oxide presents resistance switching [50, 51] and antiferromagnetic (AFM) behaviour [52], it is an interesting candidate to utilize in explorative research on next generation non-volatile memories. Finally, we briefly explore two potential applications, reporting the first successful growth of NiO wires by FEBIP displaying resistive switching and exchange coupling in Co/NiO bilayers, indicative for an exchange-bias effect.

The deposits have been studied using energy dispersive x-ray spectroscopy (EDS), high resolution transmission

electron microscopy (HRTEM), electrical measurements by four-probe method at temperature range (from 295 K to 5 K) and magneto-optical Kerr microscopy.

2. Experimental details

2.1. Ni deposits grown by FEBID and FIBID

Ni deposits were grown in a FEI Helios NanoLab 650 Dual Beam System. The bismethylcyclopentadienyl-nickel $(\text{MeCp})_2\text{Ni}$ was used as a precursor material. The Ni gas injection system (GIS) uses a standard needle $500 \mu\text{m}$ in diameter positioned at an angle of $\sim 30^\circ$ with the horizontal sample, $100 \mu\text{m}$ from the interest area in x , y and $50 \mu\text{m}$ from the substrate in the z direction. The deposits were grown on a boron doped Si substrate with a few nanometres of native SiO_2 on top, except for the Ni deposits used for electrical measurements which were grown on pre-patterned gold contacts on Si/ SiO_2 (500 nm) substrates.

Typical deposition parameters used for the FEBID process were: voltage = 5 kV, current = 1.6 nA, dimensions $(L \times w \times t) = 1 \times 1 \times 0.4 \mu\text{m}^3$; dwell time = $10 \mu\text{s}$, overlap = 50%, pitch = 8.8 nm, scanning mode = serpentine, $T_{\text{precursor}} = 57^\circ\text{C}$, $P_{\text{base}} \sim 1 \times 10^{-6}$ mbar, $P_{\text{process}} \sim 1 \times 10^{-5}$ mbar (since we cannot give real data of the effective pump speed for $(\text{MeCp})_2\text{Ni}$ molecules in our equipment, the molecular flux (molecules/ cm^2s) that reaches the surface has not been estimated). The resultant volume per dose using these parameters was $\sim 5.9 \times 10^{-3} \mu\text{m}^3 \text{nC}^{-1}$. Similar to other metal-organic precursors, variations on voltage, current and dwell time did not significantly improve the metal content (15 at. % $\pm$ 5 at. %) on the Ni deposits [7, 26, 53, 54]. Thus, the reported parameters in our study were chosen to improve volume per dose and deposition resolution.

Typical deposition parameters used for the FIBID process were: voltage = 30 kV, current = 24 pA, dimensions $(L \times w \times t) = 1 \times 1 \times 0.7 \mu\text{m}^3$; dwell time = 200 ns, overlap = -150% , pitch = 32 nm, scanning mode = serpentine, $P_{\text{base}} \sim 1 \times 10^{-6}$ mbar, $P_{\text{process}} \sim 7.5 \times 10^{-6}$ mbar, $T_{\text{precursor}} = 57^\circ\text{C}$. The resultant volume per dose using these parameters was $\sim 0.97 \mu\text{m}^3 \text{nC}^{-1}$.

2.2. Focused electron beam induced processing under O_2 flux

The post-treatment consists of a FEB irradiation under O_2 flux at room temperature. The O_2 GIS uses a needle $160 \mu\text{m}$ in diameter positioned at an angle of 16.5° with the horizontal sample, $100 \mu\text{m}$ from the interest area in x , y and $100 \mu\text{m}$ from the substrate in the z direction. The FEB irradiation parameters were: voltage = 5 kV, current = 26 nA, pattern dimensions $(L \times w) = 1 \times 1 \mu\text{m}^2$; dwell time = $10 \mu\text{s}$, overlap = 50%, pitch = 7.7 nm, scanning mode = serpentine, $P_{\text{base}} \sim 1 \times 10^{-6}$ mbar, maximum $P_{\text{process}} \sim 6.5 \times 10^{-5}$ mbar.

After performing the Ni deposition and closing the Ni GIS we waited for at least 15 min before starting the e-beam post-irradiation to avoid undesirable Ni deposits under the

Figure 1. Sketch illustrates the two-step sequential process for the fabrication of NiO deposits. The colour scheme for the circles depicted in the sketch indicates the different atoms which compose the starting materials, volatile products and non-volatile products. Red circles represent the carbon atoms, green ones the hydrogen atoms, light blue ones the nickel atoms and dark blue ones the oxygen atoms. (a) Step 1: Ni FEBID process. (b) Step 2: FEB irradiation under O₂ flux at room temperature.

FEB irradiation. To study the contribution of the O₂ molecular flux that reaches the surface [54], it was increased from $\sim 9.1 \times 10^{18}$ molecules (cm² s)⁻¹ to $\sim 7.7 \times 10^{19}$ molecules (cm² s)⁻¹ varying the P_{O_2} from 7.6×10^{-6} mbar to 6.4×10^{-5} mbar. To investigate the FEB dose contribution, it was increased from $0 \mu\text{C} \mu\text{m}^{-2}$ to $12 \mu\text{C} \mu\text{m}^{-2}$.

2.3. Composition of as-grown Ni deposits and post-treated Ni deposits

The composition of deposits was studied *in situ* by energy dispersive x-ray spectroscopy (EDS) using a detector with ~ 135 eV energy resolution calibrated for a Si K α line and EDAX Genesis software. The spectra were collected at an acceleration voltage of 5 kV and electron beam current of 0.80 nA.

2.4. Microstructure of as-grown Ni FEBID deposits and post-treated NiO deposits

The microstructure of deposits was studied by high resolution transmission electron microscopy (HRTEM) in a JEOL ARM200FCS equipped with a 100 mm² Centurio SDD EDS detector. The compositional analysis was carried out by performing EDS in scanning TEM—high angle annular dark field (HAADF) mode. The sample preparation for this analysis was performed by the standard SEM/FIB lamella preparation method.

2.5. Study of the electrical transport properties

As mentioned in section 2.1, pre-patterned substrates with four gold (100 nm in thickness) electrodes on top of Si/SiO₂ substrates fabricated by UV lithography and lift-off processes were used for the electrical transport study. We have deposited Ni wires with dimensions $12 \times 1 \times 0.2 \mu\text{m}^3$ by FEBID and FIBID on top of these substrates. A FEB irradiation dose of $2.6 \mu\text{C} \mu\text{m}^{-2}$ was employed in those wires that we want to

oxidize into NiO wires. The deposition and the FEB irradiation parameters were already mentioned in sections 2.1 and 2.2. The samples were wire-bonded on a specific chip carrier for the electrical measurements. The four-point probe measurements were performed in an *ex situ* electrical transport setup with Keithley sourcemeters 2400, 6430 and a He flow cryostat at different temperatures ranging from 295 to 5 K. By FIB cross-sectional view of the wires after the electrical characterization, their real thickness was measured for determining their resistivity.

2.6. Fabrication of exchange biased bilayer

Fabrication of bilayer wires composed of Co (ferromagnetic, FM)/NiO (AFM) layers were carried out by FEBIP processes. First, NiO wires with dimensions $10 \times 1 \times 0.07 \mu\text{m}^3$ were fabricated using our two sequential *in situ* step method detailed in sections 2.1 and 2.2 and sketched in figure 1. Second, high-purity Co FEBID deposits with dimensions $10 \times 1 \times 0.02 \mu\text{m}^3$ were grown on top of the NiO wires forming bilayer wires, and on top of a piece of silicon substrate to use them as magnetic signal reference. Cobalt deposits were grown in a FEI Nova Nanolab 600 dual beam system using Co₂(CO)₈ as a precursor material. By tuning deposition parameters, cobalt content above 90 at.% in Co deposits was obtained, ensuring their ferromagnetic behaviour [25]. The magnetic characterization of Co/NiO wires has been studied by magneto-optical Kerr microscopy. Since the shape anisotropy and in-plane magnetization govern the magnetization reversal in Co wires, a longitudinal Kerr effect configuration and an in-plane magnetic field oriented parallel to the easy axis were used. The hysteresis loops are obtained by measuring the intensity of the image of the Co/NiO and Co wires as a function of the magnetic field providing their magnetic information.

Figure 2. (a) Dependence of the composition of post-treated Ni FEBIP deposits on the O_2 flux (indicated as the oxygen pressure, $P_{O_2} = P_{\text{process}} - P_{\text{base}}$) at two FEB doses. Solid lines indicate a FEB dose of $2.4 \mu\text{C}/\mu\text{m}^2$, dashed lines indicate a FEB dose of $4.8 \mu\text{C}/\mu\text{m}^2$. (b) Typical EDS spectra of as-grown Ni FEBID and post-treated NiO deposits. (c)–(e) SEM images of FIB cross-sectional view of Ni FEBIP deposits are indicated in the bottom panels. (c) As-grown Ni FEBID deposit; (d) post-treated Ni FEBIP deposit exposed to O_2 flux, $J \sim 9.1 \times 10^{18} \text{ molecules (cm}^2 \text{ s)}^{-1}$ ($P_{O_2} = 7.6 \times 10^{-6}$ mbar) and FEB dose: $2.4 \mu\text{C}/\mu\text{m}^2$; (e) post-treated Ni FEBIP deposit exposed to O_2 flux, $J \sim 7.7 \times 10^{19} \text{ molecules (cm}^2 \text{ s)}^{-1}$ ($P_{O_2} = 6.4 \times 10^{-5}$ mbar) and FEB dose: $4.8 \mu\text{C}/\mu\text{m}^2$.

3. Results and discussion

3.1. Ni deposits grown by FEBID and FIBID

In this section we report on a study of Ni deposits grown by FEBID and FIBID (see section 2.1 for experimental details).

First, we have investigated the composition of Ni FEBID deposits as a function of the electron beam current, voltage and dwell time. As expected in deposits grown by FEBID using organometallic precursors, no significant changes in Ni content (18 at.% Ni, 82 at.% C) were observed above the nA range [1]. Regarding the beam voltage and the dwell time, we did not observe noteworthy composition changes in the studied range (from 1 kV to 5 kV and from 10 μs to 500 μs). We conclude that it is not possible to produce highly pure Ni deposits by FEBID just by tuning the deposition parameters. Second, rather than FEBID we explored FIBID to grow Ni. A typical Ni FIBID deposit (see section 2.1 for experimental details) has a composition of 22 at.% Ni, 69 at.% C and 9 at.% Ga. An EDS spectrum of a typical deposit is shown in the supporting information. As in the case of FEBID, by tuning the deposition parameters the composition of Ni FIBID deposits does not exhibit sizeable changes. Although our results substantially improve the values already reported in the literature [26].

The slight differences in the Ni content in deposits grown by FEBID and FIBID were not considerable mainly due to the

incomplete dissociation of the precursor molecule under our specific experimental conditions. While a certain Ga content is added in the latter ones due to the Ga^+ FIB. Similar behaviour has been reported for platinum deposits grown by FEBID and FIBID using organometallic compounds as precursor materials [7, 53]. As a conclusion, the use of Ga^+ FIB instead of FEB does not notably improve the quality of deposits in terms of Ni content. Since the gallium contribution into the Ni deposits could impair the functionality of the final deposits, from now on we decided to focus the post-treatment study on deposits grown by FEBID.

3.2. Post-treated Ni deposits

Inspired by reports on the purification of FEBID deposits, transforming them in pure metals using an *in situ* method [32, 34, 39], we attempted to apply this method to our Ni FEBID deposits. The clue of this approach is a post-treatment process at room temperature based on the FEB irradiation under oxygen flux, which produces the carbon removal from deposits. The FEBIP post-treatment process applied to the as-grown Ni FEBID deposits is extensively described in section 2.2 and sketched in figure 1.

In order to investigate the effect of the FEB post-irradiation under O_2 flux to as-grown Ni deposits, they were exposed to two different FEB doses at a series of O_2 fluxes. In figure 2(a), we clearly identify a dependence in the

Figure 3. Ni FEBID deposits exposure under O_2 flux ($J \sim 7.7 \times 10^{19}$ molecules $(\text{cm}^2 \text{ s})^{-1}$, $P_{\text{O}_2} = 6.4 \times 10^{-5}$ mbar) at different FEB doses ranging from 0 to $12 \mu\text{C} \mu\text{m}^{-2}$. (a) Composition of Ni FEBIP deposits. (b) Ni_xO_y thickness. Linear fit is indicated.

composition of deposits on FEB dose and O_2 flux (indicated as the oxygen pressure, $P_{\text{O}_2} = P_{\text{process}} - P_{\text{base}}$). The normalized content of Ni and O increases as a function of the O_2 flux and FEB dose (solid lines: $2.4 \mu\text{C} \mu\text{m}^{-2}$, dashed lines: $4.8 \mu\text{C} \mu\text{m}^{-2}$), while the C content decreases till ~ 10 at.%. EDS spectra of as-grown Ni and optimized post-treated Ni deposits are shown in figure 2(b). By FIB cross-sectional view of the Ni FEBIP deposits, the effect of the FEB post-irradiation into the deposit thickness was investigated. Figures 2(c)–(e) show SEM images of post-treated Ni deposits. The image of figure 2(d) is a typical example of post-processed deposits which are composed of two different layers, a Ni_xO_y layer (bright contrast) on top of the carbonaceous Ni layer (dark contrast), except for the last one which is a homogeneous NiO deposit (see figure 2(e)). We surely observe the decrease in the total thickness from ~ 400 nm in the as-grown Ni FEBID (figure 2(c)) to ~ 70 nm in the NiO deposit (figure 2(e)) due to the carbon matrix removal during the post-treatment process.

The first appreciable effect of the proposed post-treatment process at room temperature is the amorphous carbon removal from the Ni FEBID deposit, where contributions of both O_2 flux and FEB irradiation are required, as has been recently reported with a MeCpPtMe_3 precursor by Villamor *et al* [32]. It indicates that the process could be limited by the oxygen flux, thus a high O_2 concentration becomes crucial for the process. In addition, SEM images illustrate that our post-treated FEBIP procedure (FEB irradiation under O_2 flux) is a top-down process, which suggests that the carbon removal and the Ni oxidation is starting from the surface of the as-grown Ni deposit. This method involves the total thickness of the deposit decreasing and the oxygen reactive species could penetrate deeper into the deposit.

The second effect of our method is the oxidation of Ni atoms forming a continuous and homogeneous nickel oxide deposit. Figure 2(e) shows a highly pure NiO deposit ($1 \times 1 \times 0.07 \mu\text{m}^3$) according to its microstructure measured by TEM and electron diffraction as will be depicted in section 3.2.

The mechanism which governs our proposed post-treatment is explained in the following. By FEB interaction with the Ni deposit, the generated secondary and backscattered electrons dissociate and ionize the O_2 molecules adsorbed on it, resulting in radicals, ionized oxygen molecules and ionized oxygen atoms. These species react with the carbon matrix forming volatile products such as carbon monoxide (CO) and carbon dioxide (CO_2), while the Ni atoms oxidize them into a Ni_xO_y compound.

Moreover, results from Monte Carlo simulations using the CASINO package [55] provide information about the electron trajectories in the sample and the x-ray generation (see supporting information). Evaluating the maximum value of the penetration depth of electron trajectories in as-grown Ni deposit and post-treated one, similar values (~ 110 nm) for the two different deposits were found. In addition, the maximum value of the penetration depth of electron trajectories that will escape the sample surface is ~ 30 nm for the two different deposits as well. Furthermore, for these deposits the x-ray intensity of each element exhibits similar values as a function of the deposit depth. Thus, no large differences in the NiO composition along the thickness could be produced during the post-treatment process.

In order to identify the role of contributions such as FEB dose, FEB penetration depth and O_2 flux in the fabrication of Ni_xO_y deposits, we made three batches of Ni FEBID deposits with dimensions $1 \times 1 \times 1.5 \mu\text{m}^3$ exposed to three different post-treatment processes. In the first batch, as-grown Ni deposits were exposed to an O_2 flux ($J \sim 7.7 \times 10^{19}$ molecules $(\text{cm}^2 \text{ s})^{-1}$, $P_{\text{O}_2} = 6.4 \times 10^{-5}$ mbar) at 5 kV and at different FEB doses ranging from 0 to $12 \mu\text{C} \mu\text{m}^{-2}$. Figure 3 shows compositional analysis (in atomic %) extracted from the EDS spectra and the thickness of Ni_xO_y layer in those deposits. In accordance with the experiments previously shown in figure 2(a), the Ni and O content increase whereas the C content decreases as a function of the FEB dose.

In particular, the C content is lower than 10 at.% at the highest FEB dose, indicating that the fabrication of highly pure NiO is feasible for thicker as-grown Ni deposits. Figure 3(b) shows that the thickness of the Ni_xO_y layer on top of the

Figure 4. Ni_xO_y thickness as a function of FEB voltage in the post-treatment process. FEB dose of $2.4 \mu\text{C } \mu\text{m}^{-2}$ and O_2 flux ($J \sim 7.7 \times 10^{19}$ molecules $(\text{cm}^2 \text{ s})^{-1}$, $P_{\text{O}_2} = 6.4 \times 10^{-5}$ mbar). The red line indicates the linear fit of the data. SEM images of a cross-sectional view of two deposits post-treated at 20 kV and 5 kV.

carbonaceous Ni linearly increases with FEB dose. During this process, the top part of the as-grown Ni FEBID deposit is transformed into a Ni_xO_y layer with ~ 200 nm thickness. These results are consistent with the FEB dose-limited mechanism which governs the process in our specific experimental conditions. Taking into account this linear dependence, it is feasible to fabricate Ni_xO_y deposits in a wide range of thicknesses, limited just by the FEB penetration depth. For higher FEB doses (results not shown here), two effects could be noticed. The first is the complete carbon removal from a certain thickness of our deposit which corresponds with the FEB penetration depth as previously mentioned. The second is that the metallic nickel could be transformed into nickel oxide (NiO) and dinickel trioxide (Ni_2O_3).

In the second batch, deposits were exposed to the same O_2 flux ($J \sim 7.7 \times 10^{19}$ molecules $(\text{cm}^2 \text{ s})^{-1}$, $P_{\text{O}_2} = 6.4 \times 10^{-5}$ mbar), but at fixed FEB dose ($2.4 \mu\text{C } \mu\text{m}^{-2}$) and varying the FEB voltage, ranging from 5 to 25 kV. Figure 4 shows such a dependence of the FEB voltage in the post-treatment process. It is well known that the efficiency in the FEBIP in terms of yield in both additive and subtractive processes is inversely proportional to the FEB voltage [2, 56]. This provides a clear evidence of the essential role of low energy electrons which reach the substrate surface dissociating adsorbed molecules. This argument is fully consistent with the results shown in figure 4 where the thickness of the Ni_xO_y layer on top of the Ni deposit linearly decreases with the FEB voltage in the studied range. As the FEBIP process is less efficient at higher beam voltage, for the same final result a higher FEB dose will be required.

In the third batch, deposits were again exposed to O_2 flux ($J \sim 7.7 \times 10^{19}$ molecules $(\text{cm}^2 \text{ s})^{-1}$, $P_{\text{O}_2} = 6.4 \times 10^{-5}$ mbar), but without FEB irradiation for the same time and O_2 flux as used in the first batch of deposits (maximum time ~ 23 min). EDS analysis on a cross-sectional sample prepared from these deposits showed a small oxygen

contribution in the surface of the deposit and no carbon removal, which is a key point of this process. Their overall composition is not modified (Ni-carbonaceous matrix along the full thickness of the deposit), except for their first nanometres. The measured oxygen content is comparable to those observed in samples exposed to ambient conditions for one week, which indicates that some Ni grains embedded in the first nanometres of the amorphous carbonaceous matrix have been oxidized. We highlight that neither a Ni_xO_y layer on top of the carbonaceous matrix nor the carbon removal from the deposit were observed. This insight certainly proves the essential role of both the FEB irradiation and O_2 flux in the synthesis of highly pure NiO deposits and in the proposed mechanism. Moreover, this method works at room temperature, which is very valuable for future applications.

3.3. Microstructure of as-grown Ni FEBID and highly pure NiO deposits

In order to figure out the microstructure of the as-grown Ni deposits and highly pure NiO, high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) studies on typical samples (see section 2 for experimental details) have been carried out. Additionally, TEM-EDS analysis on this highly pure NiO deposit is shown in the supporting information available at stacks.iop.org/NANO/27/065303/mmedia.

A HRTEM image of the as-grown Ni FEBID deposit is shown in figure 5(a). The microstructure of these deposits is mainly composed of very small Ni clusters, 1–2 nm embedded in an amorphous carbon matrix. The SAED pattern in the inset of the image displays two diffuse rings. This set of rings can be assigned to neither Ni nor NiO phases. This effect could be explained by the amorphous nature of the Ni-containing clusters, explaining a diameter of the rings deviating from those expected for crystalline Ni.

Concerning the microstructure of the NiO deposit, it reveals a polycrystalline structure with crystals of ~ 5 nm, as shown in figure 5(b). A study of the microstructure along the deposit thickness (not shown here), displayed that all the observed SAED patterns are identical, indicating that the crystal structure is the same throughout the entire film. The ring patterns studied in the SAED image suitably match the rocksalt structure of NiO, which is cubic (fcc, Fm-3m, $a = 0.418$ nm). The experimental lattice spacings examined in the inset of the figure 5(b) (0.242, 0.209, 0.147, 0.125 and 0.119 nm) are consistent with the distance between (111), (200), (220), (311) and (222) lattice planes of the NiO structure, respectively. We highlight that these patterns do match neither the cubic Ni structure, nor the hexagonal Ni_2O_3 phase. This cubic structure could also correspond to the paramagnetic phase of NiO above the Néel temperature $T_N = 523$ K [52]. Below T_N the cubic NiO crystal structure where the Ni^{2+} spins is ferromagnetically ordered and could experience antiferromagnetic behaviour [57, 58].

In summary, we proved that the tuned post-treatment method proposed here transforms the as-grown Ni FEBID into a homogeneous NiO deposit, with a cubic structure.

Figure 5. HRTEM images and electron diffraction patterns of a typical (a) as-grown Ni FEBID deposit and (b) NiO deposit.

Figure 6. Four-probe I - V measurements of as-grown Ni FEBID deposits at different temperatures. The inset shows the detailed measurements at 50 and 20 K.

3.4. Study of the electrical transport mechanism

By using a four-probe method in an *ex situ* setup (described in section 2.4), the electrical transport mechanism for as-grown Ni FEBID, Ni FIBID and highly pure NiO deposits has been studied.

We have systematically measured the current (I) as a function of voltage (V) in as-grown Ni FEBID wires at different temperatures, ranging from 295 K to 5 K such as shown in figure 6. A linear I - V behaviour at 270 K in the studied voltage range (from -1 to 1 V), which corresponds to $\sim 1 \times 10^6 \Omega$ in resistance and $\sim 40 \Omega\text{cm}$ in resistivity, has been observed. This resistivity value is $\sim 6 \times 10^6$ times higher than in bulk Ni ($6.7 \mu\Omega\text{cm}$). I - V measurements become non-linear at lower temperatures as expected in semiconductor materials such as the typical nanogranular deposits grown by FEBID [7]. The later dependence may occur by electron hopping between Ni nanograins, mainly described by a tunnelling conduction mechanism. For

Figure 7. Dependence of the resistivity as a function of the temperature ($T^{-0.5}$). (a) As-grown Ni FEBID wire, (b) as-grown Ni FIBID wire. The inset in (a) shows ρ versus T in both wires.

temperatures below 50 K, the non-linear behaviour becomes more pronounced, following an exponential-type energy barrier conduction dependence as observed in the inset of figure 6. The conductance increases with the voltage, as is consistent with semiconductor materials in the regime of hopping conduction [59].

To achieve further insight into the electrical behaviour of as-grown Ni FEBID and a Ni FIBID wires, the dependence of

the resistivity (ρ) as a function of the temperature has been studied (see figure 7).

ρ was calculated from $\rho = R \frac{w \times t}{L}$, where w is the width, t the thickness and L the length of the wire. The width and length were measured by SEM inspection, while the thickness was measured using a FIB cross-section process.

In general, resistivity strongly drops with temperature. This behaviour is again consistent with the hopping regime for low metallic doped amorphous semiconductors, with a low conductance of $0.025 \Omega^{-1} \text{cm}^{-1}$ in Ni FEBID and $8.8 \Omega^{-1} \text{cm}^{-1}$ in Ni FIBID deposits at room temperature. In particular, for the Ni FEBID deposit, the lowest value of ρ (275 K) corresponds to $\sim 1 \times 10^6 \Omega$ in resistance, while the highest one to $\sim 7 \times 10^9 \Omega$ (5 K). In the case of the Ni FIBID deposit, the lowest value of ρ (295 K) corresponds to $\sim 3.6 \times 10^3 \Omega$ in resistance, while the highest one to $\sim 8.8 \times 10^6 \Omega$ (5 K). The resistivity of the Ni FIBID deposit is $0.113 \Omega \text{cm}$ at room temperature, $\sim 1.7 \times 10^4$ times higher than in bulk Ni and $\sim 3.5 \times 10^2$ times lower than as-grown Ni FEBID. The conduction in the semiconducting amorphous matrix is increased in those wires because the higher metallic (~ 1.7 times) content. In conclusion, both types of wires experience a semiconductor behaviour and appropriately follow the equation $\rho(T) \sim \rho_0 \exp(T_0/T)^{1/2}$ where ρ_0 is the pre-exponential factor and T_0 is the characteristic temperature (see figure 7). This behaviour indicates that the electronic conduction is dominated by electron hopping in a band of localized states, which needs to overcome an activation energy to move them from one state to another. This mechanism is well described as variable range hopping [60] and has been already studied in granular FEBID and FIBID structures [6, 7].

Finally, electrical measurements were carried out in highly pure NiO deposits. Their electrical resistivity is $\sim 2000 \Omega \text{cm}$ at room temperature, being ~ 73 and $\sim 1.8 \times 10^4$ times higher than our as-grown Ni FEBID and Ni FIBID, respectively. For NiO thin films a range of resistivity values from $1 \Omega \text{cm}$ to $10^5 \Omega \text{cm}$ have been reported in literature [61–63]. Such strong differences could be due to alterations in stoichiometry and/or microstructure. Most excitingly, current versus voltage measurements in our NiO wires reveal a reproducible resistance switching phenomenon at relatively low voltages (see figure S5 in the supporting information). The origin of these conducting paths is not fully understood, although it could be related to the microstructure, nickel defects and oxygen vacancies in our NiO deposits [50, 51]. To understand the voltage switching behaviour and its related mechanism further study will be needed which is beyond the scope of the present study.

3.5. Co/NiO exchange biased bilayers

Another area of interest concerns the physics of FM/AFM bilayers. This type of system is attractive because its potential applications in magnetoelectronic nanodevices such as spin valve systems. FM/AFM systems can experience at their interface an exchange anisotropy (exchange bias), when the AFM spins at the interface are aligned with the FM spins. By

Figure 8. Hysteresis loops extracted from magneto-optical Kerr measurements on Co/NiO wire and Co wire used as a reference.

using such an interface coupling effect it is possible to pin the magnetization direction of the FM layer, resulting in a shift of the hysteresis loop along the field direction and/or a coercive field increase [64, 65]. Because of its well-known cubic crystallographic structure (see section 3.4) and anti-ferromagnetic order, NiO deposit is considered a good candidate for a FM (Co or Fe)/AFM bilayer system [66].

Figure 8 shows the hysteresis loops for a Co wire and a Co/NiO bilayer (see section 2.6 for experimental details), where 50 averaged intensity values of the images result in the measured signal for each applied magnetic value. The noise over the signal is around 20%.

An increase in H_c is observed in the Co/NiO bilayer compared to the Co wire taken as a reference. The experimental hysteresis loop shows a coercivity enhancement of $\Delta H_c \sim 1.5 \text{ mT}$, almost 40% with respect to the reference. Such an effect could be explained in terms of the small magnetic anisotropy of the NiO deposit due to its nanometric sized and polycrystalline structure (see section 3.3), which is able to pin the magnetization of the Co layer just enhancing its coercivity. This behaviour is well established in systems that display an exchange-bias effect. By annealing the samples very close to the T_N (250 °C) and zero field cooling, the coercivity enhancement vanishes, indicating that the exchange coupling in the Co/NiO bilayer is responsible for the noticed coercivity enhancement. Thus, we believe that our FEBIP NiO is indeed a promising candidate for exchange biased magnetic devices, entirely made by FEB processes.

4. Conclusion

We have successfully fabricated and characterized Ni deposits fabricated by FEBID and FIBID techniques using $(\text{MeCp})_2\text{Ni}$ as a precursor. The first type has a Ni content of 18 at.% and is composed of very small Ni clusters (1–2 nm in size) embedded in an amorphous carbonaceous matrix. Its

resistivity value at 270 K is $\sim 40 \Omega\text{cm}$. The Ni deposits grown by FIBID have a higher metallic content and their resistivity is $0.113 \Omega\text{cm}$ at room temperature. Both kind of deposits experience an electronic conduction mechanism governed by electron hopping in a band of localized states. This mechanism is well known for nanogranular systems as variable range hopping.

Additionally, we have demonstrated for the first time a successful method to synthesize binary oxides at room temperature by FEBIP. The fabrication method consists of two sequential *in situ* steps: (1) Ni FEBID and (2) FEB irradiation under O_2 flux. By tuning the FEB dose and O_2 flux for the second step, it results in well-defined and homogeneous highly pure nickel oxide deposits. These deposits have a polycrystalline structure with a grain size of $\sim 5 \text{ nm}$ which properly fits with the cubic (fcc) rocksalt. Their electrical measurements showed a resistivity value of $\sim 2000 \Omega\text{cm}$ at room temperature and a non-ohmic behaviour.

We have shown the first effective growth of a resistive switching NiO wire [50, 51] and an exchange biased (Co/NiO) wire [52] by FEBIP. These results are highly interesting in view of future applications in memory resistors and devices exploiting an exchange-bias effect.

This work could give new insights and inspire further research on synthesis of compounds such as binary oxides, magnetic alloys, broadening the horizon of focused beam induced processing techniques for high-speed data processing devices and high-density memories.

Supporting information

Compositional analysis of Ni deposits. Monte Carlo simulations via CASINO software. EDS analysis in post-treated NiO deposit at the nanoscale.

Acknowledgements

This work was supported by the project FOM-08.1898, a programme supported by the Dutch Government. The authors thank the FEI company for giving us the opportunity to use the proposed FEBIP method. Solliance is acknowledged for funding the TEM facility.

References

- [1] Utke I, Hoffmann P and Melngailis J 2008 Gas-assisted focused electron beam and ion beam processing and fabrication *J. Vac. Sci. Technol. B* **26** 1197–276
- [2] van Dorp W F and Hagen C W 2008 A critical literature review of focused electron beam induced deposition *J. Appl. Phys.* **104** 81301
- [3] Sadki E S, Ooi S and Hirata K 2004 Focused-ion-beam-induced deposition of superconducting nanowires *Appl. Phys. Lett.* **85** 6206–8
- [4] Guillamón I, Suderow H, Vieira S, Fernández-Pacheco A, Sesé J, Córdoba R, De Teresa J M and Ibarra M R 2008 Nanoscale superconducting properties of amorphous W-based deposits grown with a focused-ion-beam *New J. Phys.* **10** 093005
- [5] Córdoba R *et al* 2013 Magnetic field-induced dissipation-free state in superconducting nanostructures *Nat. Commun.* **4** 1437
- [6] Fernández-Pacheco A, De Teresa J M, Córdoba R and Ibarra M R 2009 Metal–insulator transition in Pt–C nanowires grown by focused-ion-beam-induced deposition *Phys. Rev. B* **79** 174204
- [7] De Teresa J M, Córdoba R, Fernández-Pacheco A, Montero O, Strichovanec P and Ibarra M R 2009 Origin of the difference in the resistivity of As-grown focused-ion- and focused-electron-beam-induced Pt nanodeposits *J. Nanomater.* **2009** 936863
- [8] Bret T, Utke I, Bachmann A and Hoffmann P 2003 *In situ* control of the focused-electron-beam-induced deposition process *Appl. Phys. Lett.* **83** 4005–7
- [9] Faraby H, DiBattista M and Bandaru P R 2014 Reduced electrical impedance of SiO_2 , deposited through focused ion beam based systems, due to impurity percolation *J. Appl. Phys.* **116** 204301
- [10] Lavrijsen R *et al* 2011 Fe:O:C grown by focused-electron-beam-induced deposition: magnetic and electric properties *Nanotechnology* **22** 025302
- [11] Córdoba R *et al* 2012 Giant anomalous Hall effect in Fe-based microwires grown by focused-electron-beam-induced deposition *J. Phys. D: Appl. Phys.* **45** 035001
- [12] Fernández-Pacheco A, Serrano-Ramón L, Michalik J M, Ibarra M R, De Teresa J M, O'Brien L, Petit D, Lee J and Cowburn R P 2013 Three dimensional magnetic nanowires grown by focused electron-beam induced deposition *Sci. Rep.* **3** 1492
- [13] Gavagnin M, Wanzenboeck H D, Wachter S, Shawrav M M, Persson A, Gunnarsson K, Svedlindh P, Stöger-Pollach M and Bertagnolli E 2014 Free-standing magnetic nanopillars for 3D nanomagnet logic *ACS Appl. Mater. Interfaces* **6** 20254–60
- [14] Gavagnin M, Wanzenboeck H D, Belić D and Bertagnolli E 2013 Synthesis of individually tuned nanomagnets for nanomagnet logic by direct write focused electron beam induced deposition *ACS Nano* **7** 777–84
- [15] De Teresa J M and Córdoba R 2014 Arrays of densely packed isolated nanowires by focused beam induced deposition plus Ar + milling *ACS Nano* **8** 3788–95
- [16] Fernández-Pacheco A, De Teresa J M, Córdoba R, Ibarra M R, Petit D, Read D E, O'Brien L, Lewis E R, Zeng H T and Cowburn R P 2009 Domain wall conduit behavior in cobalt nanowires grown by focused electron beam induced deposition *Appl. Phys. Lett.* **94** 192509
- [17] Fernández-Pacheco A *et al* 2009 Magnetization reversal in individual cobalt micro- and nanowires grown by focused-electron-beam-induced-deposition *Nanotechnology* **20** 475704
- [18] Botman A *et al* 2008 Investigation of morphological changes in platinum-containing nanostructures created by electron-beam-induced deposition *J. Vac. Sci. Technol. B* **26** 2464
- [19] Botman A, Hesselberth M and Mulders J J L 2008 Improving the conductivity of platinum-containing nano-structures created by electron-beam-induced deposition *Microelectron. Eng.* **85** 1139–42
- [20] Peña-Quesada L, Mitra J and Dawson P 2007 Non-linear electronic transport in Pt nanowires deposited by focused ion beam *Nanotechnology* **18** 215203
- [21] Tao T, Ro J S, Melngailis J, Xue Z L and Kaesz H D 1990 Focused ion-beam induced deposition of platinum *J. Vac. Sci. Technol. B* **8** 1826–9
- [22] De Marzi G, Iacopino D, Quinn A J and Redmond G 2004 Probing intrinsic transport properties of single metal

- nanowires: direct-write contact formation using a focused ion beam *J. Appl. Phys.* **96** 3458–62
- [23] Lin J F, Bird J P, Rotkina L and Bennett P A 2003 Classical and quantum transport in focused-ion-beam-deposited Pt nanointerconnects *Appl. Phys. Lett.* **82** 802–4
- [24] Barry J D, Ervin M, Molstad J, Wickenden A, Brintlinger T, Hoffman P and Meingailis J 2006 Electron beam induced deposition of low resistivity platinum from Pt(PF₃)₃ [sub 4] *J. Vac. Sci. Technol. B* **24** 3165
- [25] Fernández-Pacheco A, De Teresa J M, Córdoba R and Ibarra M R 2009 Magnetotransport properties of high-quality cobalt nanowires grown by focused-electron-beam-induced deposition *J. Phys. D: Appl. Phys.* **42** 055005
- [26] Perentes A, Sinicco G, Boero G, Dvir B and Hoffmann P 2007 Focused electron beam induced deposition of nickel *J. Vac. Sci. Technol. B* **25** 2228–32
- [27] Botman A, Mulders J J L and Hagen C W 2009 Creating pure nanostructures from electron-beam-induced deposition using purification techniques: a technology perspective *Nanotechnology* **20** 372001
- [28] Córdoba R, Sesé J, De Teresa J M and Ibarra M R 2010 High-purity cobalt nanostructures grown by focused-electron-beam-induced deposition at low current *Microelectron. Eng.* **87** 1550–3
- [29] Mehendale S, Mulders J J L and Trompenaars P H F 2013 A new sequential EBID process for the creation of pure Pt structures from MeCpPtMe₃ *Nanotechnology* **24** 145303
- [30] Plank H, Noh J H, Fowlkes J D, Lester K, Lewis B B and Rack P D 2014 Electron-beam-assisted oxygen purification at low temperatures for electron-beam-induced Pt deposits: towards pure and high-fidelity nanostructures *ACS Appl. Mater. Interfaces* **6** 1018–24
- [31] Sachser R, Reith H, Huzel D, Winhold M and Huth M 2014 Catalytic purification of directly written nanostructured Pt microelectrodes *ACS Appl. Mater. Interfaces* **6** 15868–74
- [32] Villamor E, Casanova F, Trompenaars P H F and Mulders J J L 2015 Embedded purification for electron beam induced Pt deposition using MeCpPtMe₃ *Nanotechnology* **26** 095303
- [33] Lewis B B, Stanford M G, Fowlkes J D, Lester K, Plank H and Rack P D 2015 Electron-stimulated purification of platinum nanostructures grown via focused electron beam induced deposition *Beilstein J. Nanotechnol.* **6** 907–18
- [34] Mehendale S, Mulders J J L and Trompenaars P H F 2015 Purification of Au EBID structures by electron beam post-irradiation under oxygen flux at room temperature *Microelectron. Eng.* **141** 207–10
- [35] Stanford M G, Lewis B B, Noh J H, Fowlkes J D, Roberts N A, Plank H and Rack P D 2014 Purification of nanoscale electron-beam-induced platinum deposits via a pulsed laser-induced oxidation reaction *ACS Appl. Mater. Interfaces* **6** 21256–63
- [36] Roberts N A, Fowlkes J D, Magel G A and Rack P D 2013 Enhanced material purity and resolution via synchronized laser assisted electron beam induced deposition of platinum *Nanoscale* **5** 408–15
- [37] Frabboni S, Gazzadi G C and Spessot A 2006 Transmission electron microscopy characterization and sculpting of sub-1 nm Si-O-C freestanding nanowires grown by electron beam induced deposition *Appl. Phys. Lett.* **89** 113108
- [38] Botman A, Mulders J J L, Weemaes R and Mentink S 2006 Purification of platinum and gold structures after electron-beam-induced deposition *Nanotechnology* **17** 3779–85
- [39] Belić D, Shawrav M M, Gavagnin M, Stöger-Pollach M, Wanzenboeck H D and Bertagnolli E 2015 Direct-write deposition and focused-electron-beam-induced purification of gold nanostructures *ACS Appl. Mater. Interfaces* **7** 2467–79
- [40] Shimojo M, Takeguchi M, Mitsuishi K, Tanaka M and Furuya K 2008 Formation of nanoscale platinum and iron oxide structures using electron beam induced deposition techniques *J. Phys.: Conf. Ser.* **100** 052016
- [41] Plank H, Kothleitner G, Hofer F, Michelitsch S G, Gspan C, Hohenau A and Krenn J R 2011 Optimization of postgrowth electron-beam curing for focused electron-beam-induced Pt deposits *J. Vac. Sci. Technol. B* **29** 051801
- [42] Frabboni S, Gazzadi G C, Felisari L and Spessot A 2006 Fabrication by electron beam induced deposition and transmission electron microscopic characterization of sub-10 nm freestanding Pt nanowires *Appl. Phys. Lett.* **88** 213116
- [43] Geier B, Gspan C, Winkler R, Schmied R, Fowlkes J D, Fitzek H, Rauch S, Rattenberger J, Rack P D and Plank H 2014 Rapid and highly compact purification for focused electron beam induced deposits: a low temperature approach using electron stimulated H₂O reactions *J. Phys. Chem. C* **118** 14009–16
- [44] Winhold M, Schwalb C H, Porra F, Sachser R, Frangakis A S, Kaempken B, Terfort A, Auner N and Huth M 2011 Binary Pt-Si nanostructures prepared by focused electron-beam-induced deposition *ACS Nano* **5** 9675–81
- [45] Porra F, Begun E, Winhold M, Schwalb C H, Sachser R, Frangakis A S and Huth M 2012 Room temperature L1₀ phase transformation in binary CoPt nanostructures prepared by focused-electron-beam-induced deposition *Nanotechnology* **23** 185702
- [46] Porra F, Kämpken B, Terfort A and Huth M 2013 Fabrication and electrical transport properties of binary Co-Si nanostructures prepared by focused electron beam-induced deposition *J. Appl. Phys.* **113** 53707
- [47] Bresin M, Chamberlain A, Donev E U, Samantaray C B, Schardien G S and Hastings J T 2013 Electron-beam-induced deposition of bimetallic nanostructures from bulk liquids *Angew. Chem. Int. Ed. Engl.* **52** 8004–7
- [48] Shawrav M M, Belić D, Gavagnin M, Wachter S, Schinnerl M, Wanzenboeck H D and Bertagnolli E 2014 Electron beam-induced CVD of nanoalloys for nanoelectronics *Chem. Vap. Depos.* **20** 251–7
- [49] Che R C, Takeguchi M, Shimojo M, Zhang W and Furuya K 2005 Fabrication and electron holography characterization of FePt alloy nanorods *Appl. Phys. Lett.* **87** 223109
- [50] Seo S et al 2004 Reproducible resistance switching in polycrystalline NiO films *Appl. Phys. Lett.* **85** 5655
- [51] Kim S I, Lee J H, Chang Y W, Hwang S S and Yoo K-H 2008 Reversible resistive switching behaviors in NiO nanowires *Appl. Phys. Lett.* **93** 033503
- [52] Roth W 1958 Magnetic structures of MnO, FeO, CoO, and NiO *Phys. Rev.* **110** 1333–41
- [53] Langford R M, Wang T X and Ozkaya D 2007 Reducing the resistivity of electron and ion beam assisted deposited Pt *Microelectron. Eng.* **84** 784–8
- [54] Friedli V and Utke I 2009 Optimized molecule supply from nozzle-based gas injection systems for focused electron- and ion-beam induced deposition and etching: simulation and experiment *J. Phys. D: Appl. Phys.* **42** 125305
- [55] Drouin D, Couture A R, Joly D, Tastet X, Aimez V and Gauvin R 2007 CASINO V2.42—A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users *Scanning* **29** 92–101
- [56] Randolph S, Toth M, Cullen J, Chandler C and Lobo C 2011 Kinetics of gas mediated electron beam induced etching *Appl. Phys. Lett.* **99** 213103
- [57] Mironova-Ulmane N, Kuzmin A, Grabis J, Sildos I, Voronin V I, Berger I F and Kazantsev V A 2011 Structural and magnetic properties of nickel oxide nanopowders *Solid State Phenom.* **168–169** 341–4
- [58] Hutchings M T and Samuelsen E J 1972 Measurement of spin-wave dispersion in NiO by inelastic neutron scattering and its relation to magnetic properties *Phys. Rev. B* **6** 3447–61

- [59] Yu D, Wang C, Wehrenberg B L and Guyot-Sionnest P 2004 Variable range hopping conduction in semiconductor nanocrystal solids *Phys. Rev. Lett.* **92** 216802
- [60] Mott N F 1971 Conduction in non-crystalline systems .7. Non-ohmic behaviour and switching *Phil. Mag.* **24** 911
- [61] Kögeler C, Weng R, Schroeder H, Symanczyk R, Majewski P, Ufert K-D, Waser R and Kund M 2010 Study on the dynamic resistance switching properties of NiO thin films *Thin Solid Films* **518** 2258–60
- [62] Patil P and Kadam L 2002 Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films *Appl. Surf. Sci.* **199** 211–21
- [63] Kohmoto O, Nakagawa H, Isagawa Y and Chayahara A 2001 Effect of heat treatment on the oxygen content and resistivity in sputtered NiO films *J. Magn. Magn. Mater.* **226-230** 1629–30
- [64] Nogués J and Schuller I K 1999 Exchange bias *J. Magn. Magn. Mater.* **192** 203–32
- [65] Nogués J, Sort J, Langlais V, Skumryev V, Suriñach S, Muñoz J S and Baró M D 2005 Exchange bias in nanostructures *Phys. Rep.* **422** 65–117
- [66] Ohldag H, van der Laan G and Arenholz E 2009 Correlation of crystallographic and magnetic domains at Co/NiO(001) interfaces *Phys. Rev. B* **79** 052403