Micro-patterning of NdFeB and SmCo magnet films for integration into micro-electro-mechanical-systems

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Abstract

The integration of high performance RE-TM (NdFeB and SmCo) hard magnetic films into Micro-Electro-Mechanical-Systems (MEMS) requires their patterning at the micron scale. In this paper we report on the applicability of standard micro-fabrication steps (film deposition onto topographically patterned substrates, wet etching and planarization) to the patterning of 5 µm thick RE-TM films. While NdFeB comprehensively fills micron scaled trenches in patterned substrates, SmCo deposits are characterized by poor filling of the trench corners, which poses a problem for further processing by planarization. The magnetic hysteresis loops of both the NdFeB and SmCo patterned films are comparable to those of non-patterned films prepared under the same deposition/annealing conditions. A micron-scaled multipole magnetic field pattern is directly produced by the unidirectional magnetization of the patterned films. NdFeB and SmCo show similar behavior when wet etched in an amorphous state: etch rates of approximately 1.25µm/minute and vertical side walls which may be attributed to a large lateral over-etch of typically 20 µm. Chemical-Mechanical Planarization (CMP) produced material removal rates of 0.5-3µm/min for amorphous NdFeB. Ar ion etching of such films followed by the deposition of a Ta layer prior to film crystallization prevented degradation in magnetic properties compared to non-patterned films.

Introduction

There are many potential applications for high performance micro-magnets in magnetic MEMS.[1] However, the emergence of magnetic MEMS has been hindered by the challenge of integrating high quality magnets using techniques compatible with today's MEMS technologies.[2] One of the most promising reports to date, from the viewpoint of integration, concerns the fabrication of $Co_{80}Pt_{20}$ magnets {cylinders of height 2 μm and diameter 5 or 10 μm, μ_0H_c = 0.5 T, $(BH)_{max}$= 52 kJ/m^3) by electro-deposition at room temperature.[3] The successful integration of RE-TM magnets into devices, for which much higher coercivities and energy densities may be expected, should provide a significant boost to the field of magnetic MEMS. To achieve this, two challenges are faced. The first of these is the preparation of thick film magnets (1-100 μm) at reasonable deposition rates over relatively large surface areas. High rate triode sputtering has been shown to be suitable for the preparation of thick films of both SmCo[4] and NdFeB[5] alloys and we have recently used this technique to prepare high energy product 5 μm thick films of these materials on Si substrates ($SmCo_7$ - 140 kJ/m^3, NdFeB - 400 kJ/m^3). [6,7]

The second challenge to be solved is the lateral structuring of the films at the micron-scale. The use of Si substrates greatly facilitates lateral structuring using standard micro-technology processes. However, the use of these standard processes for the structuring of rare earth based alloys, in particular steps based on chemical attack, is challenging because of the poor resistance of these alloys to oxidation. Features of size 5x5 μm up to 100x100 μm were wet-etched into 1 μm thick NdFeB films sputtered onto AL_2O_3 substrates using salpetric acid.[8] Reports exist on both the dry and wet etching of SmCo films deposited on Al_2O_3 substrates. [9,10] Wang et al. compared the etching rates achieved using different Ar based plasmas and found that addition of Cl_2 to an Ar plasma led to a 10-fold increase in etching rate (a maximum value of 0.7 μm/min. was reported) compared with a pure Ar plasma.[9] Budde et al. reported an increase in etching rate of SmCo from 0.02 μm/min for dry etching to 12.5μm/min for wet etching.[10] A major concern is whether coercivity is altered during structuring. Budde et al. referred to the magnetic properties of the non-patterned films but not to those of the wet etched films, [10] while Wang et al. only gave the magnetic properties of films etched at very low rates.[9] Lemke et al. reported that no significant change was observed in the coercivity of their patterned NdFeB films, which however, had relatively low coercivities to begin with (0.2 T). [8]

In this paper we report on a study of three different processes ((i) film deposition onto patterned substrates, (ii) wet etching and (iii) planarization) for the micro-patterning of RE-TM films. The influence of the processing steps on the magnetic properties of the hard magnetic material is presented.

Experimental details

Patterned Si/SiO_2 substrates containing trench motifs with individual trenches of depth 6 μm, length 500 μm and trench/wall widths on the scale of 5-100 μm were prepared by standard micro-fabrication processes: deposition of 6μm of SiO_2 on Si followed by photo-lithography through a mask containing the trench motif and finally dry etching of the SiO_2. The magnetic (NdFeB, SmCo) and buffer/capping (Ta,Cr) layers were deposited using DC triode sputtering at rates of the order of 18 μm/hour,[6,7] onto patterned Si/SiO_2 wafers and standard Si wafers. The NdFeB films were deposited at temperatures ≤ 400°C, and were thus amorphous.[7] The SmCo films were deposited in both the amorphous (no-substrate heating) and crystallised state (T_{sub}=400°C).[6] Post-deposition annealing of amorphous films was carried out at 750°C for 10 minutes under secondary vacuum (10^{-6}mbar) either in-situ (full wafer) or ex-situ on samples of typical surface area 5 x 5 mm. Film thicknesses were measured using a Dektak profilometer. Magnetic measurements were made at 300 K on a

Vibrating Sample Magnetometre (VSM) with a maximum magnetic field of 8T. Observations were made with an FEG-SEM (Gemini 1530).

Results and discussion

1) Micro-patterning of RE-TM films

I - Deposition of RE-TM films onto patterned substrates

SEM images of fractured cross-sections of pieces of {Ta(100nm)/NdFeB(8µm)/Ta(100nm)} and {Cr(100nm)/SmCo(8µm)/Cr(100nm)} films, deposited onto non-heated, patterned Si/SiO_2 substrates, are shown in figures 1a,b. It was found that NdFeB fills comprehensively and continuously the patterns even for trenches with an aspect ratio of 1.2 (6µm deep, 5µm wide). Though SmCo fills the trenches, the film structure is different at the trench corners, appearing granular and less dense than the rest of the film (fig 1c). Note that because the substrates were not heated during deposition, the as-deposited films are amorphous. Deposition of SmCo in the crystallized state, achieved by heating the substrate to 400°C during deposition,[6] did not lead to an improvement of the trench corners. Nor did a decrease in the sputtering rate from 18 to 10µm/h, achieved by decreasing the target potential from 900 to 300V. The difference in trench filling behavior of the NdFeB and SmCo alloys is not presently understood.

The amorphous as-deposited films were annealed at a temperature of 750°C for 10 minutes to crystallize the hard magnetic $Nd_2Fe_{14}B$ and $SmCo_7$ phases.[6,7] Post-deposition annealing of the entire 100 mm patterned wafers with NdFeB layers did not lead to film fracture or peel-off. This is in contrast with the case of continuous planar films deposited onto 100 mm Si wafers, for which peel-off occurs in the central region of the film.[7] In contrast, annealing of the amorphous SmCo films deposited on the patterned wafers does lead to film peel-off, as was already observed with continuous planar films deposited on Si substrates.[6] Peel-off occurs via fracture below the SmCo/substrate interface (i.e. some SiO_2 remains adhered to the SmCo film). When deposited directly in the crystallized state (T_{sub} = 400°C), peel-off from patterned SmCo films does not occur in the trenched regions, but only in the continuous planar regions between different motifs.

Film peel-off is attributed to the build up of strain due to the difference in thermal expansion coefficients of the magnetic layer and the Si wafer. While Si has a thermal expansion coefficient of 2.6 $x10^{-6}$/K, values in the range of 6 $x10^{-6}$/K to 12 $x10^{-6}$/K have been measured for RE-TM alloys at 750°C.[11] The fact that NdFeB films have distinctly less tendency to peel-off than $SmCo_7$ films may be attributed to two particular features. The first is that $Nd_2Fe_{14}B$ has a lower thermal expansion anisotropy than $SmCo_5$ ($SmCo_7$ is closely related to the $SmCo_5$ phase).[11] The second is the fact that $Nd_2Fe_{14}B$ is an Invar system. A large positive magnetovolume anomaly develops in the ferromagnetic state, below 592 K, which reduces very significantly the material's thermal expansion. Note finally that a study of the mechanical properties of these films as a function of the film dimensions is underway.

II – Wet etching of RE-TM films

Wet etching trials on non-capped 5µm thick RE-TM films were carried out on continuous planar films in the amorphous state. This is because it is expected that amorphous films should be less prone to oxidation than crystalline films, due to the absence of grain boundaries which can act as paths for oxygen diffusion. Optical lithography was used to define mm sized patterns in a resist layer deposited on the RE-TM film. Removal rates of approximately 1.25µm/min. were achieved for both NdFeB and SmCo wet etched at room temperature in an acidic bath containing $(NH_4)_2S_2O_8$, H_2O and H_2SO_4. A large lateral over-etch of typically 20 µm occurred in both materials. The side walls of the etched films are relatively vertical (Figure 2). Budde had also reported vertical flanges for wet-etched SmCo films, which he attributed to large lateral over-etching. [9] Note that patterns as small as a few tens of µm in size could in principle also be defined this way, the actual size used here was chosen to suit the overall process flow being studied (see below).

III – Planarization of NdFeB films

Chemical-Mechanical-Planarization can be used to eliminate topographical relief. This step was developed for NdFeB only, as the poor quality of the trench corners of SmCo deposited on patterned substrates and stress issues render them unsuitable for planarization. 5µm thick NdFeB films were deposited onto non-heated planar Si substrates. Wet etching was used to topographically pattern the magnetic films. These patterned films were planarized to a final thickness of 1 µm using chemical-mechanical planarization (CMP). Film removal rates of 0.5 to 3µm/min were achieved by varying the composition of the polishing slurry.

2) Magnetic properties of micro-magnets

The extrinsic properties of a permanent magnet (coercivity, remanence, loop squareness…) depend on both the material's intrinsic magnetic properties and the magnet's microstructure (grain size, grain boundary quality, oxygen content, crystallographic texture…). As the latter may be influenced by how the magnet is prepared, the different steps involved in the micro-patterning of magnets may be expected to influence the micro-magnet's extrinsic properties. The magnetic properties of micro-magnets prepared using the various steps described above were thus evaluated.

I – Magnetic properties following deposition onto patterned substrates

VSM measurements of RE-TM films deposited onto patterned substrates are compared with those of films deposited onto non-patterned substrates and processed under similar conditions (Figure 3). More specifically, the NdFeB films were deposited amorphous at 400°C and crystallised during a post-deposition anneal (750°C/10 minutes), while the SmCo films were deposited in the crystallised state (T_{sub} = 400°C). These deposition temperatures were chosen to induce crystallographic texture and thus maximize the remanent magnetization and energy product of the hard magnetic material.[6,7] It can be seen that, for a given material, the hysteresis loops of the patterned and planar films are very similar.

The patterned NdFeB films, which have an out-of-plane texture, were magnetized by the application of an out-of-plane magnetic field of 7T. A polar Kerr image of a uniaxial Magneto-Optic-Indicator-Film (MOIF)[12] placed on top of the magnetized patterned NdFeB film is shown in Figure 4. The black/white contrast corresponds to the up/down direction of magnetization in the MOIF. This image reveals that the patterned sections of the film produce micron scaled multi-polar magnetic field patterns at the position of the MOIF with a pole pitch approximately equal to the pitch of the trench walls (note that the non-patterned sections of film between motifs do not produce enough stray field to saturate the MOIF). This is only a qualitative image and quantitative imaging using a planar MOIF is underway. The relevance of this result is that following a simple fabrication procedure (deposition + annealing of the magnetic layer), the trivial application of a uniaxial magnetic field can be used to produce a micron-scaled multi-polar field pattern. These micropatterned films have been used to levitate diamagnetic beads,[13] and have potential applications in lab-on-chip experiments.

II - Magnetic properties following etching and planarization

Rare earth elements have a high affinity for oxygen and it is well known that surface oxidation of RE-TM magnets leads to degradation in their magnetic properties.[14] Thus fabrication steps involving chemicals could be critical for the processing of RE-TM films. To assess the impact of the etching/planarization steps, the 1 μm thick amorphous NdFeB patterns produced were further processed under two different conditions : (#1) simple annealing and (#2) annealing following Ar ion etching during 5 min (to remove any damaged surface layer produced during the chemical attack) and deposition of a Ta capping layer. The annealing treatments were carried out at 750°C for 10 min. in a rapid heating furnace.[15] In-plane VSM measurements of these samples are compared in figure 5. It can be seen that good magnetic properties (single phase behavior, high coercivity ($\mu_0 H_C$ = 1.5 T), good squareness for an isotropic sample) are achieved for the sample #2 which was cleaned and capped before annealing. Sample #1 shows approximately the same coercivity value but it has poor loop squareness indicative of a wide distribution in coercivity values of individual grains. Note that samples which were capped with Ta but not etched prior to annealing had a small amount of a soft magnetic phase (data not shown). It can be concluded that light etching serves to remove some damaged material and that the Ta capping layer protects the magnetic film from oxidation during the annealing step.

Conclusions

The applicability of some standard micro-fabrication steps has been tested for 5 μm thick rare earth transition metal (NdFeB and SmCo) films. It has been found that the deposition of films onto pre-patterned Si/SiO_2 substrates with trench motifs with individual trenches of depth 6 μm and trench/wall widths on the scale of 5-100 μm works better for NdFeB than for SmCo. While NdFeB fills comprehensively and continuously the trenches, the SmCo deposits are characterized by poor filling of the trench corners (i.e. full density is not achieved in these areas). The use of patterned substrates was found to improve the mechanical behavior of the RE-TM films. In contrast to the case of films deposited on non-patterned substrates, film fracture did not occur during the post-deposition high temperature (750°C) annealing treatment of amorphous NdFeB films deposited on patterned wafers. However fracture still occurs upon annealing of amorphous SmCo films deposited on patterned wafers, which should thus be directly deposited in the crystallized state. The magnetic properties (hysteresis loops) of patterned NdFeB and SmCo films are comparable to those of non-patterned films prepared under the same deposition/annealing conditions. The unidirectional magnetization of such a topographically patterned film directly produces a micron-scaled multi-pole magnetic field pattern.

Wet etching of NdFeB and SmCo gave very similar results: etch rates of approximately 1.25μm/min., large lateral over-etch of typically 20 μm and vertical side walls.

Chemical-Mechanical Planarization was studied for NdFeB films. Material removal rates of 0.5 to 3μm/min were achieved. Degradation in magnetic properties of the thus patterned NdFeB films, relative to continuous planar films, was prevented by the application of Ar ion etching of the film surface followed by the deposition of a Ta layer prior to film annealing.

The first fully integrated magnetic micro-switch was made with electrodeposited hexagonal close packed CoPtP magnets with relatively low values of coercivity and remanence (μ_0H_c= 0.3 T, μ_0M_r= 0.3 T).[16] The integration of high performance NdFeB into a modified version of this micro-switch, by the consecutive application of the processing steps developed in this work (figure 6), is presently being studied.[17] Note that in this process flow the wet etching step is not used to define the final size of the magnet but as a coarse patterning step prior to CMP. Thus the large lateral over-etch observed does not pose a problem. The applicability of these micro-fabrication steps to thicker RE-TM films needs to be established. Finally, it should be noted that the high processing temperatures needed for producing NdFeB (550-750°C) films dictate that these films need to be integrated onto a given wafer before other temperature sensitive components. On the other hand, SmCo alloys, which are produced at relatively low temperatures (350-400°C), may be processed "above IC" (integrated circuit).

Acknowledgments

This work was carried out in the framework of the ANR "Nanomag2" project. R.G. is grateful for a CNRS visiting research fellowship at Institut Néel.

References

[1] O. Cugat, J. Delamare and G. Reyne, IEEE Trans. Mag. **39**, 3608 (2003)

[2] O. Gutfleisch and N.M. Dempsey, in *Magnetic Nanostructures in Modern Technology*, edited by G. Asti, L. Pareti and M. Ghidini, (Springer, 2007), p. 167.

[3] I. Zana, G. Zangari, Jin-Woo Park and M. G. Allen, J. Magn. Magn. Mat. 272–276, e1775-e1776 (2004)

[4] R.P. Allen, S.D. Dahlgren, H.W. Arrowsmith and J. P. Heinrich, Technical report AFML-TR-74-87 (1974)

[5] B.A. Kapitanov , N.V. Kornilov, Ya.L Linetsky, and V.Yu. Tsvetkov, J. Magn. Magn. Mater. **127**, 289 (1993).

[6] A. Walther, D. Givord, N.M. Dempsey, K. Khlopkov and O. Gutfleisch, J. Appl. Phys. **103** 043911 (2008)

[7] N.M. Dempsey, A. Walther, F. May and D. Givord, K. Khlopkov and O. Gutfleisch, Appl. Phys. Lett. 90 092509 (2007)

[8] H. Lemke, T. Lang, T. Giiddenhenrich and C. Heiden, J. Magn. Magn. Mater. **148**, 426 (1995)

[9] J. J. Wang, J. R. Childress, S. J. Pearton, F. Sharifi, K. H. Dabmen, E. S. Giliman F. J. Cadieu, R. Rani, X. R. Qian, and Li Chen, J. Electrochemical Soc. **145** 2512 (1998)

[10] T. Budde and H. H. Gatzen, J. Appl. Phys. **99**, 08N304 (2006)

[11] C. H. Chen, M. S. Walmer, M. H. Walmer, W. Gong and Bao-Min Ma, J. Appl. Phys. **85**, 669 (1999)

[12] R. Grechishkin, S. Chigirinsky, M. Gusev, , O. Cugat and N.M.Dempsey, in *Magnetic Nanostructures in Modern Technology*, edited by G. Asti, L. Pareti and M. Ghidini, (Springer, 2007), p. 195

[13] H. Chetouani, V. Haguet, C. Jeandey, C. Pigot, A. Walther, N.M. Dempsey, F. Chatelain, B. Delinchant and G. Reyne, Solid-State Sensors, Actuators and Microsystems Conference, 2007. TRANSDUCERS'07, 715 (2007)

[14] Katter, M., K. Ûstüner and R. Blank, Proc. of the 19th Int. Workshop on Rare Earth Magnets and their Appl., Beijing, China (2006) 87.

[15] A. Walther, K. Khlopkov, O. Gutfleisch, D. Givord and N.M. Dempsey, J. Magn. Magn. Mat. 316, 174 (2007)

[16] C. Dieppedale, B. Desloges, H. Rostaing, J. Delamare, O. Cugat, J. Meunier-Carus, Proceedings of IEEE Sensors 2004, 493-496 (2004)

[17] The fabrication of a fully integrated RF micro-switch using RE-TM magnets is being studied within the framework of the ANR (French National Research Agency) "Nanomag2" project, which is a collaborative action between CEA-LETI, G2Elab, Institut Néel and Alcatel Alenia Space.

Figure captions

Figure 1: SEM cross sectional images of RE-TM films deposited onto patterned wafers (this particular section has trench and wall widths of 20 μm): (a) NdFeB, (b) SmCo and (c) zoom of a trench corner for the SmCo film.

Figure 2: SEM cross sectional images of a fracture surface of wet etched RE-TM films.

Figure 3: Comparison of the hysteresis loops of non-patterned continuous (cont.) and patterned (pattn.) RE-TM films: NdFeB (top), SmCo (bottom). Note that the NdFeB films were measured out-of-plane and the loops corrected with a demagnetization factor N = 1 while the SmCo films were measured in-plane.

Figure 4: Polar Kerr optical image of a Magneto-Optic-Indicator-Film (MOIF) placed on top of a patterned NdFeB film (this particular section contains two motifs, one with trench and wall widths of 10 μm and one with trench and wall widths of 20 μm, i.e. trench width/pitch of 10/20 and 20/40 μm, respectively)

Figure 5: Comparison of the hysteresis loops of 1 μm thick NdFeB films which were etched and planarized in an amorphous state and then further processed under different conditions: (#1) simple annealing (no Ta), (#2) annealing following Ar ion etching (5min) and deposition of Ta capping layer (etched + Ta).

Figure 6: Process flow diagram for the micro-patterning of magnetic films.

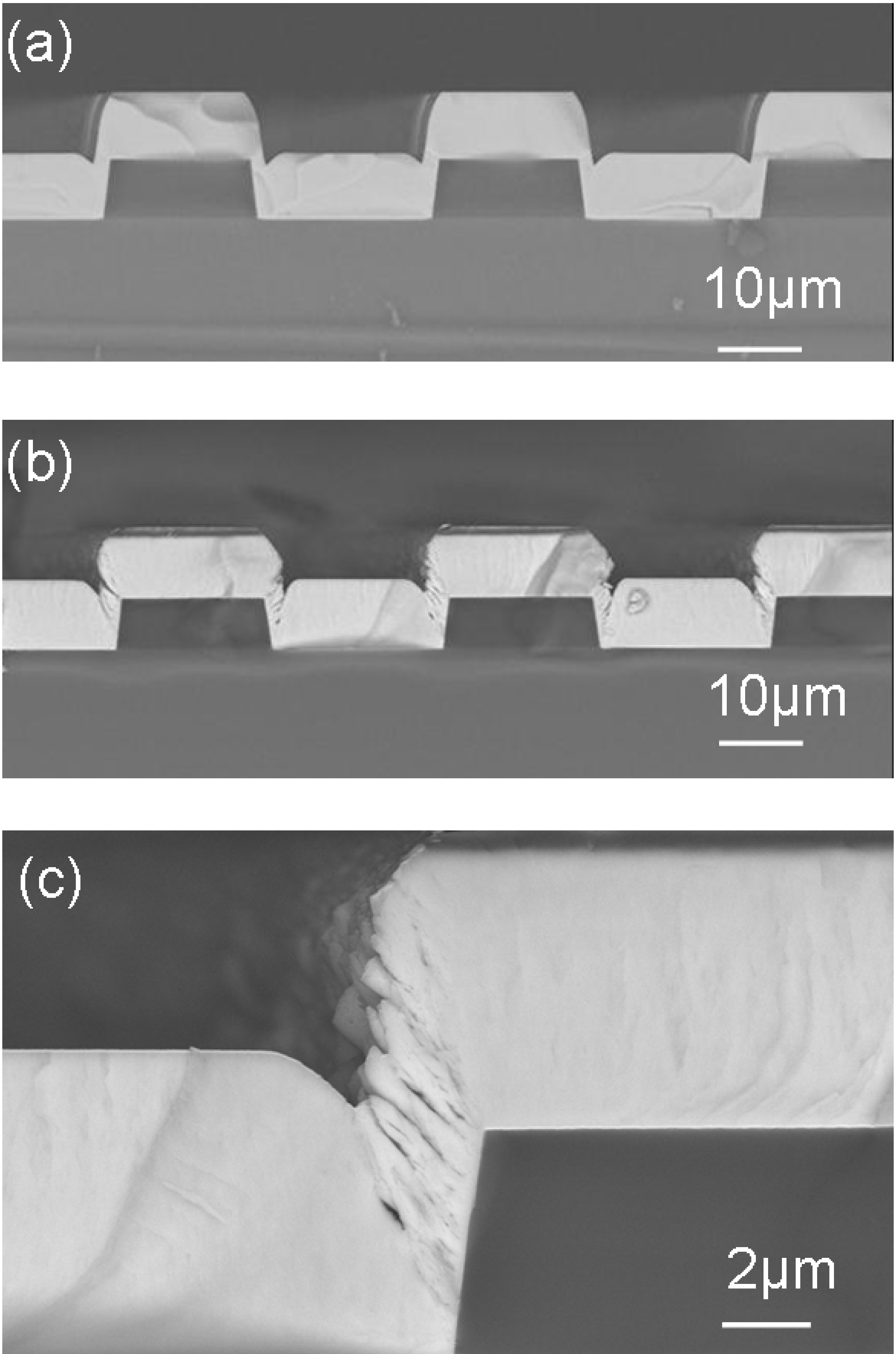


Fig. 1

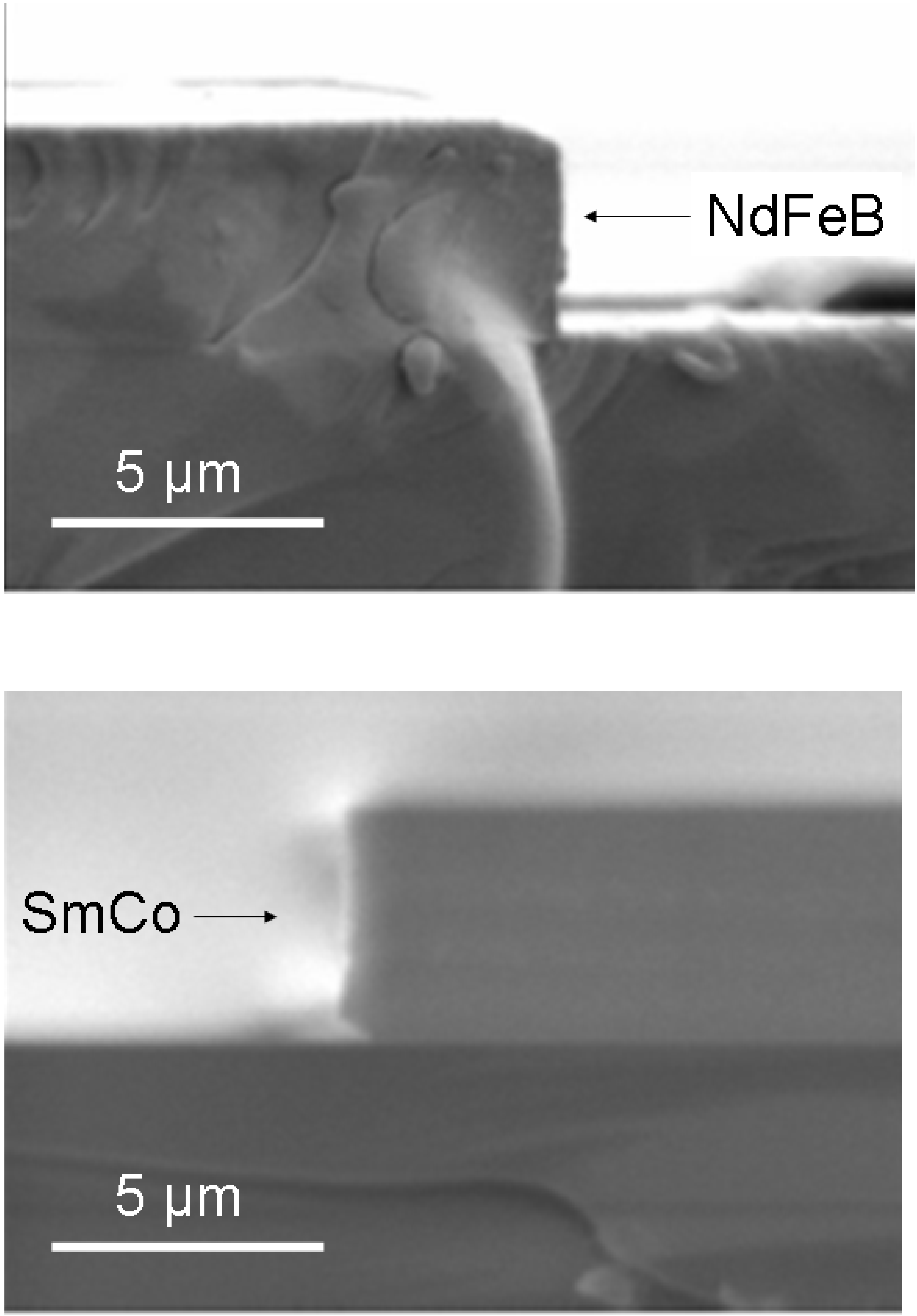
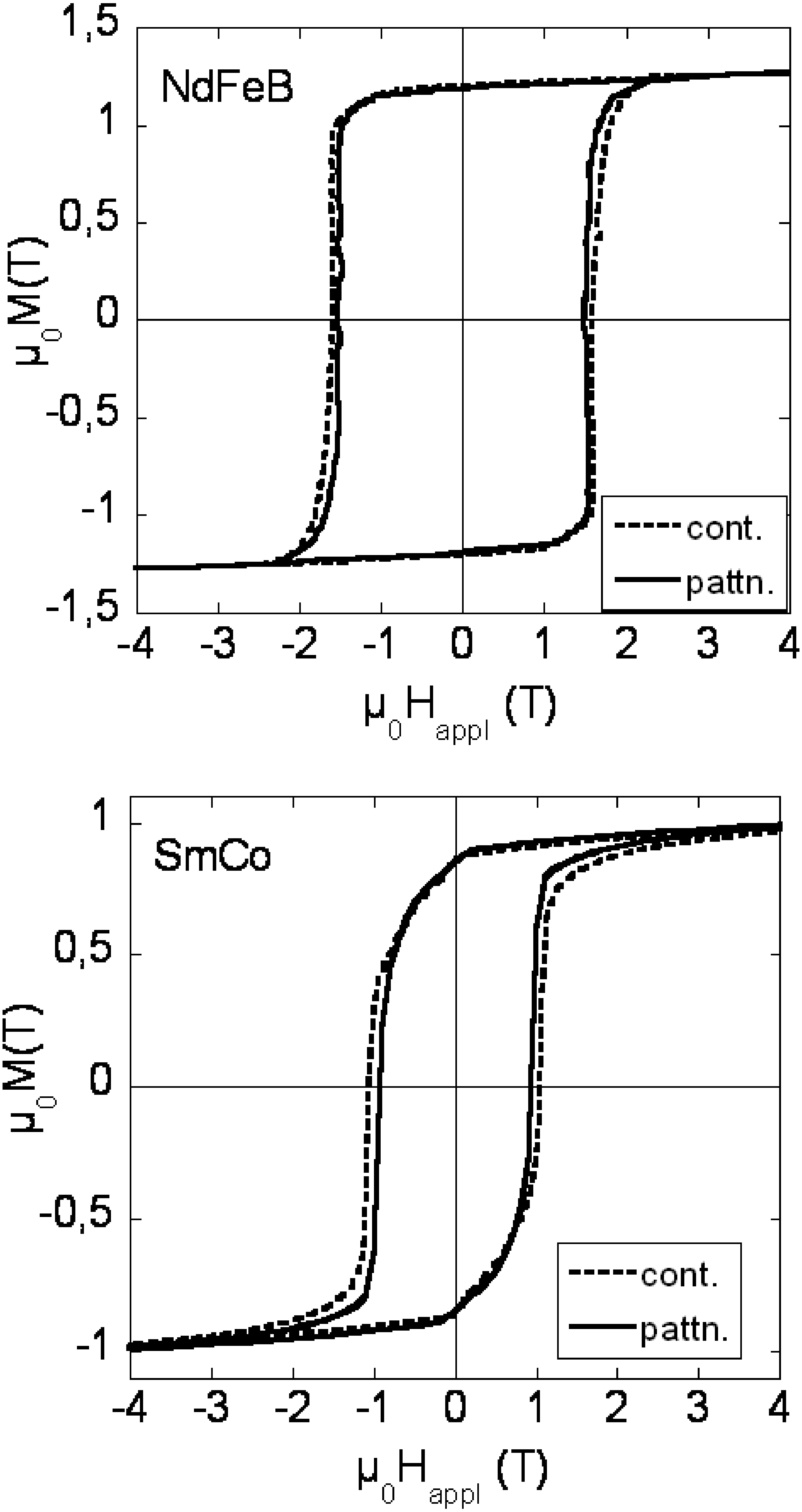


Fig. 2



NdFeB
1,5
1
0,5
0
-0,5
-1
-1,5
$\mu_0 M(T)$
-4
-3
-2
-1
0
1
2
3
4
$\mu_0 H_{appl}$ (T)
cont.
pattn.
SmCo
1
0,5
0
-0,5
-1
$\mu_0 M(T)$
-4
-3
-2
-1
0
1
2
3
4
$\mu_0 H_{appl}$ (T)
cont.
pattn.

Fig. 3

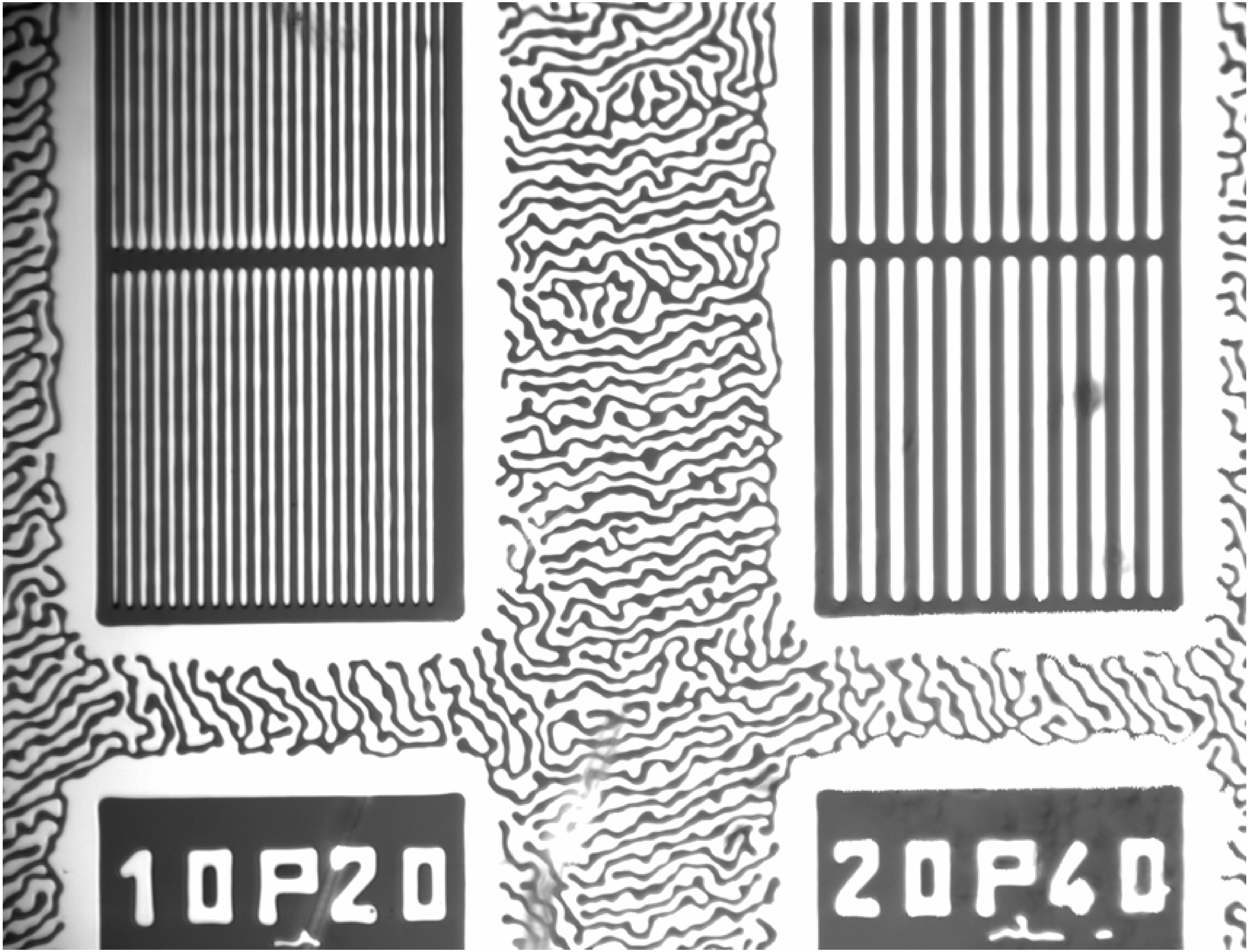


Fig. 4

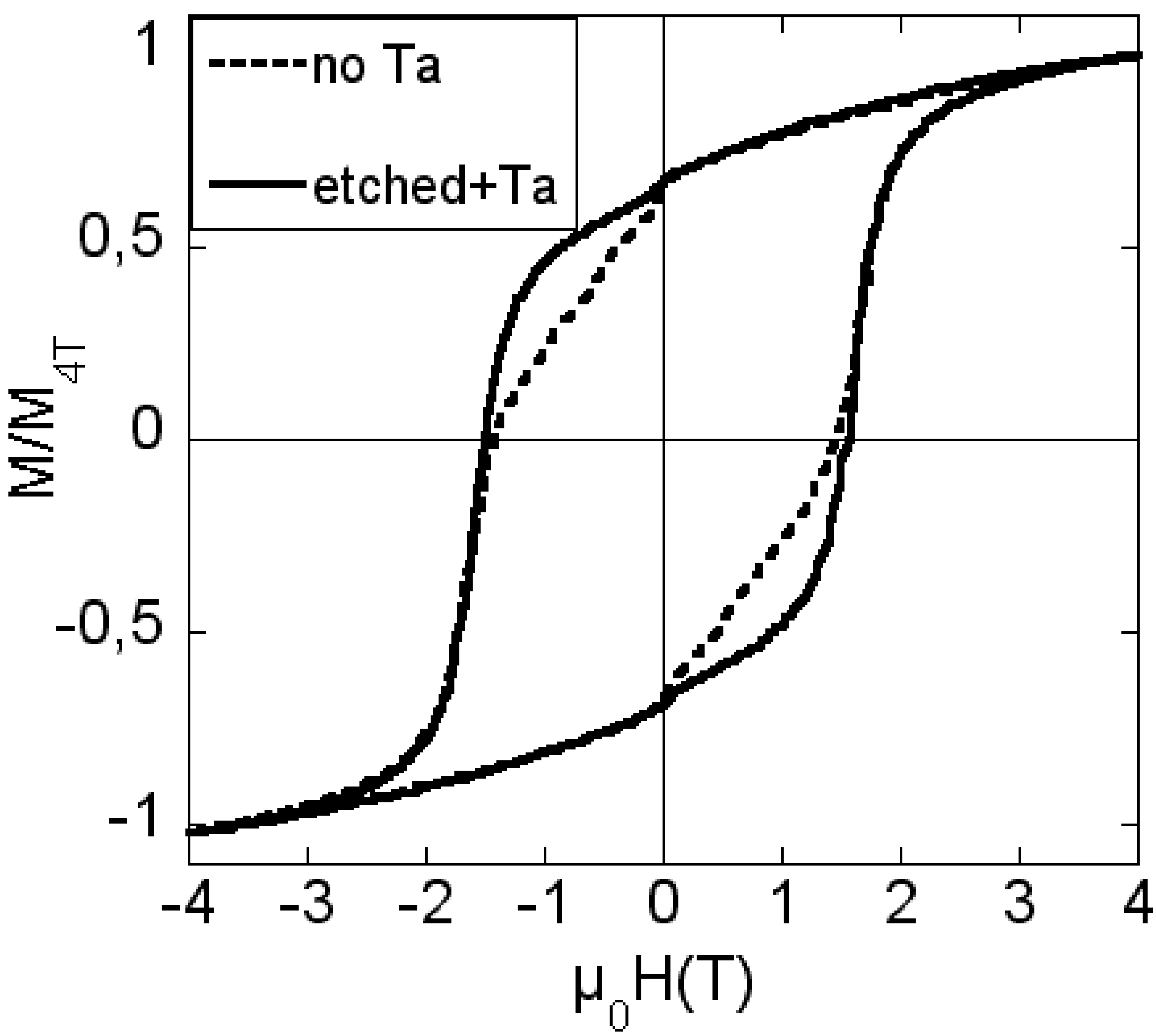


Fig. 5

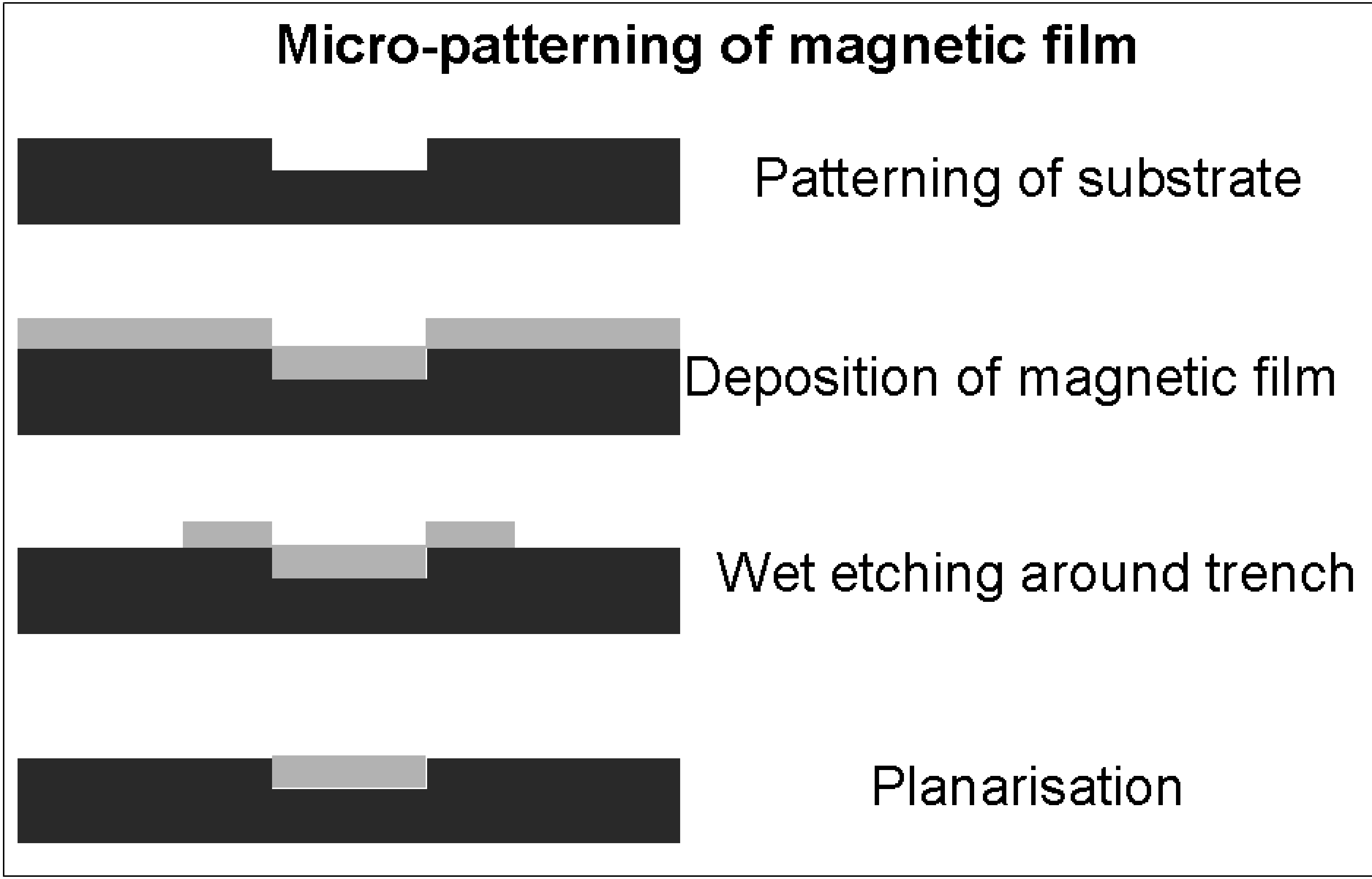

Micro-patterning of magnetic film
Patterning of substrate
Deposition of magnetic film
Wet etching around trench
Planarisation

Fig. 6