Self-patterning of epitaxial Ni-Mn-Ga/MgO (001) thin films

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Abstract

In this work, a detailed report on the growth of elongated bar-like crystallites with a definite crystallographic orientation, forming a self-organized patterned surface layer, with a thickness of about 100 nm, onto 900 nm thick ferromagnetic shape memory alloy Ni-Mn-Ga films epitaxially grown on MgO(001) is presented. The phenomenon appears above a threshold of lattice mismatch ($\approx 2\%$) between the film and substrate. The structural, magnetic and transformation properties of such films are described and analyzed. Particularly, the different magnetic states of the two film layers are discerned by ferromagnetic resonance. The feasibility of creating a ferromagnetic shape memory alloy with a nanoscale self-patterned surface, during the very same process of film deposition, can be interesting for potential applications where control of the surface architecture would be needed.

Keywords: Ni-Mn-Ga/MgO(001) thin films composites, Martensitic transformation, Surface self-patterning, Ferromagnetic resonance.

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1. Introduction

Ferromagnetic shape memory alloys (FSMAs), such as the Ni_2MnGa Heusler compound and its off-stoichiometric equivalents, represent a new type of active materials showing interesting “giant” multifunctional or "smart" properties [1]. A strong coupling between crystal structure and magnetism, alongside an anomalously low elastic shear modulus, enables outstanding features of these materials in the martensite state, as magnetically induced reorientation of twin variants, leading to strains up to 12%, in bulk single crystals under a moderate magnetic field [2,3]. The high frequency response to the applied magnetic signal [4,5] and the large power density [6] encourage the research and development of FSMAs as magnetic actuators or sensing devices (see [7,8] and references therein).

Whereas high performance of Ni-Mn-Ga single crystalline FSMAs has been widely proved in bulk [9,10] and implemented in different technical solutions [7,11], a deeper comprehension of its behavior is needed when the material is reduced to the micro- or nanoscale, as in the case of thin films (see [12,13] and references therein). When in form of thin film, there are a number of physical and technological factors that influence the performance of FSMAs, such as thickness, deposition rate, substrate type and temperature, internal stress or the growth conditions. If films are deposited by the sputtering technique [14,15], one of the most common deposition methods, it is important that deposition parameters such as power, Ar pressure or substrate temperature are optimized, because film properties, such as crystal structure, texture and magnetic anisotropy, strongly depend on them [16,17].

Deposition of the FSMA thin films with tunable functional properties would allow the elaboration of new elements for magnetically operated microelectromechanical systems (MEMS) [18,19]. As far as single-crystals of FSMAs provide much more

1 efficiency in their performance, attention has been paid to the preparation and study of
2 the epitaxial Ni-Mn-Ga films grown on MgO (001) [17,20,21]. As Si technology is well
3 established and widely used in microelectronics, Si (001) substrates have been also
4 explored for a deposition of Ni-Mn-Ga thin films. So far, highly textured polycrystalline
5 FSMA films have been obtained onto Si [22,23].

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12 In the present work we have studied Ni-Mn-Ga thin films with different
13 compositions sputter-deposited on a MgO (001) substrate. By surface imaging, we
14 found that in some of them the epitaxial growth was interrupted by the self-organized
15 growth of a highly textured top layer. Other Ni-Mn-Ga films deposited on the same
16 substrate, however, remain epitaxial throughout all their thickness (see also
17 Refs.[20,24,25]). The encountered top layer represents a rectangular pattern with a
18 depth varying between 50 and 100 nm. The pattern is formed by elongated crystal
19 grains, self-assembled in a perpendicular way to each other.

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31 One of the patterned film was selected as a model object for a detailed examination
32 of its properties by means of surface imaging, structural, magnetic and electric
33 measurements. The results and their analysis are main focus of the paper. The patterned
34 Ni-Mn-Ga thin films is the first example of FSMAs with a nanoscale self-patterned
35 surface, which can be interesting for applications where the functional properties
36 depend on the crystal structure, magnetic anisotropy and morphology. For instance, the
37 martensitic transformation can produce huge changes of the electromagnetic radiation
38 scattering or the wettability of the surface, because of the deformation of the specific
39 patterning already present. Such effects will be not observed in even surfaces.

40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 **2. Experimental**

57 58 *2.1. Preparation of self-patterned Ni-Mn-Ga/MgO(001) thin film composite*

Five Ni-Mn-Ga thin films with different thickness and composition were deposited at 500 °C on MgO(001) by a DC magnetron sputtering using several targets and different sputtering parameters, in a Pfeiffer Classic Vacuum 500 sputtering chamber. The high deposition temperature was used to promote the crystalline ordered growth, avoiding subsequent heat treatment. The film thickness was determined by profilometry, using a KLA Tencor D-100 device. Energy-dispersive X-ray spectroscopy (EDS) was used to determine, with an accuracy better than 0.5 at.%, the chemical compositions of the films, which are shown in Table 1.

Table 1 Chemical compositions, sputtering parameters, film thicknesses and self-patterning effect of Ni-Mn-Ga/MgO (001) thin film composites.

Composition	Ar Pressure (mbar)	Power (W)	Thickness (μm)	a_0 (nm)	Lattice mismatch (%)	Self-patterned
Ni _{52.3} Mn _{26.8} Ga _{20.9}	$2.6 \cdot 10^{-2}$	150	0.5	0.5850 [17]	1.82	No
Ni _{48.8} Mn _{25.4} Ga _{25.8}	$2.8 \cdot 10^{-3}$	200	1.0	0.5860 [26]	1.65	No
Ni _{51.5} Mn _{24.4} Ga _{24.1}	$2.6 \cdot 10^{-2}$	150	0.5	0.5824 [27]	2.28	Yes
Ni _{48.5} Mn _{30.9} Ga _{20.6}	$2.6 \cdot 10^{-2}$	150	1.0	0.5820 [28]	2.35	Yes
Ni _{46.7} Mn _{30.1} Ga _{23.2}	$2.6 \cdot 10^{-2}$	150	1.0	0.5820	2.35	Yes

For the rapid surface exploration, the secondary electron imaging at 10 kV with a JEOL JSM-7000F scanning electron microscope equipped with a field emission gun was used. Table 1 illustrates that the self-patterned surface has been found in three films while other two are fully epitaxial.

The last patterned film from Table 1 was selected as a model object for a detailed examination of its properties by means of surface, structural, magnetic and electric measurements as described in this paper.

2.2. Experimental technique

1 The $\text{Ni}_{46.7}\text{Mn}_{30.1}\text{Ga}_{23.2}$ (at.%) film with calculated valence electron concentration of
2 $e/a = 7.47$ was selected from Table 1 as a model object to investigate a phenomenon of
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4 the film self-patterning. The target with a composition of $\text{Ni}_{45.9}\text{Mn}_{31.4}\text{Ga}_{22.7}$ was used to
5
6 sputter-deposit this film. The base and Ar pressures were 4.1×10^{-7} mbar and 2.6×10^{-2}
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8 mbar, respectively. A power of 150 W was applied, and target-substrate distance was 9
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10 cm. The surface structure of the films was investigated by means of a Bruker Dimension
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12 Icon atomic force microscope in tapping mode, and with scanning electron microscopy
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14 using secondary electron imaging at 10 kV with a JEOL JSM-7000F scanning electron
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16 microscope equipped with a field emission gun. The crystallographic orientation of the
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18 different parts of the film was studied by electron backscatter diffraction (EBSD), at 10
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20 kV accelerating voltage.
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26 The crystal structure of the film was analyzed with X-ray diffraction in θ -2 θ
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28 configuration, using a Bruker D8 Discover diffractometer with CuK_α radiation.
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30 Temperature evolution of the lattice parameters was determined taking diffractograms
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32 every 5 °C from -150 to 200 °C.
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36 A vibrating sample magnetometer (VSM) was used to measure in-plane and out-
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38 of-plane magnetization curves of the film in martensitic and austenitic phases, at -100
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40 °C and 20 °C respectively. The thermomagnetization curve was measured at a low DC
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42 magnetic field of 100 Oe from -135 to 130 °C with a 5 °C step, using a liquid nitrogen
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44 flow to control the sample temperature. The temperature dependence of AC
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46 susceptibility was recorded by applying an alternating field of 1 Oe amplitude and 20
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48 Hz frequency.
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53 Ferromagnetic resonance spectra were recorded using Bruker ELEXIS E500 EPR
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55 spectrometer with automatic goniometer within -70 °C - +120 °C temperature range at
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57 9.46 GHz.
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The electrical resistivity was measured as a function of temperature by the four-probe method, between -110 and 150 °C at every 2 °C. An electric current of 5 mA being switched alternatively in the opposite directions was used to average measurements of the resistance.

3. Results

In the present work we found that the epitaxial deposition of Ni-Mn-Ga films can be interrupted by the growth of a self-patterned layer. As evidenced from Table 1, the occurrence of film patterning depends mainly on the lattice mismatch between the film and substrate: the films which have a low mismatch (1.82% and less) with the substrate present a continuous epitaxial growth, whereas those having a larger mismatch (2.28% and more) do not preserve the epitaxy resulting in a self-patterned morphology. Hereafter, the detailed behavior of the $\text{Ni}_{46.7}\text{Mn}_{30.1}\text{Ga}_{23.2}/\text{MgO}(001)$ patterned film composite is presented.

3.1. Structural characterization

The X-ray diffraction pattern of the film at room temperature is depicted in Fig. 1. It shows three peaks attributed to the Ni-Mn-Ga film that can be indexed as (220), (400) and (440) of the cubic austenite with a lattice parameter of $a_0=5.82 \text{ \AA}$. The absence of other diffraction maxima indicates 110 and 100 textures in the films.

The temperature dependence of the diffraction pattern reveals the martensitic transformation (MT) below -70 °C, in agreement with the other measurements (see Sec. 3.3) and with the expected value in bulk samples with a similar composition [29]. The low transition temperature is explained by the reduced Ni content, and the corresponding low electron concentration (e/a) [30]. Although the actual composition

suggests a 5M pseudo-tetragonal structure, diffraction data for the martensitic phase revealed, instead, a (pseudo-)orthorhombic structure [21] with lattice parameters: $c=5.60 \text{ \AA}$, $b=5.82 \text{ \AA}$ and $a=6.07 \text{ \AA}$. The orthorhombic structure may be stabilized by the stress coming from the substrate, as will be analyzed below.

Figure 2 shows the temperature evolution of the lattice parameters and the unit cell volume, as calculated from the (220)- and (400)-type reflections. The lattice parameter in cubic austenite displays a slope change at the Curie temperature (located at about 110 °C, see Sec. 3.3). An estimation of the linear thermal expansion coefficients in the ferromagnetic and paramagnetic phases gives $\alpha_{\text{Ferromagnetic}}=3.11 \times 10^{-5} \text{ K}^{-1}$ and $\alpha_{\text{Paramagnetic}}=1.25 \times 10^{-5} \text{ K}^{-1}$, respectively. The specific volume exhibits a magnetovolume contraction below the Curie temperature, as does the bulk [30]. On the contrary, the martensitic transformation (MT) during cooling is accompanied by about 1% of specific volume increase, whereas the volume effect in the bulk has opposite sign. Such inversion of the volume effect at MT was previously observed in Ni-Mn-Ga thin films deposited onto silicon, and explained as an effect of the internal stresses [31].

3.2. Morphology and lattice orientation

The secondary electron image in Fig. 3 reveals a topography pattern unusual for Ni-Mn-Ga surfaces. This pattern is formed as a result of a partial loss of epitaxial growth and consists of the elongated single crystal grains self-assembled in a perpendicular manner to each other. As follows from Fig. 3, the long axes of these grains are aligned with the [100] and [010] directions of the substrate. The approximate size of the separate grain is about $1 \times 0.1 \times 0.1 \text{ \mu m}^3$, as also confirmed by the AFM depth profile shown in Fig. 3. Incidentally, the film underneath of this patterned structure is formed by a continuous layer with a thickness of about 0.9 $\text{\mu m}$.

To get insight into the rich morphology of the film, the lattice orientation of the different constituents of the film was studied by EBSD. As shown in Fig. 4, the (100) pole figure reveals three different orientations of the crystallites which are present in the film. First, type 1, and second, type 2, are out-of-plane equivalent orientations presenting 110 texture in this direction, but differing in a 90° rotation in plane. Whilst the first type has the $[100]_{\text{NiMnGa}}$ direction parallel to the $[100]_{\text{MgO}}$ direction of the substrate, the second type is parallel to the $[010]_{\text{MgO}}$. The third type, type 3, has a (100) out-of-plane orientation and $[100]_{\text{NiMnGa}}$ and $[010]_{\text{NiMnGa}}$ directions along $[110]_{\text{MgO}}$ and $[1-10]_{\text{MgO}}$, respectively. All three orientations types of each crystal unit cell are sketched in the lower part of Fig. 4, indicating their relative orientation in respect to the substrate. These results agree with the X-ray diffraction pattern in Fig. 1.

The crystal orientation can be related to the morphological constituents of the thin film by indexing the local backscattered electron diffractograms coming from each point of the scanned area. Fig. 5 represents the crystal orientation map, where the color contrast for each orientation types, is given by the orientation difference between different grains. Fig. 5 reveals a clear lattice correspondence between the main body of film and the orthogonally arranged crystallites of the surface layer: in (110) out-of-plane textured grains, those oriented with $[100]_{\text{NiMnGa}}$ direction parallel to the $[100]_{\text{MgO}}$ (type 1) tend to grow along the $[010]_{\text{MgO}}$ direction, while the grains with $[100]_{\text{NiMnGa}}$ parallel to $[010]_{\text{MgO}}$ (type 2) grow along $[100]_{\text{MgO}}$. Namely, the crystals with 110 out-of-plane texture grow along their $[110]_{\text{NiMnGa}}$ axes. The 100 out-of-plane epitaxially grown main body of the film continuously extends throughout the whole area underneath the patterned layer. Comparing the orientation details of the patterned layer with the topographic image in Fig. 3 in terms of shape and dimensions, it can be easily deduced that the top superficial structures seen by SEM correspond to the (110) out-of-plane

type 1 and type 2 crystallites, while the film main body continuous layer can be ascribed to the type 3 part, with (100) out-of-plane orientation.

3.3. Transformation behavior

Both the magnetization and resistivity temperature dependences depicted in Fig. 6 show a reversible MT with characteristic temperatures $M_s = -55$ °C, $M_f = -73$ °C, $A_s = -65$ °C, $A_f = -49$ °C and a small hysteresis. Some features are present at -30 °C. At this temperature the thermomagnetization curve shows a slight magnetization drop, and the resistivity curve shows a slope change, both indicating a premartensitic transformation [32], expected to occur because of the low transformation temperature. The narrow transformation temperature range of MT in Fig. 6, as compared to that of Ni-Mn-Ga thin films deposited on Si [23], indicates a high compositional and structural homogeneity resulting from the epitaxial growth of the film on MgO(001). Structural homogeneity is also reflected by the large in-plane magnetic anisotropy in the martensite, resulting in the 45% drop of the low-field magnetization at MT (Fig. 6a), in contrast to the small drop usually seen in randomly oriented polycrystalline films. A thermal hysteresis of MT, about 7 °C, appears between the cooling and heating curves. Both the magnetization and resistivity curves show the Curie temperature in the vicinity of 110 °C, which is in agreement with the value correspondent to the valence electron concentration of the studied alloy [33].

3.4. Magnetic properties

(a) Magnetometry

The magnetization process in the film was characterized by VSM. The hysteresis loops, presented in Fig. 7, have been measured at -100 and 20 °C corresponding to the

1 martensitic and austenitic phases, respectively. A large difference can be seen between
2 the in-plane and the out-of-plane curves, due to different anisotropy contributions. In
3 the austenitic phase (measured at 20 °C), the anisotropy is almost fully given by the
4 shape factor, as the demagnetizing field, $H_D=6$ kOe, coincides with the anisotropy field.
5 However, the out-of-plane loop for martensite (measured at -100 °C), shows a
6 noticeably higher anisotropy field, which means that the hard magnetization axes are
7 preferentially oriented out-of-plane. Consequently, the direction of easy magnetization
8 axis, which is the crystallographic c direction, lies in the film plane. The saturation
9 magnetization taken from Fig. 7 is about 50 emu/g in the martensite, and 40 emu/g in
10 the austenite, being comparable to that of Ni-Mn-Ga bulk crystals [34,35]. These mass-
11 magnetization values might be slightly underestimated as the film mass was calculated
12 not considering the voids of the top layer.

31 (b) Ferromagnetic resonance

32 Usually, the resonance spectra for Ni-Mn-Ga thin films contain a single resonance
33 peak (see, e.g., [36] and references therein). In our case, however, the resonance
34 spectrum is complicate (Fig. 8). The spectrum can be presented as a superposition of
35 two lines. The first line (A) is a single peak, which is typical for continuous
36 ferromagnetic films with flat surfaces. The second line is a multipeak which is
37 characteristic for the films with embrasured surfaces and nanomeshes, where a
38 nonuniform magnetization precession takes place [37]. In our film, the line A can be
39 ascribed to the main body of film, whereas the line B can be associated with the top
40 patterned layer.

41 Overlapping of the resonance lines does not allow a correct determination of the
42 cubic anisotropy fields from in-plane angular dependence of the resonance peaks, but

one can state that these fields do not exceed 25 Oe. Furthermore, the different angular behavior of the main peaks A and B (not shown in the figure) implies different crystalline orientation for these two layers, which was already clarified in Sec. 3.2. Moreover, we need to take into consideration the structure of self-assembled pattern of the surface layer of the film and the different magnetization easy axes orientation to explain the multipeak character of the B resonance.

The temperature dependences of the resonance field for both main peaks are presented in Fig. 9. Taking into account a small value of anisotropy fields, the experimental data can be described by a simple formula

$$\omega / \gamma = H_r - 4\pi M_{eff}$$

Here, ω is the microwave frequency, γ is the giromagnetic ratio, H_r is the resonance field, $4\pi M_{eff} = (N_{\perp} - N_{\parallel})M_s - H_{A\perp}$ is the effective magnetization, $N_{\perp}$ and $N_{\parallel}$ are the perpendicular-to-the-film-plane and in-plane demagnetizing factors, M_s is the saturation magnetization, $H_{A\perp}$ is the perpendicular anisotropy field. For both film layers, the effective magnetization should be less than saturation magnetization because of tensile stresses at the film-substrate interface resulting in a perpendicular anisotropy [36] and because of the surface roughness leading to the decrease of the perpendicular demagnetizing factor ($N_{\perp} - N_{\parallel} < 4\pi$). However, the evaluation of the saturation magnetization at room temperature provides the value ~ 50 emu/g, which is typical for this material and represents a fairly good approximation for the experimentally obtained value (Fig. 7).

Above 100 °C, both layers became paramagnetic. In Fig. 9 below -50 °C, the decrease of the resonance field and increase of the resonance linewidths manifest the austenite-martensite transformation [38]. In fact, we should not expect a substantial

temperature variation of the A resonance linewidth [36] in the ferromagnetic austenitic phase, as it is really the case between the Curie and MT temperatures.

The situation is different for the patterned layer resonance, B. The magnetic inhomogeneity which is responsible for resonance linewidth is due to the surface patterned layer and, as a result, the resonance linewidth should be proportional to the magnetization, which really holds for all peaks of line B (see Fig. 9).

4. Discussion

In this work, two very distinct layers of Ni-Mn-Ga film grown on MgO (001) substrate are found. Whereas the lower part of the film attached directly to the substrate shows an epitaxial relationship with the substrate, the crystallites of the upper patterned layer exhibit only a partial lattice correspondence with the continuous part of the film. The observed structure of the entire film can be interpreted in terms of the lattice matching between different atomic layers. The lower layer of Ni-Mn-Ga grows epitaxially on the MgO single crystal for about 900 nm, presenting the (001) direction out-of-plane, with the unit cell rotated 45° around this axis, in agreement with the already observed epitaxial structures on MgO [36,39]. This kind of structure generates a tensile stress in the film due to the 2.35% mismatch between $a_{0\text{NiMnGa}}=5.82 \text{ \AA}$ and $\sqrt{2} \cdot a_{\text{MgO}}=5.96 \text{ \AA}$.

As already mentioned, the patterned crystalline grains in the 100 nm surface layer do not preserve the crystal orientation of the epitaxial layer. This fact could be attributed to the strain relaxation and switching to the deposition growth mechanism, leading to a preference of 110-type out-of-plane orientation typical for the annealed Ni-Mn-Ga/MgO (001) thin films [40]. The stress relaxation evolution has been observed in Ni-Mn-Ga films deposited on MgO (001) where several critical thicknesses were established. As

1 thickness increased, films presented substrate-constrained austenitic phase,
2 transformation between the austenite and a single variant martensite, and finally the
3 transformation to a multivariant martensitic phase [41]. We suggest that, in our case,
4 transformation to a multivariant martensitic phase [41]. We suggest that, in our case,
5 after achieving the 900 nm thickness, the film growth mode switches from the Frank-
6 van der Merwe mechanism, which proceeds atomic layer by layer, to the Volmer-Weber
7 mechanism, consisting in nucleation and growth of individual crystal grains [42]. This
8 combined growth mode, known as Stranski-Krastanov mechanism, has been previously
9 observed in thin films under internal stress coming from the lattice mismatch [43]. The
10 relaxation of the stress happens at a critical thickness at which the epitaxy is broken.
11 This thickness depends on the lattice properties (typically decreasing with increasing
12 lattice mismatch) and growth conditions, being in our case 900 nm. At this point, the
13 single crystalline continuous film growth is interrupted by the formation of discrete
14 orthogonal bar-like crystalline domains that match the epitaxial layer only
15 unidirectionally. Specifically, the lattice matching of these domains is accomplished by
16 the in-plane $\langle 100 \rangle$ and $\langle 1-10 \rangle$ directions correspondent to (110) out-of-plane
17 orientation.

18 For the present thin film, the mismatch with the substrate results in a tensile strain
19 of 2.35%. The associated stress, together with the intrinsic stress in the film coming
20 from defects, originates the switch to the Volmer-Weber growth mode as it can be
21 relieved by the formation of surface undulations which are typical in significantly
22 strained epitaxial films [44,45]. According to this, the (110) out-of-plane oriented grains
23 of the top layer of the film present an elongated shape and grow along the $[100]_{\text{MgO}}$ or
24 $[010]_{\text{MgO}}$ directions. These two possible growing directions generate the orthogonal
25 crosslinked pattern of the surface layer observed in Fig. 3. Different out-of-plane
26 orientations of the continuous film and the upper crystallites give rise to the appreciably

different magnetic anisotropy fields resulting in the occurrence of two lines in the FMR spectrum (Fig.8). The patterned surface layer provides also a distinct temperature behavior of FMR signal width (Fig.9). These distinctions would be even more pronounced in the martensitic state and the further challenge would be the micromagnetic studies. In any case, the different magnetic states would mean that the magnetic field actuation might be different for the main body and surface pattern thereby evoking an idea about “smart” surfaces feasibility in FSMAs. The described film was obtained by “natural” engineering, much simpler than surface morphology produced by artificial methods, such as the lithographic approach or surface templates.

5. Conclusions

In the present work we have found that the epitaxial deposition of Ni-Mn-Ga films on MgO(001) can be interrupted by the growth of a self-patterned layer. One of such films, $\text{Ni}_{46.7}\text{Mn}_{30.1}\text{Ga}_{23.2}$, was studied in detail. It was shown that this film exhibits a low-hysteresis martensitic transformation in the vicinity of -50 °C, between the cubic and orthorhombic phases. During martensitic transformation, the unit cell volume undergoes an inverse to the bulk jump-like behavior due to the stress imposed by the substrate. The surface layer of the film presents a naturally formed self-organized morphology, being formed by elongated bar-like shaped crystal grains parallel to the [100] and [010] directions of the substrate. The formation of this surface layer is explained in terms of the change of the growth conditions caused by the stress coming from the lattice mismatch: after achieving of some thickness, the epitaxial continuous growth is interrupted by a discrete formation of out-of-plane 110-type oriented crystallites as a result of surface stress relaxation. Meanwhile, these crystallites exhibit in-plane directional growth which has been explained in terms of the unidirectional

lattice correspondence. Magnetization measurements show essentially larger magnetic anisotropy of the martensitic phase compared to the austenitic one. FMR measurements in the cubic phase clearly discern magnetic states of the main body of film and upper layer.

To summarize, the film thoroughly studied in the present work shows unusual properties. It can be considered as a first example of FSMA with the self-assembled patterned surface system interesting for possible smart nanoscale applications.

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Figures Captions

Fig. 1. X-ray diffraction pattern at room temperature. The peaks marked with arrows correspond to the Ni-Mn-Ga film in the austenitic phase. Other peaks belong to the MgO substrate.

Fig. 2. (a) Temperature evolution of the lattice parameters of the orthorhombic martensite and cubic austenite. (b) Dependence of the unit cell volume with temperature, showing an inverse volume effect at the martensitic transformation and change of slope in the vicinity of Curie temperature of austenite marked by arrow.

Fig. 3. Upper micrographs show scanning electron microscopy (left) and atomic force microscopy (right) images of the film, revealing a particular surface layer pattern. Lower picture depicts AFM depth profile of the film surface layer. It represents a rectangular self-assembled pattern with a depth varying between 50nm and 100 nm. The sample edge on the SEM image was damaged by cutting with a diamond-tipped stylus.

Fig. 4. Upper schematic shows (100), (110) and (111) pole figures of the Ni-Mn-Ga film obtained by electron backscatter diffraction. Each color (shape) of the poles makes reference to a different crystal orientation. Lower schematic shows the unit cells of the three crystal orientations present in the Ni-Mn-Ga film referred to the coordinate system of the substrate. The color underneath corresponds to the poles above.

Fig. 5. Orientation map of the crystalline components forming the Ni-Mn-Ga film, represented by the colors indicated in Fig. 5. The image presents a preferential growth direction of the (110)-type crystallites on the top and an epitaxial (100) layer underneath them. The coordinate axes for each Ni-Mn-Ga orientation and for the MgO substrate are indicated.

Fig.6. Temperature dependences of magnetization at $H=100$ Oe and electrical resistance, both revealing martensitic transformation (M_s , M_f , A_s , A_f) and Curie temperature (T_C).

Fig. 7. In-plane (1) and out-of-plane (2) magnetization curves of the film in martensitic phase (a) and austenitic phase (b).

Fig. 8. Resonance spectrum of the film recorded at 70°C in austenite (the two panels correspond to the first and second absorption derivative). Magnetic field is perpendicular to the film plane. The 2nd derivative is also plotted to remark the position of the absorption peak. The decomposition of the spectrum into two lines, A and B, is shown on the top panel.

Fig. 9. Temperature dependence of the resonance field for the main resonance peaks of lines A and B (see Fig. 8). Magnetic field is perpendicular to the film plane. The temperature variation of the peaks linewidth is shown in the inset.

Fig. 10. Two-dimensional scheme of the lattice correspondence between different atomic layers. Arrows show the preferential growth direction of the crystallites on top of the continuous film.

Fig. 1

Fig.2a

Fig.2b

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7a

Fig.7b

Fig.8

Fig.9

Fig.10

Self-patterned Ni-Mn-Ga/MgO(001) thin film composite