Effects of film thickness and composition on the structure and martensitic transition of epitaxial off-stoichiometric Ni–Mn–Ga magnetic shape memory films

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Abstract. Epitaxial Ni–Mn–Ga magnetic shape memory films with varied thickness and variable stoichiometry were prepared by magnetron sputtering on MgO(001) substrates and investigated by using x-ray diffraction (XRD), scanning tunneling microscopy (STM) and scanning electron microscopy (SEM). The results demonstrate that the structure of the films is either a non-modulated martensite or a seven-layer-modulated martensite. At small film thicknesses, we observe a preferential alignment of the {110} twin planes titled 45° from the substrate surface, which gives rise to the surface corrugation, whereas at large thicknesses, twin planes align additionally along the perpendicular planes. The biaxial tensile stress due to the film–substrate lattice mismatch is shown to have an important role in the selection of the possible twinning planes. An exponential relation between the stress and the film thickness is identified. In contrast, the magnetic properties of the films are found to be independent of the stress. A resistance maximum is measured close to the Curie temperature, which can be attributed to the relaxation of the lattice distortion induced by magnetoelastic coupling.

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1. Introduction

Recently, the Heusler compound Ni$_2$MnGa has attracted considerable scientific interest because of its magnetic shape memory (MSM) effect. The phenomenon refers to reversible strains or deformations caused by either martensitic variant reorientation or austenite-to-martensite transformation in response to applied magnetic fields. The largest MSM effect so far of about 10% was observed in a single-crystal Ni$_2$MnGa with seven-layer-modulated (7M) orthorhombic martensite [1, 2] and is nearly two orders of magnitude larger than the largest magnetostriction of about 0.2% measured in Tb–Dy–Fe alloys [3]. In addition, the MSM effect has a dynamic response of up to 3 kHz [4, 5], by a factor of about 10 faster compared with conventional shape memory alloys [6] driven by temperature. These properties make the MSM alloys promising materials for technological applications in sensors as well as actuators capable of large strokes (up to 5 mm) and forces (up to 2 kN) [7].

Unlike the magnetostrictive phenomenon generally occurring in structurally homogeneous samples [3], the MSM effect requires a special microstructure, i.e. twinning. It is formed by a displacive, diffusion-free structural transformation from a higher symmetry cubic austenite phase ($L_2_1$) to a lower symmetry orthorhombic or tetragonal martensite phase. The twinning emerges in the martensite phase to minimize the total shape change and thus the macroscopic strain energy over the whole sample. The twin boundary remains the lattice of the parent phase and separates two structural domains, namely twin variants with different, but symmetrical, lattice orientations. Due to the high mobility of the twin boundaries, a sample in the martensite phase can easily be deformed. Additionally, it is necessary for MSM alloys that the magnetic anisotropy energy is higher than the energy needed to move the twin boundaries, so that the twin variants are redistributed or reoriented in applied magnetic fields and then aligned in the magnetic easy axis. In the case of nanotwins caused by layer modulations [8, 9], the movement of the twin boundaries becomes easier and thus can be driven by moderate magnetic fields <1 T [4, 5].

The MSM effect is operating well for bulk materials, but is so far fraught with problems for thin films prepared on rigid substrates. This has motivated, in recent years, increased research interest in film preparation [10]–[14] and the investigation of the stress influences on film microstructures and martensitic transformations [15]. In addition to a linear length expansion, thin films are expected to show a shear strain [16] useful for micro-actuators. In addition, by
means of stress or magnetic fields applied perpendicular to the film surface, as suggested in [17], a tunnel-like or a tent-like shape emerges, where the film is released from the substrate. This is of particular interest for applications based on CMOS technology. Moreover, a tensile or compressive stress induced by a film–substrate lattice misfit and a thermal expansion difference gives rise to an increase in martensitic temperatures \( T_M \). However, in the case of thin films, a common problem exists, namely adhesion to the rigid substrate, which results in suppression of twin variant reorientations or martensitic transformations and thus impedes the MSM effect. However, recent publications show that epitaxial Ni–Mn–Ga films can be released from the substrate by using either NaCl as a dissolvable substrate [18] or Cr buffer layers on MgO(001) that can be selectively removed by chemical etching [19]. Using the latter technique, free-standing epitaxial Ni–Mn–Ga films can be produced and further implemented in actuating or sensing devices.

In this work, we have investigated the structural and magnetic properties of epitaxial Ni–Mn–Ga films sputtered from an off-stoichiometric target. The stoichiometric Ni\(_2\)MnGa compound shows an electron concentration \( e/a = 7.5 \) (here 10, 7 and 3 electrons per Ni, Mn and Ga atoms, respectively). The phase diagram measured for bulk materials [20] predicts a martensitic temperature \( T_M \) of about 210 K and a Curie temperature \( T_C \) of 376 K. The off-stoichiometric Ni–Mn–Ga target has a ratio \( e/a = 7.7 \), and \( T_M \) is expected to be above room temperature (RT) as basically required for technological applications. Due to the existence of stress in the prepared thin films, however, their properties, which are expected to deviate from bulk materials, can strongly depend on the preparation conditions, including film thicknesses and stoichiometries. The present work was carried out in the framework of a project for pressure sensor applications based on the MSM effect.

2. Experimental details

Three epitaxial films referred to as \( f_1 \), \( f_2 \) and \( f_3 \) with thicknesses of 150, 120 and 445 nm, respectively, were prepared by magnetron sputtering from an alloy target Ni\(_{50}\)Mn\(_{30}\)Ga\(_{20}\). The target is weakly ferromagnetic at RT and allows a stable Ar plasma at a low working pressure \( (3 \times 10^{-3} \text{ mbar}) \) and a low sputter power \( (36–80 \text{ W}) \). As a result, smooth and epitaxial films can be prepared. The base pressure of the sputtering chamber is \( 1 \times 10^{-7} \text{ mbar} \). MgO(001) substrates were used for the thin film growth. The substrate temperature during the film deposition was maintained at about 823 K. At this temperature, the films grow with a cubic structure of \( L2_1 \) \( (a = 0.582 \text{ nm}) \), i.e. the parent phase (austenite). The lattice parameter of cubic MgO substrates is 0.421 nm. A lattice misfit to the \( L2_1 \) phase is about 2.5% in diagonal directions. In most cases, the film composition deviates from the sputter target because of different sputter yields for different elements. After prolonged sputtering, a chemical equilibrium can be achieved in the target. In addition, we found that a pronounced evaporation of Mn from the films occurs upon annealing, especially at higher temperatures \( (>773 \text{ K}) \). In order to minimize the Mn loss, the substrate heating was stopped immediately after the deposition and a relatively larger deposition rate (sputtering power 80 W) was used for the thicker film \( f_3 \) (see table 1).

Thin film stoichiometries were measured by energy dispersive x-ray spectroscopy (EDX). Film thicknesses and lattice structures, including layer modulations in martensitic variants, were determined by means of small-angle and wide-angle x-ray scattering (SAXS and WAXS). The film topography was investigated at RT using scanning tunneling microscopy (STM) and
Table 1. Deposition rates, film thicknesses, compositions, \( e/a \) ratios, phases at RT, Curie temperatures \( T_C \) and martensitic transition temperatures \( T_M \) for different films.

| Film | Power (W) | Growth rate (nm min\(^{-1}\)) | Thickness (nm) | EDX (at.%) | Phase | \( T_C \) (K) | \( T_M \) (K) |
|------|-----------|-------------------------------|----------------|------------|--------|------------|------------|
| \( f_1 \) | 45        | 20                            | 150            | Ni 53.3    | Mn 26.7 | Ga 20.0   | 8.0        | \( M + \gamma \) | 270 | 505 |
| \( f_2 \) | 36        | 16                            | 120            | Ni 51.7    | Mn 27.3 | Ga 21.0   | 7.7        | M          | 310 | 495 |
| \( f_3 \) | 80        | 36                            | 445            | Ni 51.2    | Mn 29.6 | Ga 19.2   | 7.8        | M          | 335 | 475 |
| \( f_R \) | 175       | 105                           | 180            | Ni 48.6    | Mn 26.6 | Ga 24.8   | 7.5        | A          | 385 | 270 |

scanning electron microscopy (SEM). In situ x-ray diffraction (XRD) at variable temperature was carried out accompanied by heating the film slightly above \( T_M \) and cooling down to RT in vacuum of \( 1 \times 10^{-6} \) mbar in order to reveal structural changes due to the phase transitions. The temperature dependence of the magnetization was measured by means of superconducting quantum interference device (SQUID) magnetometry in external magnetic fields of 0.1 T. The Curie temperature \( T_C \) was extracted from these results. Furthermore, resistance measurements were carried out at different temperatures up to 350 K to gain information about additional structural changes possibly induced by magnetoelastic coupling in the martensite phase \([21, 22]\), or by pre-martensitic transitions that can occur in the temperature range from \( T_M \) to \( T_C \) for Ni\(_{2}\)MnGa samples with \( T_C > T_M \) \([22, 23]\).

For comparison, a reference film \( f_R \) was prepared at the same deposition temperature from a low-Ni target of Ni\(_{48}\)Mn\(_{31}\)Ga\(_{21}\). This target is strongly ferromagnetic at RT and needs accordingly a higher working pressure of \( 5 \times 10^{-3} \) mbar and a higher sputter power to stabilize the Ar plasma. The film \( f_R \) was found to be austenitic at RT and thus the structural properties of the austenite phase can be studied at RT, which is representative of the structure of samples \( f_1, f_2 \) and \( f_3 \) at \( T > T_M \) in the austenite state.

3. Results and discussion

3.1. Surface morphology investigation

Table 1 presents an overview of the results obtained from films \( f_1, f_2 \) and \( f_3 \), including the reference film \( f_R \). Film compositions determined by EDX differ from those of the target, mainly due to the loss of Mn during the sputter deposition. The film \( f_1 \), which was fabricated at the beginning of this study, exhibits a stronger chemical deviation compared with \( f_2 \) and \( f_3 \). This is due to the fact that the sputter target was still out of chemical equilibrium for \( f_1 \). The film \( f_3 \) has a relatively high Mn content of 29.6%, indicating that the Mn loss is effectively suppressed by increasing the deposition rate. The \( e/a \) ratios calculated from the measured composition are listed in table 1. They are 8.0 for \( f_1 \), 7.7 for \( f_2 \) and 7.8 for \( f_3 \), respectively. The reference film \( f_R \) prepared from the low-Ni target shows a composition close to stoichiometry and an \( e/a \) ratio of 7.5. The \( e/a \) ratio will be used here to predict \( T_M \) and \( T_C \) according to the phase diagram \([20]\).

The film thicknesses given in table 1 were examined by means of SAXS. Figure 1 illustrates the SAXS patterns measured for films \( f_2 \) and \( f_R \), showing oscillations with the angle indicating a high film quality. The periodicity of the oscillation determines the film thickness and the intensity decay depends on the surface roughness. The decay of the intensity for \( f_2 \) is more...
Figure 1. SAXS patterns measured for $f_2$ and $f_R$. The oscillation period determines the film thickness and the intensity decay indicates the film roughness. A larger roughness for $f_2$ arises from twinned martensite variants.

Figure 2. STM images obtained for $f_2$ (120 nm) showing surface corrugation lines that are oriented at $45^\circ$ with respect to the substrate edges (a). The twin lamella width and height can be determined from the profile (b) and yield a twin misorientation angle of $3^\circ$–$4^\circ$. The magnified STM image (c) represents nanotwins that are arranged perpendicularly on macrotwins as indicated by the arrows.

pronounced compared with $f_R$ and the oscillation ends near $2\theta = 3.0^\circ$ for $f_2$, but near $6^\circ$ for $f_R$, implying a rough surface for $f_2$. The result can be interpreted on the basis of the twinned surface of martensitic films, as described below. Twinning in martensitic films leads to a rough surface, as can be observed in the STM images (see figure 2). The film $f_R$ is austenitic with the as-prepared surface being smooth. The superposed long period oscillation in the SAXS curve for $f_R$ originates most likely from the oxidized surface layer (2–3 nm thick) due to ex situ handling.

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Figure 3. SEM images obtained for films $f_1$ (a), $f_2$ (b) and $f_3$ (c) demonstrating different martensite variants depending on the composition and film thickness. Insets in (a) and (c) show cross-sectional SEM images: the precipitation of Ni$_3$Ga single-crystal whiskers (inset a) and the twin boundary selection along perpendicular planes (inset c).

Figure 2 shows constant-current STM images obtained at RT for the film $f_2$. The observed surface corrugation lines can be attributed to the twinning, which leads to a distinct decay of the SAXS intensity, as mentioned above. Well-oriented twin lamellas can be observed in two orientations parallel to the substrate diagonal. The result mirrors the lattice relation $L_2(001)[110]/\text{MgO}(001)[100]$ for the epitaxial growth. The six highest density planes [110] of the $L_2$ lattice serve as possible habit planes for twinning, four of them in 45° and two perpendicular to the substrate surface. The selection of the twins along 45° and/or perpendicular planes depends on the film thickness as a result of biaxial tensile stress in epitaxial films [15]. The film $f_2$ (120 nm) is the thinnest and the twinning observed is limited to twin planes along the 45° planes.

Figure 2(b) shows the cross-section profile, giving a twin lamella width $d_1 + d_2$ of about 40 nm and a height $h$ of about 1–1.5 nm. A twin misorientation angle $\alpha = \tan^{-1}(h/d)$ of about $3°–4°$ can be estimated. An angle $\alpha$ equal to 4.3° for tetragonal and 2.9° for orthorhombic martensites is expected [24]. Therefore, the result of $\alpha = 3°–4°$ obtained from film $f_2$ suggests that in this film a non-modulated (NM) tetragonal phase and a 7M orthorhombic phase coexist.

In the case of the 7M martensite, a shuffling of [110] planes along the [110] axis occurs with a periodicity of seven atomic planes, five toward the positive direction and two toward the negative direction. This can be described also as twinning on a nanometer scale [8, 9]. Figure 2(c) reveals these nanotwins in film $f_2$, which are perpendicularly arranged on the macrotwin stripes as indicated by the arrows. The superlattice arising from the layer modulation can be measured using XRD, as will be described below.
3.2. Structural investigation

Figure 3 presents the SEM images measured for $f_1$, $f_2$, and $f_3$, including cross-sectional images. The film $f_R$ is austenitic at RT with a smooth surface, as shown in figure 1, and therefore its SEM image (not shown here) reveals no structure. The relevant WAXS patterns are plotted in figure 4, including $f_R$, which simply shows (200) and (400) peaks from the high-symmetry cubic phase with much higher intensities compared with $f_1$, $f_2$, and $f_3$. The lattice constant measured for $f_R$ yields 0.583 nm, which is close to the value of bulk material. It is obvious from figure 3 that the film microstructure strongly depends on the chemical composition and the thickness. Likely due to a higher Ni content (53 at.%), the film $f_1$ underwent a phase precipitation during the film deposition, namely a $\gamma$-phase was observed both by SEM and WAXS. The latter shows a diffraction peak at $2\theta = 50.6^\circ$, identified as cubic Ni$_3$Ga ($a = 0.360$ nm). The precipitation occurs mostly in close proximity to grain boundaries of the parent phase in a whisker-like manner (inset of figure 3(a)). Thus, the grains of the parent phase look disc-like, in contrast to films $f_2$ and $f_3$ (figures 3(b) and (c)). Nevertheless, the twin orientation is overall identical due to the epitaxial growth. Two weak peaks located near $2\theta = 65^\circ$ and $69^\circ$ in the WAXS pattern can be identified as the martensites (004) and (400).

Figure 3(b) shows the SEM image measured for $f_2$. Similar to the STM image (figure 2), highly ordered twin variants are visible without any sign of precipitation. The surface corrugation due to twinning along the 45° planes makes the SEM image rich in contrast, but it drastically lowers the WAXS intensity, as indicated in figure 4, where the relevant diffraction peaks of the twinned martensite are almost invisible. The extremely low intensity is, besides the low symmetry of the martensite lattice, primarily due to a non-collinearity of the scattering vector and the reciprocal lattice vector in Bragg reflection conditions. For this reason, the martensite peak intensities rise upon slight tilting of the sample, as shown in figure 5(a). Here, the sample was rotated in a plane around 45°, so that the twin lamellas, the tilt axis and the incidence x-ray are nearly parallel. One can see remarkable changes in the WAXS patterns with the tilt angle, indicating the disorientation of the martensite multivariants. Five different peaks...
Figure 5. WAXS patterns measured for films f2 (a) and f3 (b) with a slight tilt. The peaks marked by arrows stem from the twinned martensite and the extra peaks marked by ‘S’ originate from the superlattice caused by layer modulations.

appear in turn and could be attributed to the NM martensites (400)_{NM} and (004)_{NM}, as well as 7M martensite (400)_{7M}, (040)_{7M} and (004)_{7M}, respectively. The peak intensity reaches the maximum at a tilt angle of 3°–4° close to the twin misorientation angle α. Similar results were observed in [9, 24] by means of the x-ray pole figure measurements. One should note that some extra peaks marked here by ‘S’ appear when the tilting is close to 3°–4°. They can be attributed to the superlattice related to layer modulations, as discussed below.

Figure 3(c) shows SEM images of the thick film f3, exhibiting two different areas labeled here as A and B. The area A corresponds to the non-even twinned martensite with clear twin lamellas parallel to the substrate diagonal, while the area B reveals twin stripes poor in contrast on the surface, but clearly visible in the film cross-section, as can be seen in the inset. These results suggest that the twin boundary selection in f3 is possible not only along the 45° planes but also along the perpendicular planes. The twin stripes on the surface of the area B show accordingly two orientations perpendicular to each other and parallel to the substrate edges. It is apparent that the influence of the biaxial tensile stress on the twin boundary selection becomes smaller in comparison to the thinner film f2. The corresponding WAXS pattern is illustrated in figure 4. Two martensite peaks (040)_{7M} and (004)_{7M} near 2θ = 65° become clearly visible and could originate from the area B, while other weak peaks, such as (400)_{NM} near 2θ = 69°, could stem from the non-even twinned area A. On the film surface, some white spots are visible, which typically appear on the surface of films with a larger thickness (thus a long deposition time) or at a higher deposition temperature. Therefore, they could be caused by local surface overheating. A γ-phase of Ni3Ga can, however, be excluded here according to the measured WAXS pattern.

Figure 5(b) presents more detailed WAXS patterns measured for f3 at a tilt angle up to 7°. Also, the sample was horizontally rotated by 45° before and thus four martensitic peaks marked here by arrows are visible even at zero tilt. They are identified accordingly as (400)_{7M}, (040)_{7M},
Table 2. Lattice constants of 7M and NM martensitic phases measured for films $f_1$, $f_2$ and $f_3$ compared with bulk values [25, 26].

| Martensite            | $f_1$  | $f_2$  | $f_3$  | Bulk [25, 26] |
|-----------------------|--------|--------|--------|---------------|
| 7M (orthorhombic)     | $a = 0.63$ nm | $a = 0.623$ nm | $a = 0.610$ nm |
| $-b = 0.58$ nm        | $b = 0.58$ nm | $b = 0.582$ nm | $b = 0.582$ nm |
| NM (tetragonal)       | $a = 0.54$ nm | $a = 0.543$ nm | $a = 0.544$ nm | $a = 0.544$ nm |

(004)$_{7M}$ and (400)$_{NM}$. The peaks (040)$_{7M}$ and (004)$_{7M}$ with a higher intensity originate most likely from the area B, as mentioned above, and their intensity hence drops drastically, as the film is slightly tilted. One should note that the relatively high intensity of the (040)$_{7M}$ peak might be a superlattice effect, as further discussed below. The peak (400)$_{NM}$ near $2\theta = 55^\circ$ with a low intensity appears at $4^\circ$ tilt, similar to film $f_2$. The position of the peaks marked by arrows is independent of the tilt, although their intensity changes remarkably. The lattice constants for 7M and NM martensite phases were evaluated from the x-ray data given in figures 4 and 5. The values with respect to the cubic $L2_1$ unit cell are listed in table 2. The extremely low diffraction intensity of $f_2$ leads to a large measurement error for the lattice parameters. However, compared with the bulk values [25, 26], both $a$ and $c$ axes of the 7M martensite measured for the films are expanded by about 2–3%, which is close to the film–substrate lattice misfit and suggests a tetragonal distortion induced by biaxial tensile stress in epitaxial films. The $b$ axis (0.582 nm) remains almost unchanged and is nearly equal to $a = 0.583$ nm of the cubic austenite in $f_R$, reflecting the structural coherence in martensite–austenite phase boundaries. For the NM martensite, however, the difference in the lattice constants (<1%) is insignificant from bulk. Figure 5(b) shows the superlattice peaks marked by ‘S’ becoming more pronounced due to a larger film thickness compared with $f_2$ (figure 5(a)). The peak (040)$_{7M}$ can also be regarded as the center peak, i.e. the zero-order maximum of the superlattice. Therefore, it exhibits a relatively high intensity at zero tilt. With increasing tilt, the superlattice peaks change linearly in position but periodically in height. They reach a maximum close to a tilt angle of $4^\circ$, corresponding to the first order of the superlattice.

Generally, in the case of the 7M martensite, the superlattice implies six additional intensity maxima along the reciprocal lattice vector [220]$^*$, as illustrated in the inset of figure 6. They are detectable here by setting the x-ray scattering vector in turn across the additional maxima (see the scheme of the inset), i.e. tilting the sample table to certain angles. Figure 6 gives the additional maxima measured from the reciprocal point (040)$^*$ to (220)$^*$ and marked here by ±1, +2, +3 and so on. The first-order maxima $+1$ and $-1$ emerge here simultaneously with high intensity, as they are the nearest neighbors to the center peak (040) and thus require a small tilt of about $3.5^\circ$. Accordingly, the second- and third-order maxima were measured at a tilt angle of about $8.0^\circ$ and $13.0^\circ$, respectively. The peak intensity decreases with the tilt angle due to reduced symmetry of the diffraction geometry. The peak positions of the high-order maxima +4, +5 and +6 are shown in figure 6. They cannot be measured here due to a necessary large tilt (>20$^\circ$), at which the sample table blocks the x-rays.
Figure 6. Superlattice peaks surrounding the center peak (040) measured for \( f_3 \) by setting the scattering vector in sequence across extra maxima located from \((040)^*\) to \((220)^*\), as schematically shown in the inset.

Figure 7. *In situ* heating XRD carried out for \( f_3 \), showing an austenite start temperature \( A_s = 465 \text{ K} \) and finish temperature \( A_f = 485 \text{ K} \) by heating and a martensite start temperature \( M_s = 475 \text{ K} \) and finish temperature \( M_f = 455 \text{ K} \) by cooling. Insets give the related diffraction patterns at different temperatures.

3.3. Influence of stress on the martensitic transition and the twin plane selection

To investigate the martensite–austenite transformation, *in situ* heating XRD experiments were carried out for the films. Because of their high intensity, both the austenite peak \((040)_A\) and the first superlattice peak \((S_-1)\) were chosen here to monitor intensity changes caused by phase transformations upon heating and cooling. Typical results measured for \( f_3 \) are plotted in figure 7. The inset of figure 7(a) shows the \((040)\) peaks observed on heating from 300 to 465 K at zero tilt,
convenient for observation of the austenite peak emerging above $T_M$. The inset of figure 7(b) presents the superlattice reflections measured at 4° tilt. The relevant peak intensities versus the temperature are given in figures 7(a) and (b), showing a hysteric temperature dependence of the phase transitions. The austenite start and finish temperatures are evaluated to be $A_s = 465$ K and $A_t = 485$ K. Simultaneously with the increase in the (040) peak, the superlattice peak intensity drops rapidly. The reverse transition takes place upon cooling, indicating the martensite start temperature at $M_s = 475$ K and the finish temperature at $M_t = 455$ K, respectively. The transition width, i.e. the difference $A_t - A_s$ or $M_s - M_t$, is about 20 K and the temperature hysteresis is about 10 K. The martensite start temperatures are listed as $T_M$ in table 1. The thin films $f_1$ and $f_2$ reveal a similar transition behavior at $T_M$ of about 505 and 495 K, respectively, slightly higher than for $f_3$. In contrast to film $f_1$, which contains a $\gamma$-phase and thus has an unknown composition in the parent phase, films $f_2$ and $f_3$ exhibit $T_M$ higher than the prediction from the phase diagram [20] according to the $e/a$ ratios. The increment of $T_M$ is about 100 K for $f_2$ and 25 K for $f_3$ and can be related to a stress-induced martensite. The biaxial tensile stress exists in the epitaxial films, which is deduced from the lattice parameters. It arises from the film–substrate lattice misfit (2.5%) and a thermal expansion difference ($\sim 0.1\%$ [15]). The stress shifts $T_M$ toward higher temperatures and can be approximately described by a generalized Clausius–Clapeyron relation, $d\sigma_c/dT_M = 2.2$ MPa K$^{-1}$ [27]–[29], deduced from uniaxial stress for bulk tetragonal martensite with $\sigma_c$ denoted as the critical stress where the austenite–martensite transformation starts upon mechanical loading. A biaxial tensile stress can be roughly estimated to be about 220 MPa for $f_2$ and about 55 MPa for $f_3$, being reasonable for the film thickness. In the martensite films, the stress is partly compensated via twin boundary formation and an unequal distribution of the martensitic variants. Obviously, the larger stress in $f_2$ confines the twin selection only along the 45° planes, as shown in figures 2 and 3(b), while the lower stress in $f_3$ allows the twin boundaries additionally along the perpendicular planes (figure 3(c)).

The $T_M$ value for $f_R$ is located below RT and was determined by means of magnetic and resistance measurements, as illustrated in figure 9(c), where the changes in resistance $R$ and magnetization $M$ occur upon transforming from martensite to austenite and vice versa. From these measurements, $M_s = 267$ K and $M_t = 259$ K upon cooling as well as $A_s = 266$ K and $A_t = 274$ K upon warming can be deduced. The value $M_s = 267$ K is 57 K higher than the 210 K expected for the stress-free bulk at $e/a = 7.5$. The increment in $T_M$ suggests a biaxial tensile stress of about 125 MPa in the epitaxial film $f_R$. Together with the data for $f_2$ and $f_3$, it can be concluded that the stress as a function of film thickness drops in an exponential-like manner, as plotted in figure 8.

3.4. Temperature dependence of the magnetization and electrical resistance

Temperature-dependent magnetizations measured for films $f_1$, $f_2$ and $f_3$ are plotted in figure 9(a), giving a Curie temperatures $T_C$ of about 270 K for $f_1$, 310 K for $f_2$ and 335 K for $f_3$, all being below $T_M$. The film $f_1$ shows the lowest $T_C$ and $M$, since it contains the $\gamma$-phase of Ni$_3$Ga, which is non-magnetic. $T_C$ for $f_2$ is slightly lower than the value of 340 K predicted from the phase diagram at $e/a = 7.7$. The film $f_3$ reveals an enhanced magnetization with $T_C$ comparable to the bulk value (330 K) at $e/a = 7.8$. The improvement in magnetic properties for $f_3$ can be attributed to its higher Mn content (table 1), because in Ni–Mn–Ga compounds about 92% of the magnetic moment originates from the Mn ions [30].
Figure 8. Tensile stress in films $f_2$, $f_3$ and $f_R$ estimated from measured $T_M$ in comparison to the stress-free bulk samples with respect to $e/a$ ratios. The exponential-like curve serves as a guide to the eyes.

Figure 9. Temperature-dependent magnetization (a) and electrical resistance (b) measured for films $f_1$, $f_2$ and $f_3$ in comparison to the reference film $f_R$ (c).

The stress influence on the magnetic properties is seemingly insignificant, based on the result that film $f_R$, in spite of a large stress, still shows a $T_C$ of about 380 K (see figure 9(c)), which is comparable to the stress-free bulk sample. Both the $T_C$ and magnetization measured for $f_R$ are higher than those for $f_3$. The result can be related to a lower chemical disorder in $f_R$ being close to stoichiometry.

The resistance $R$ measured for $f_1$, $f_2$ and $f_3$ is plotted in figure 9(b) versus temperature up to 350 K and normalized by the maximum resistance $R_{\text{max}}$ occurring at about 210 K for $f_1$, 255 K for $f_2$ and 315 K for $f_3$, coinciding with the significant drop in magnetization (see figure 9(a)). The magnetic anisotropy ($K_1$) and the magnetocrystalline anisotropy in Ni–Mn–Ga are expected to decrease near $T_C$; therefore, the decrease in $R$ with temperature suggests a structural change from a low-ordered to a high-ordered state, presumably related to relaxation of the lattice distortion induced by magnetoelastic coupling (magnon–phonon interaction) in the...
martensitic state [21]. It was observed that the slope of the elastic constant changes at $T_C$ [22]. The XRD data are insensitive to this structural change because of an extremely low intensity, as shown in figure 4. A pre-martensitic transition can, however, be excluded here because it usually takes place at a temperature slightly higher than $T_M$ and lower than $T_C$, i.e. for samples with $T_C > T_M$, which is not the case here. The film $f_R$ also shows a resistance maximum at about 237 K (figure 9(c)). This is far from $T_C$ (380 K), but rather close to $T_M$ (270 K). Thus, it is related to the martensite transition, dissimilar to the case of $f_1$, $f_2$ and $f_3$ (figure 9(b)), where the temperature for $R_{max}$ is close to $T_C$ and far from $T_M$. Additionally, the magnetic spin disorder scattering near $T_C$ may increase the electric resistance, giving rise to a negative magnetoresistance [30].

4. Conclusion

Epitaxial MSM films of different thicknesses and chemical compositions were grown on MgO(001) substrates by magnetron sputtering from a non-stoichiometric target Ni$_{50}$Mn$_{30}$Ga$_{20}$. The structural analysis of the films reveals a mixture of 7M and NM martensite phases at RT. Features of the layer-modulated martensite are visible in the STM images due to the presence of nanotwins, which are also confirmed by the WAXS patterns showing the superlattice structure. A strong impact of the chemical composition and the film thickness on the resulting crystallographic structure was observed. Increasing the Ni content (53 at.%) induces the formation of a $\gamma$-phase of the cubic Ni$_3$Ga, visible as single-crystal whiskers near the grain boundaries of the $L2_1$ parent phase and giving rise to a special microstructure. At small film thicknesses, we observe a preferential alignment of the [110] twin planes 45° to the substrate surface which gives rise to the surface corrugation, whereas at large thicknesses twin planes align additionally along the perpendicular planes. The abundance of different variants depends on the magnitude of the biaxial tensile stress in epitaxial films. The tensile stress values estimated from the measured $T_M$ values in comparison to stress-free bulk samples show an exponential-like decrease on increasing the film thickness. The magnetic properties of the films are unaffected by the stress. The electrical measurements show a resistance maximum close to $T_C$ for the martensitic films, which is explained based on the relaxation of the lattice distortion induced by magnetoelastic coupling.

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