Martensitic Transformation and Microstructure of Sputter-Deposited Ni–Mn–Ga Films

Volodymyr A. Chernenko¹, Manfred Kohl², Victor A. L’vov³, Volodymyr M. Kniazkyi³, Makoto Ohtsuka⁴ and Oliver Kraft⁵

¹Institute of Magnetism, Vernadsky str. 36-b, Kyiv 03142, Ukraine
²IMT, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany
³Taras Shevchenko University, Radiophysics Dept., Kyiv 03127, Ukraine
⁴IMRAM, Tohoku University, Sendai 980-8577, Japan
⁵IMF, Forschungszentrum Karlsruhe, D-76021 Karlsruhe, Germany

The martensitic transformation and microstructure of Ni–Mn–Ga films deposited on an alumina substrate and annealed at 1073 K for 36 ks are studied. Electrical resistivity and calorimetry measurements reveal a non-monotonous thickness dependence of the martensitic start temperature, \( T_{ms} \), at submicron film thickness. Focused Ion Beam (FIB) and standard SEM techniques are used to clarify the film microstructure. A martensitic morphology of films is confirmed by the FIB imaging to be a laminated twin structure aligned almost parallel to the film plane in each crystallite as a consequence of \{110\}-type crystallographic texture. A thermodynamic model based on the Landau formalism, taking into account the substructure of the film and the elastic interaction between film and substrate describes the essential features of the thickness dependence of \( T_{ms} \).

(Received September 26, 2005; Accepted November 29, 2005; Published March 15, 2006)

Keywords: nickel–manganese–gallium thin films, alumina substrate, martensitic transformation temperatures, martensitic morphology, modeling

1. Introduction

The ferromagnetic thermoelastic martensites, such as those inherent to the prototype Ni–Mn–Ga alloy system,¹ represent a novel type of materials with a strong spin–lattice coupling resulting in a unique combination of the magneto-mechanic/electric/caloric properties. These materials processed by a novel type of materials with a strong spin–lattice coupling resulting in a unique combination of the magneto-mechanic/electric/caloric properties. These materials processed by a thin film technology are promising for implementation as the built-in functional elements of microsystems.²,³ The transformation behavior and structural features of the submicron thin films are important aspects to be clarified in view of their crucial influence on the magnetic properties and their dependence on the possible strong constraint conditions superimposed by a substrate. Noteworthy, an epitaxially grown Ni–Mn–Ga film does not show a reverse martensitic transformation until it is released from substrate⁴ while in case of the submicron Ni–Mn–Ga films prepared by the other sputtering methods, a transformation behavior is similar to the bulk specimens (see, e.g., Refs. 5–7). The thickness dependence of both the transformation characteristics and magnetic properties was found in Refs. 6, 7). This was speculated to be a consequence of the particular martensitic substructure of the film.

A systematic study of the thickness effect on the martensitic transformation (MT), in combination with the direct observations of film substructure, is presented in this work. Two series of the submicron Ni–Mn–Ga thin films deposited on alumina ceramic and annealed at 1073 K for 36 ks are used for the measurements. The experimental results are explained in a framework of the Landau-type theory.

2. Experimental Results

Two series of films with the compositions of Ni₅₁₄Mn₂₈·₃-Ga₃₀·₃ (A) and Ni₅₃·₅Mn₂₃·₅Ga₂₂·₇ (B) deposited on alumina ceramic by the magnetron sputtering (see Refs. 6, 7) were vacuum annealed at 1073 K for 36 ks. The crystallographic features of annealed films were analyzed before⁶,⁷ and were attributed to 10M/14M martensitic structure for film A/B, respectively. Just-mentioned structure can be considered in the cubic coordinates as 5-layer/7-layer modulated tetragonal/orthorhombic lattice, respectively.⁸ In addition, a strong \{110\} in-plane texture of all the films was deduced.⁶,⁷

In this work, the films are characterized by the measurements of temperature dependencies of electrical resistivity, DSC ramps and FIB/SEM microstructural observations being made with a corresponding technique.⁶,⁷

Resistivity curves for both series of films are shown in Figs. 1(a) and (b). They demonstrate that the MT which is accompanied by the hysteretic anomaly occurs at the temperatures higher than room temperature but below Curie point characterized by the kink-like anomaly for films A, while films B show only hysteretic anomaly reflecting the fact that the ferromagnetic ordering occurs in these films in close vicinity to the MT. The magnitude of resistivity jump at MT as a function of the transformation temperature is correlated with previous results.⁹ The values of \( T_{ms} \) determined from Figs. 1(a) and (b) by the tangential method are listed in Table 1. According to the Table 1, they are subject to a notable variation in comparison with the values for the films of 5 µm thickness typifying the bulk behavior. The DSC measurements were only possible to perform for the latter films which were peeled off the substrate. DSC profiles shown in Figs. 2(a) and (b) and calculated values of transformation heats equal to 5.3 J/g for film A and 8.5 J/g for film B confirm the characteristics being typical for the bulk.⁹

Figures 3(a), (b) and (c) show the typical SEM images of in-plane surface and its cross-section obtained after fractur-
ing the films in a liquid nitrogen. The in-plane ripple surface which is characteristic for both the as-sputtered and annealed films consists of cellular fragments having size between roughly 1 and 0.1 µm. A distinct pattern of columnar structure with the similar width size dispersion is observed for the as-sputtered and annealed specimens [Figs. 3(b), (c), Ref. 10]. The enhanced resolution of FIB technique turned out to be more appropriate to visualize a cross-sectional microstructure of the martensitic phase of annealed films as it follows from inspection of Fig. 4. Alongside with the columnar-like grains, one can see an internal nanostructure of each column. The fascinating feature, each column is the laminate consisting of lamellae parallel to the substrate surface, each lamella can be considered as a twin variant. An average width of black and white lamellae is about 40 nm. Figure 5 represents an idealized geometrical model of the observed nanotwin structure with the details described in theoretical sections below.

3. Theoretical Treatment

3.1 Stress–strain evolution of the Ni–Mn–Ga film on cooled substrate

It is found (see Table 1) that $T_{ms}$ for submicron Ni–Mn–Ga films exceeds this value for the bulk specimen of the same alloy. It will be argued below that MT may be promoted by the mechanical stressing of the film, which appears owing to a difference between the thermal contraction of film and substrate on cooling from annealing temperature $T_0 = 1073 K$ to $T_{ms}$. It will be shown that the particular martensitic microstructure in Figs. 4 and 5 provides the most effective stress relaxation in the macroscopic fragments of the film attached to the substrate and undergoing MT.

Let the coordinates $x$, $y$, and $z$ are aligned with the ⟨100⟩ crystallographic directions of cubic lattice with spacing $d_0$, whereas the coordinates $ξ$, $η$, $ξ_1$ are associated with the film, i.e. $ξ$-axis is perpendicular to the film with $ξ_1 = 0$ at the interface between film and substrate while the axes $ξ$ and $η$ lie in the film plane (Fig. 5). The free-standing film is considered...
as unstressed at every temperature value. In contrast, a cooling of the film attached to $\text{Al}_2\text{O}_3$ substrate from $T_0$ down to $T_{\text{ms}}$ is accompanied by its stretching because of the difference between thermal expansion coefficient of the film, $\alpha_1$, and alumina substrate, $\alpha_2$. Thus, the in-plane tension, which arises on cooling of the circle-shaped film, is described by the strain tensor components $\varepsilon_{xx} = \varepsilon_{yy} \equiv \varepsilon(\xi, T) > 0$ and $\varepsilon(0, T) = (\alpha_1 - \alpha_2)(T_0 - T)$.

Below the MT temperature every column of the film is internally twinned. Let the twins shown in Fig. 5 be formed by the $x$- and $y$-variants of tetragonal crystal lattice, which means that the short $c$-axes in these variants are oriented close to $x$ and $y$ directions, respectively.

It may be assumed that $z$-axis is directed at the angle $\varphi$ to the $\zeta$-axis and this angle is different for different martensitic columns. A transition from crystallographic coordinates to the coordinates related to the film results in the following strain components:

$$
\varepsilon_{\zeta\zeta} = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{xy}) \cos^2 \varphi
+ \varepsilon_{zz} \sin^2 \varphi + \frac{1}{\sqrt{2}} (\varepsilon_{xz} - \varepsilon_{yz}) \sin 2\varphi,
$$

$$
\varepsilon_{\eta\eta} = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{xy}) \sin^2 \varphi
+ \varepsilon_{zz} \cos^2 \varphi - \frac{1}{\sqrt{2}} (\varepsilon_{xz} - \varepsilon_{yz}) \sin 2\varphi,
$$

$$
\varepsilon_{\xi\xi} = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy} + 2\varepsilon_{xy}),
$$

$$
\varepsilon_{\zeta\eta} = \frac{1}{2} (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{xy}) \sin 2\varphi
- \frac{1}{\sqrt{2}} (\varepsilon_{xz} - \varepsilon_{yz}) \cos 2\varphi.
$$

---

**Fig. 3** Typical SEM images of in-plane surface for annealed film A (a), cross-sectional view for as-received film B (b) and cross-sectional view for an annealed film B (c).

**Fig. 4** FIB image of the columnar grain structure of martensitic Ni–Mn–Ga film: the nanostructure of each column consists of lamellae parallel to the substrate surface which is the black bottom part of image. The film is covered by the contrast layer of Pt which is the top gray part of image.
3.2 Evaluation of martensite start temperature for stressed Ni–Mn–Ga film

An influence of the uniform axial stress on the transformation temperature of Ni–Mn–Ga alloy was analyzed in Ref. 11) using Clausius–Clapeyron relationship and Landau expansion for the Helmholtz free energy

\[
F = \frac{1}{2} c_2(u_x^2 + u_y^2) + \frac{1}{3} a_4 u_z(u_x^2 - 3u_y^2) + \frac{1}{4} b_4 (u_y^2 + u_z^2)^2
\]

(4)

where \(c_2 = C/3\), \(C\) is a shear modulus, \(a_4\) and \(b_4\) are the linear combinations of the third-order and forth-order elastic modules, respectively and

\[
u_2 = \sqrt{3}(\varepsilon_{xx} - \varepsilon_{yy}), \quad u_3 = 2\varepsilon_{zz} - \varepsilon_{yy} - \varepsilon_{xx},
\]

(5)

are the linear combinations of the strain tensor components, which are the basic functions of two-dimensional irreducible representation of the cubic symmetry group.

In the moment preceding the start of MT, the Ni–Mn–Ga film is inhomogeneously stressed due to its interaction with the substrate. Thus, an appropriate shift of MT start temperature should be evaluated using the energy function with gradient terms:

\[
F_{GL} = F + F_{\text{ang}}
\]

(6)

where

\[
F_{\text{ang}} = g\left[(\nabla_x u_2)^2 + (\nabla_y u_2)^2\right] + (h + g/3)
\]

\[
\times \left[(\nabla_x u_3)^2 + (\nabla_y u_3)^2\right] + (\sqrt{3}h - 2g/\sqrt{3})
\]

\[
\times \left[(\nabla_x u_2)(\nabla_y u_3) - (\nabla_y u_2)(\nabla_x u_3)\right].
\]

(7)

g and \(h\) are the phenomenological constants introduced in Ref. 12). For the isotropically stretched film, the stress depends on one coordinate only and \(u_2 = 0\) so, the eq. (6) is reduced to the form

\[
F_{GL} = g_0(u_3d_3/d\xi^2) + c_2u_3^2/2 + au_3^3/3 + bu_3^4/4,
\]

(8)

where \(g_0 = h + g/3\).

The function \(u_3(\xi)\) provides the minimal value to the Ginzburg–Landau functional

\[
F_0 = \int F_{\text{GL}}d\xi
\]

(9)

when

\[
dF_{\text{GL}} = \frac{dF}{du_3} = \frac{dF}{d(\nabla_x u_3)} = 0.
\]

(10)

The eqs. (8) and (10) result in the nonlinear differential equation

\[
c_2[\frac{u_3^2(\nabla_x u_3)^2}{u_3} - a_4u_3^2] - b au_3^4 + b au_3^4 = 0.
\]

(11)

As long as the in-plane elastic strain \(\varepsilon\) is substantially smaller than MT strain \(\varepsilon_0\), the eq. (11) has an approximate solution

\[
u_3 = A_1 \exp(-\xi/l_0) + A_2 \exp(-2\xi/l_0) + A_3 \exp(-3\xi/l_0)
\]

(12)
where \(l_0 = \sqrt{2\varepsilon_0/C_2}\) is a characteristic thickness of the strained layer of the film and \(A_3 \ll A_2 \ll A_1\). A thorough consideration shows that the last term in the eq. (12) is negligible so, the solution of eq. (12) can be expressed as

\[
u_3 = A_1 \exp(-\xi/l_0) + \frac{\sigma_2 A_2^2}{C'} \exp(-2\xi/l_0),
\]

where \(C'\) is the shear modulus of the alloy and \(A_1\) is expressed as

\[
A_1 = \left(0.5/C_2\right) - \frac{1}{6} \left(\sigma_3 \nu_3 + \sigma_3 \nu_3^3\right).
\]

Then, the minimum condition for Gibbs potential

\[
G = F - \frac{1}{6} \left(\sigma_2 \nu_3 + \sigma_3 \nu_3^3\right)
\]

with

\[
\sigma_2 = \sqrt{3}(\sigma_{xx} - \sigma_{yy}), \quad \sigma_3 = 2\sigma_{zz} - \sigma_{yy} - \sigma_{xx}
\]

shows that the nonzero value \(\nu_3\) corresponds to the stress

\[
\sigma_3 = 6\delta F/\delta \nu_3 = c_2 \nu_3 + a_2 \nu_3^2 + b_2 \nu_3^3.
\]

This stress shifts the MT temperature so, the local MT temperature is

\[
T_{ms}(\xi) = T_{ms}^{bulk} + (\partial T_{ms}/\partial \sigma_3)\sigma_3(\xi).
\]

The mathematical expression (18) is independent on the mode of creation of nonzero \(\sigma_3\) value. According to Ref. 11, a compression of the Ni–Mn–Ga specimen in [110] direction with the stress \(\sigma < 0\) results in the notable shift of martensite start temperature with \(\partial T_{ms}/\partial \sigma \approx -0.1\) K/MPa. For this mode of compression, \(\sigma_3 = -\sigma\) holds. Hence, the value close to 0.1 K/MPa may be expected also for \(\partial T_{ms}/\partial \sigma_3\).

In the vicinity of martensite start temperature, both the value \(C' \approx 60\) GPa\(^{13}\) and the relationships \(a_4 = 4C'/9e_0, b_4 = a_4/3e_0\)\(^{13}\) are used for the evaluation of energy parameters involved in the eqs. (13)–(18). The value \(\varepsilon_0(0) = e_0/8 = 0.5\%\) is also taken into account. A substitution of all estimated values into the eq. (18) results in \(T_{ms}(0) \approx 380\) K for the films A. The preliminary attempt of applying similar approach to the films B gives rise to \(T_{ms}(0) \approx 430\) K. Either of the numerical estimation is very reasonable to conclude that the mechanical stress arising on cooling of the Ni–Mn–Ga film deposited on \(\text{Al}_2\text{O}_3\) substrate can be considered as the origin of experimentally observed differences in the martensite start temperatures of the films and the bulk specimen.

The only adjustable parameter involved in the eqs. (13)–(18) is \(l_0\). The continuous changes of “local” martensite start temperature along \(\xi\)-axis computed using \(\partial T_{ms}/\partial \sigma_3 \approx 0.12\) K/MPa and \(l_0 = 0.2\) \(\mu\)m are shown in Fig. 6 together with the experimental data from the Table 1 plotted as a function of thickness. The satisfactory coincidence of some part of the experimental data with theoretical curve in Fig. 6 is in line with the suggested idea about the influence of constraints from substrate on the transformation behavior of Ni–Mn–Ga films. From the other hand, two experimental points on each graph have a regular deviation from the theoretical curve. This, probably, indicate that some other mechanisms like the transformation kinetics may contribute giving rise to the non-monotonous dependence of transformation temperature on the film thickness. The last point can be clarified by the further studies.

4. Conclusions

The experimental and theoretical results obtained for two series of submicron martensitic Ni–Mn–Ga films deposited on \(\text{Al}_2\text{O}_3\) substrate and annealed at 1073 K for 36 ks illustrate an important role of the elastic interaction between the film and substrate. A particular laminated nanotwin structure formed in the textured films was experimentally observed. It is found that transformation behavior of films is strongly influenced by the substrate which promotes the martensitic transformation by means of elastic stressing of the film resulting in the considerable increase of the martensite start temperature. In this situation, a forward martensitic transformation is accompanied by the formation of aforementioned martensitic structure resulting in the almost complete stress relaxation on the macroscopic scale.

A theoretically estimated increase of the martensite start temperature agrees with the values measured for the films with submicron thickness. However, the non-monotone character of the dependence of martensite start temperature on the thickness of the film needs a more detailed experimental and theoretical treatment.

Acknowledgements

V.A.C. is grateful for financial support from the guest scientist program of Forschungszentrum Karlsruhe.

REFERENCES