Recent Progress Towards Active Epitaxial Ni-Mn-Ga Magnetic Shape Memory Films

S. Fähler, O. Heczko, M. Thomas, R. Niemann, J. Buschbeck, L. Schultz
IFW Dresden, P.O. Box: 270116, 01171 Dresden, Germany

Abstract:
Bulk magnetic shape memory alloys like Ni-Mn-Ga single crystals reach high strains up to 10% in a moderate magnetic field. Epitaxial Ni-Mn-Ga films with a tailored microstructure are required for the integration into micro actuators. After shortly reviewing the recent progress towards active epitaxial films, this paper focuses on optimum growth conditions. The influence of deposition temperature on structure, ordering, transformation temperatures, magnetic hysteresis, composition and existence of magnetically induced reorientation (MIR) effect is analyzed in detail.

Keywords: Magnetic Shape Memory Alloys, Epitaxial Film, Magnetically Induced Reorientation

Introduction

Magnetic shape memory alloys reach strains up to 10%, which is about two orders of magnitude larger than common magnetostrictive and piezoceramic materials. In these alloys a magnetic field can force a modification of the microstructure whereby the variants of a low-temperature and low-symmetry martensitic phase are re-arranged. This magnetically induced reorientation (MIR) of twin variants is also called magnetic shape memory (MSM) effect.

Epitaxial films are seen as the most promising approach to prepare active films for microactuators as a significant strain in bulk MSM materials to date is only obtained in single crystals. Epitaxial growth of Ni-Mn-Ga has so far only been reported on GaAs (001) substrates using a Sc0.3Er0.7As buffer [1], on Al2O3 (110) [2], and on MgO(100) [3], exhibiting the martensitic phase only at low temperatures. Recently we reported on epitaxial films grown on MgO [4] and SrTiO3 [5] which are martensitic and ferromagnetic at room temperature. In these films the MIR effect was observed within the orthorhombic phase though the overall film extension was constrained by the rigid substrate. The existence of MIR was deduced from the typical hysteresis within the first quadrant in magnetization curves. The microstructural changes caused by MIR had been confirmed by additional texture measurement without and in the presence of a magnetic field. The external magnetic field changes the distribution of the variants without changing the macroscopic length of the film. This reorientation in a constrained film can only happen in the orthorhombic phase as this has an additional degree of freedom due to its three different crystallographic axes.

Compared to bulk, we observed that the martensitic transformation temperature can be significant higher in Ni-Mn-Ga films than expected for a particular composition [6]. We could attribute this due to a stress induced transformation. The stress state shifts the martensitic transformation temperature to higher values, stabilizing the martensitic phase. For a film deposited on MgO(100) at 400°C we showed that a tensile biaxial stress of 105 MPa shifts the martensitic transformation temperature to a 60 K higher value, in agreement with the shift expected from the film composition [6]. Part of the biaxial stress originates from the different thermal expansion coefficient of substrate and film. Using this concept, an increase of the martensitic transformation temperature of 0.045 K is calculated, when increasing deposition temperature by 1 K.

This key process towards active films had been obtained by optimizing film growth. Here we will focus on the required growth conditions and analyze the influence of deposition temperature on structure, transformation temperatures, magnetic hysteresis and composition.

Experimental

For deposition a DC sputter deposition process in a 10⁻⁹ mbar base pressure range was used in order to avoid oxidation of the films. The 4” sputtering target was an arc-melted stoichiometric Ni50Mn25Ga25 alloy. The films were prepared on MgO(100) substrates at deposition temperatures ranging from 300 to 600°C with a thickness around 500 nm as measured by a quartz microbalance (Inficon XTM). The thickness of a selected film deposited at 400°C was confirmed by a Focused Ion Beam (FIB) cut [4]. The magnetic properties were measured in a Quantum Design PPMS using a Vibrating Sample Magnetometer (VSM). Structural studies were performed using X-ray diffraction (Co Kα radiation) in a Philips X pert machine. The composition of the films was determined with an accuracy of about 0.5 at.% by electron dispersive X-ray analysis (EDX) using a bulk Ni50Mn25Ga25 standard.
Phase formation

The X-ray diffraction (XRD) pattern measured at room temperature in Bragg-Brentano geometry of a sample series deposited at different temperatures is shown in fig. 1. The vertical dotted lines mark the positions of peaks corresponding to polycrystalline cubic Ni$_2$MnGa austenite ($a = 0.5821$ nm) [7]. Two very pronounced and sharp peaks in the measured diffractograms originate from the single crystalline MgO(001) substrate with a lattice constant $a = 0.4194$ nm. The film deposited at 300°C exhibits only a single (400) reflection, as expected for the austenite state ($c/a = 1$). As no reflections of other lattice planes are observed, this film exhibits a high degree of fiber texture, indicating presumably epitaxial growth. When increasing the deposition temperature to 350°C and 400°C, two distinctive convolutions of peaks close to the (400)$\lambda$ and (200)$\lambda$ austenite lines appear. Three overlapping peaks at the angle close to the (400)$\lambda$ austenite peak can be indexed as a (pseudo-)orthorhombic phase with the lattice constants: $a = 0.609$ nm, $b = 0.578$ nm, $c = 0.554$ nm using the coordinates related to the parental cubic austenite phase [8]. Analyzing pole figure measurements the epitaxial orientation Ni-Mn-Ga(100)[110] || MgO(100)[100] had been determined for this sample [4]. An increase of deposition temperature to 450°C results in an even larger peak splitting giving a $c/a$ ratio of 1.22. A tetragonal martensite with a similar $c/a$ is known from bulk, but exhibits no MIR. A further increase of deposition temperature to 600°C results in several reflections, which could not be indexed unambiguously.

For the films deposited at 350° and 400°C a series of three reflections is observed within a few degrees around the austenite (200)$_\lambda$ line, whereas no reflection in this region is observed for the film deposited at 300°C. The presence of these (200)$_\lambda$ superstructure reflections indicates a high degree of chemical order in the off-stoichiometric films. Apparently the elevated deposition temperature provides sufficient mobility for the atoms on the surface to achieve ordering in the Heusler alloy. For Ni$_2$MnGa however X-ray is not very suitable to quantify the degree of order as for a sample with exact stoichiometry the atomic structure factors nearly cancel out and this reflection can vanish [9]. To decide, if the film deposited at 300°C might be ordered, also the film composition has to be measured and compared with other films.

Phase transformations

Fig. 2 shows the temperature dependence of the susceptibility from which the transformation parameters can be obtained, as described previously [4]. The increase of susceptibility from zero indicates a ferromagnetic transition. The strong decrease of the susceptibility denotes the transformation from a soft magnetic austenite to a martensite with high magnetocrystalline anisotropy. This decrease is similar for the two films having an orthorhombic phase ($T_D= 350$ and 400°C), but the susceptibility of the film deposited at lower temperatures exhibits two different slopes, possibly due to an inhomogeneous or two stage (possibly premartensitic) transition. The relative decrease of susceptibility is significantly lower for the film exhibiting the austenite phase at room temperature ($T_D= 300°C$), suggesting that a different martensite occurs in this film (not accessible by room temperature XRD).
Table 1: Summary of transition temperatures (Curie temperature $T_c$, martensitic start $M_s$, martensitic finish $M_f$, austenitic start $A_s$, austenitic finish $A_f$) and electron density $e/a$ for films deposited at different temperatures $T_D$.

<table>
<thead>
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<th>$T_D$ (°C)</th>
<th>$e/a$</th>
<th>$T_c$ (K)</th>
<th>$M_s$ (K)</th>
<th>$M_f$ (K)</th>
<th>$A_s$ (K)</th>
<th>$A_f$ (K)</th>
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<td>363</td>
<td>275</td>
<td>269</td>
<td>281</td>
<td>287</td>
</tr>
<tr>
<td>350</td>
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<td>356</td>
<td>303</td>
<td>296</td>
<td>304</td>
<td>309</td>
</tr>
<tr>
<td>400</td>
<td>7.64</td>
<td>352</td>
<td>319</td>
<td>314</td>
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<td>325</td>
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<tr>
<td>450</td>
<td>7.72</td>
<td>350</td>
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The film deposited at 450°C transforms to martensite above $T_c$ and thus no decrease of susceptibility is observed.

The transformation temperatures are summarized in Table 1. As described in the introduction, the differences of thermal expansion coefficients suggest an increase of the martensitic temperature by 2.3 K per 50 K increase of deposition temperature. The observed shift is significantly higher; hence other influences have to be examined.

Magnetic Hysteresis

Magnetization curves were measured in $[100]$ Ni-Mn-Ga in-plane direction of the epitaxial films. The magnetization curves accessible in austenite state ($T_D=300$ to 450°C) are rectangular, exhibit a low coercivity and do not differ significantly (not shown). The magnetization curves of films in the martensitic state (Fig. 3) differ significantly from this rectangular shape. When transforming to martensite the microstructure splits into many variants with different orientations. In tetragonal martensite there are three variants having two different orientations with respect to the magnetic field. Due to a tetragonal distortion and twinning these directions are only approximately parallel. The magnetization curve of the film prepared at 450°C exhibits an initially sharp increase of magnetization and then a slow approach to saturation due to magnetocrystalline anisotropy. This type of curve is expected for a multivariant sample consisting of variants with their easy plane and hard axis along the field direction [10].

Films deposited at 350°C and 400°C posses an orthorhombic structure with a hard, medium and easy axes and thus the curve consists of four distinctive parts, which had been analysed in detail [4]. The important feature is the hysteresis in the first and third quadrant shown in inset of Fig. 3, exhibiting characteristic steps indicating magnetically induced reorientation [4].

Fig. 3: Magnetization curves of the films in martensitic state. The inset shows details at low fields. Black (full line) - film deposited at 450°C red (dash) – film deposited at 400°C, green (dot) -film deposited at 350°C, all measured at 297 K, blue (dash-dot) - film deposited at 300°C, measured at 270 K. As these films exhibit different transformation temperatures, also different measurement temperatures had to be used. This affects saturation magnetization and thus for better clarity all curves are normalize to magnetization in a field of 2 T.

The height of the steps gives the amount of reorientation, which is largest for the film deposited at 400°C.

The magnetization curves of the films deposited at 300°C and 450°C do not exhibit this feature. The film deposited at 450°C is in the tetragonal martensite phase with $c/a>1$ which is known from bulk not to exhibit the MIR effect. This phase has no uniaxial anisotropy but is an easy plane magnet which can explain the very low coercivity observed in this film. Contrary to this, the film deposited at 300°C exhibits the highest coercivity. Probably due to low chemical ordering and variant misalignment, the curve has a roundish shape and the approach to saturation is slow.

Film compositions

It was found that the film composition strongly depends on deposition temperatures (fig. 4). When increasing deposition temperature a decrease of Mn and Ga content and thus an increasing amount of Ni is observed. It is suggested, that this occurs due to the higher vapor pressure of elements like Mn and Ga compared to Ni at higher temperatures. This is more important in thin films exhibiting a larger surface/volume fraction than in bulk.

It is known that the phase formation in Ni-Mn-Ga strongly depends on the density of electrons per unit cell (the $e/a$ ratio) and thus phase formation can be also controlled by adjusting the composition of the film. From bulk it is known that increasing the $e/a$ ratio the martensite transformation temperature goes up and Curie temperature slightly decreases. The
changing c/a explains the observed decrease of $T_c$ and increase of martensitic transformation temperatures with higher deposition temperatures from 350°C to 450°C.

However it can hardly explain the difference between the films deposited at 300°C and 350°C, having a very similar composition. The similar composition of both films, however, allows to attribute the relative intensity of the (200) superstructure line to ordering. The absence of this line for the film deposited at 300°C (Fig. 1) suggests that this low deposition temperature is not sufficient for ordering. From bulk it is known that absence of chemical order lowers the martensitic transformation temperature [9], which can explain the differences between these two samples.

**Fig.4:** Composition variation with deposition temperature for films prepared on MgO substrate. The composition of the target is also shown. The structure of the films at room temperature is noted. The error bar is shown for Ga and is similar for the other elements.

### Conclusions

The deposition temperature strongly influences the properties of Ni-Mn-Ga films. Temperatures above 300°C are necessary to obtain a sufficient degree of order. A higher temperature further results in a loss of Mn and Ga, very likely due to evaporation of these elements. This increases the e/a ratio and in agreement with bulk martensitic transformation temperatures rise. A deposition temperature of 600°C results in non-Heusler structure suggesting that this high temperature range should be avoided. In the deposition temperature range from 300 to 450°C only (001) reflections of the Ni-Mn-Ga phase are observed, indicating that the epitaxial growth of this phase is quite robust and uncomplicated. These trends should be valid in general, though the specific film compositions are expected to depend on target composition and the specific sputtering conditions. Deposition temperature can be used for fine tuning of film composition and in the present experiments an optimum for a high MIR is observed when depositing at 400°C.

On a rigid substrate however no length change is possible; hence for actuation free standing films are required. Recently we reported on an approach to peel off epitaxial films to obtain such free standing films [11]. Recently free standing epitaxial film were also prepared by dissolving NaCl substrate [12].

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### References