Effect of substrate on processing of multi-gun sputter deposited, near-stoichiometric Ni$_2$MnGa thin films

B.C. Bayer $^{a,*}$, A.F. Khan $^b$, M. Mehmood $^b$, Z.H. Barber $^a$

$^a$ Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK
$^b$ Department of Chemical and Materials Engineering/National Centre for Nanotechnology, Pakistan Institute of Engineering and Applied Sciences, P.O. Nilore, 45650, Islamabad, Pakistan

**A R T I C L E   I N F O**

Article history:
Received 30 March 2009
Received in revised form 11 August 2009
Accepted 13 August 2009
Available online 23 August 2009

Keywords:
Sputtering
Ferromagnetic shape memory alloys
Heat treatment
Silicides

**A B S T R A C T**

Near-stoichiometric Ni$_2$MnGa thin films were sputter deposited with a multi-gun sputter deposition system onto sapphire, silicon dioxide and silicon substrates and exposed to heat treatments in vacuum. The multi-gun setup was proven to be feasible for switching compositions quickly and reliably. Using chemical, morphological, magnetic and structural characterisation methods the effects of the different substrates on the Ni$_2$MnGa film properties as a function of heat treatment temperature were studied: sapphire and silicon dioxide provided a metallurgically inert substrate for Ni$_2$MnGa thin films and resulted in films showing room temperature magnetizations of up to ~350 kA/m and austenitic/martensitic structures upon heat treatments at 700 °C. The highest mechanical stability of Ni$_2$MnGa occurred on sapphire substrates, due to the closest match of the thermal expansion coefficients. Silicon substrates led to silicide formation for heating temperatures of 550 °C and above, leading to the loss of ferromagnetism and the austenite/martensite structure in the films.

© 2009 Elsevier B.V. All rights reserved.

---

1. Introduction

Ferromagnetic Shape Memory Alloys (FSMAs) have been studied extensively because they incorporate both the Shape Memory Effect (SME) and ferromagnetic behaviour [1]. This is in contrast to well known, common Shape Memory Alloys (SMAs) like NiTi which lack ferromagnetism. In both SMAs and FSMAs the SME is ascribed to a martensitic transformation between two phases (martensite and austenite) and its reversal. This transformation allows a common SMA to restore its initial shape after deformation upon the application of heat and/or stress. In FSMAs this martensitic transformation is linked to the magnetic state of the material, which allows triggering of the SME under certain conditions not only by heat or stress but also by the application of a magnetic field. For a review of FSMAs see Ref. [2].

FSMAs have great potential for application as actuators and sensors since magnetic triggering gives fast response times (in comparison with heat transport for actuation of common shape memory materials such as NiTi). They can also show larger strains than magnetostriective and piezoelectric materials. Response times below 1 ms, when triggered magnetically [3] and strains up to ~10% [4] have been reported. Furthermore, magnetically controlled FSMAs can be used in environments in which ordinary shape change technologies face particular limitations, e.g. in liquids or biomedical applications.

The most extensively studied FSMA is the Heusler alloy Ni$_2$MnGa [5,6]. All parameters of Ni$_{2+x+y}$Mn$_{1-x-y}$Ga$_x$ such as structure and transformation temperatures (e.g. martensitic phase transformation onset temperature, $M_s$, and magnetic Curie temperature, $T_C$) are very sensitive to the chemical composition. Hence material properties may be precisely engineered for specific applications by optimising the composition. Bulk Ni$_2$MnGa is highly brittle [7], a disadvantage which can be overcome in single crystals and thin films [8]. As single crystal Ni$_2$MnGa is costly and difficult to shape [9], thin films are the more promising solution to the problem of brittleness as well as offering opportunities for miniaturisation. Initial proof of principle and theoretical studies of Micro-electro-mechanical systems type applications of Ni$_2$MnGa was reported [10–15], however for bio-applications an initial study showed that the biocompatibility of Ni$_2$MnGa is questionable [16].

Ni$_2$MnGa thin film properties are controlled by the chosen fabrication technique and process conditions as well as type and properties of the substrate. This opens up a large parameter space for film properties which has, as yet, only been explored to a small extent: Pulsed Laser Deposition [17–23], Molecular beam epitaxy [24–26] and Flash evaporation [27–34] have been used, but sputter deposition is the technique for fabrication of Ni$_2$MnGa which has shown greatest potential for films exhibiting shape change on both thermal and magnetic triggering [7,8,10–13,35–41]. Mainly single target sputtering, using a pre-alloyed target with near-stoichiometric composition...
has been used to sputter deposit Ni$_2$MnGa. However, use of a multi-gun approach with separately controllable elemental or alloy targets has been shown to provide a simple way of producing films with varying, closely controlled compositions, thereby engineering the film properties (e.g., [42], for FePd [43], NiTi and NiTi films alloyed with a third element [44–46]).

In a multi-gun setup the film composition is simply controlled via the powers applied to the different sputtering targets, whilst substrates may be rotated in front of the sputter targets to achieve a homogeneous film composition (Fig. 1). This offers direct control over film composition and easy switching between compositions, without the need to change the “hardware”. In addition, it offers flexibility for adjustments required when varying other deposition parameters, such as sputtering gas pressure, which affect the film composition.

In this study we show that multi-gun sputter deposition is a highly flexible method for deposition of Ni$_{2+x+y}$Mn$_{1-3}$.Ga$_{1-y}$ films of varying compositions and elucidate material interactions upon heat treatments between the deposited films and their substrates which strongly affect the properties of the films.

2. Experimental setup

Substrates of r-plane sapphire (Al$_2$O$_3$), fused quartz (SiO$_2$) and silicon (1 0 0) (incl. a native oxide layer, Si) were cut, ultrasonically cleaned and loaded into an ultra-high vacuum multi-gun sputtering system [47], consisting of three independent DC magnetron targets (35 mm × 55 mm, target-substrate distance ~50 mm) mounted on a 200 mm flange for deposition of the Ni$_2$MnGa films. The targets used were Ni, Mn and Ni$_2$Ga$_3$ (due to stability problems with pure Ga). The substrate support (diameter 110 mm) was rotated in front of the targets at 5 rpm and the substrates remained unheated. Shielding between the targets and the substrate support allowed pre-sputtering of the targets, without exposing the substrates to the depositing flux, in order to pre-clean the target surfaces and make adjustments to the deposition parameters (pressure, target powers) before commencing the deposition. A constant flow of the sputtering gas Ar during film deposition was achieved with a leak valve, where different Ar pressures were controlled by throttling the gate valve to the main pump. During the deposition run the pressure was monitored and controlled manually (±0.05 Pa of the desired value). Three custom-built power supplies (either manually monitored or computer-controlled via Labview programme) were used for simultaneous deposition from the three magnetron targets. After loading samples into their pre-sputter positions the system was pumped down and baked out overnight yielding a base pressure of ~10$^{-7}$ Pa. The residual gas composition was checked by a residual gas analyser, before introducing the Ar flow. After igniting the plasma and setting up of stable conditions with the samples in their shielded pre-sputter position the computer-controlled, continuous rotation of the sample stage was started, exposing the substrates consecutively to the three targets. The total deposition time was used to control the final film thickness.

Post-deposition heat treatments were undertaken by resting samples on a custom-built resistive heater strip in a vacuum system (10$^{-6}$Pa). The strip was heated by applying a set current from a voltage/current source which was calibrated using an optical pyrometer (temperatures used were 400 °C, 550 °C and 700 °C at ramps of 10 °C/min with an uncertainty of ±50 °C).

High magnification imaging and chemical analysis were performed with a Scanning Electron Microscope (SEM)/Energy Dispersive X-ray Spectroscopy System (EDX) JEOL 5800LV SEM (acceleration voltage: 16–20 kV). The chemical composition was measured at several spots on reference samples from each deposition run. Structural investigations were carried out using a Bruker AXS D8 advance X-ray diffractometer (XRD) (Bragg-Brentano geometry, Theta-Theta scans, Cu X-ray source: 1.541 Å). To measure (in-plane) magnetic hysteresis curves a Princeton Measurements Corp. Model 2900 MicroMag Vibrating Sample Magnetometer with an accessible temperature range of 80 K to 473 K was used. Estimated uncertainty in magnetisation was 5% for room temperature hysteresis curves. The magnetisation versus temperature measurements for acquiring Curie Temperatures were less accurate due to fast heating (±50 °C). The magnetisation values were corrected for substrate effects and the film volume to obtain magnetisation per volume ($M_{\text{vol}}$). The volume of the films was estimated from the sample area and the film thickness which was measured by a Veeco Dektak 6M Stylus Profiler (scanning over the step height on partially masked Si or SiO$_2$ substrates (“thickness monitors”). All stated magnetisation per volume values have an estimated uncertainty of ±10% attached to them.

3. Results and discussion

3.1. As deposited films

In several deposition runs the flexibility in varying the film composition with the multi-gun setup was tested. After depositing several calibration films (O-series), the A series and the B series had constant deposition parameters within each series but were deposited alternately, i.e. switching from A- to B series from run to run. The A series yielded consistently a Mn-rich film with deficiency in Ga and near-stoichiometric Ni. The B series was nearer to stoichiometry in Mn and Ga content, with a higher Ni level (see Table 1). The uncertainty in the obtained values comes 1. from the EDX/SEM setup (0.5 at.% to 1 at.%), and 2. a spread in composition over the substrate holder. A region of stable composition on the substrate holder was identified (for Mn up to ±3 at.% for Ni up to ±3 at.% for Ga up to ±4 at.%). For samples kept within that region the feasibility of a multi-gun setup for depositing varying compositions was shown (in comparison with single-gun deposition). However, a very close monitoring of the deposition process was required in this more complex setup (i.e. maintenance of constant powers on the three separate targets).

As deposited films on all substrates looked uncracked and smooth by SEM and had a metallic, silver appearance. The as deposited composition was not a function of the substrate type.

3.2. Heat treated films

Heat treatments were performed on separate samples from each deposition run, i.e. no consecutive heating of one sample was performed. Heat treatment runs included several samples on different substrates and were repeated for reproducibility. Sample positions on the heater were kept constant to rule out local heating effects and samples were neither measured nor processed prior to heating to rule out cross-contamination. Nevertheless, we found significant variation in the magnetic and structural properties from one heating run to the other which indicated that the quality of the vacuum and the sample/substrate...
heater thermal contact varied in between runs. Introducing more stringent vacuum conditions improved the results, although there remains room for further improvement of the heating setup.

Upon heating, the samples developed different properties depending on their substrate:

Ni$_2$MnGa films on Al$_2$O$_3$ remained uncracked after heat treatments up to 700 °C in vacuum. See Fig. 3, left. However, they changed their surface colour from metallic silver to red, blue or green (depending on sample) which is attributed to the formation of surface layers which act as interference layers. There was no correlation of the surface colour developed and other film properties. SiO$_2$ showed a similar evolution with heating, however films were likely to crack and flake off (Fig. 3, middle). Films on Si showed an evolution similar to the other substrates up to 400 °C, but after heat treatments above 550 °C films become optically matt and the smooth, featureless surface changed into a distinct surface pattern with Jan-sized features of darker contrast. See Fig. 3, right.

The comparatively bad adhesion upon heat treatment of the films on SiO$_2$ is ascribed to the different thermal expansion coefficients of Al$_2$O$_3$ ($7.4 \times 10^{-6} \text{K}^{-1}$), Si ($2.5 \times 10^{-6} \text{K}^{-1}$) and SiO$_2$ ($0.4 \times 10^{-6} \text{K}^{-1}$) [48]. As the thermal expansion coefficient of near-stoichiometric Ni$_5$MnGa is higher ($>10 \times 10^{-6} \text{K}^{-1}$) [49,50], the low expansion of SiO$_2$ upon heating leads to stress in the substrate to surface composition (thickness, deposition rate, composition) for the runs undertaken.

<table>
<thead>
<tr>
<th>Run</th>
<th>Ar-pressure/Pa</th>
<th>Power Ni/W</th>
<th>Power Ni$_2$Ga$_3$/W</th>
<th>Power Mn/W</th>
<th>Time of run/min</th>
<th>Thickness/nm</th>
<th>Deposition rate/(nm/min)</th>
<th>Mn/at.%</th>
<th>Ni/at.%</th>
<th>Ga/at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2</td>
<td>22</td>
<td>20</td>
<td>11.3</td>
<td>200</td>
<td>880±80</td>
<td>4.4±0.4</td>
<td>24±2</td>
<td>51±2</td>
<td>25±2</td>
</tr>
<tr>
<td>A1</td>
<td>1.25</td>
<td>22</td>
<td>20</td>
<td>11.3</td>
<td>180</td>
<td>1100±45</td>
<td>6.1±0.3</td>
<td>30±1</td>
<td>48±2</td>
<td>22±2</td>
</tr>
<tr>
<td>A2</td>
<td>1.25</td>
<td>22</td>
<td>20</td>
<td>11.3</td>
<td>180</td>
<td>1020±60</td>
<td>5.7±0.3</td>
<td>28±2</td>
<td>50±3</td>
<td>22±2</td>
</tr>
<tr>
<td>A3</td>
<td>1.25</td>
<td>22</td>
<td>20</td>
<td>11.3</td>
<td>180</td>
<td>980±50</td>
<td>5.5±0.3</td>
<td>31±2</td>
<td>53±2</td>
<td>16±3</td>
</tr>
<tr>
<td>B1</td>
<td>1</td>
<td>19.3</td>
<td>20</td>
<td>7.9</td>
<td>180</td>
<td>885±40</td>
<td>4.9±0.2</td>
<td>24±2</td>
<td>51±2</td>
<td>25±2</td>
</tr>
<tr>
<td>B2</td>
<td>1</td>
<td>19.3</td>
<td>20</td>
<td>7.9</td>
<td>180</td>
<td>850±30</td>
<td>4.8±0.2</td>
<td>25±3</td>
<td>52±2</td>
<td>23±4</td>
</tr>
<tr>
<td>B3</td>
<td>1</td>
<td>19.3</td>
<td>20</td>
<td>7.9</td>
<td>180</td>
<td>850±40</td>
<td>4.8±0.2</td>
<td>25±3</td>
<td>54±3</td>
<td>21±4</td>
</tr>
</tbody>
</table>

In-plane magnetisation curves were recorded at room temperature for heated and as deposited samples. A typical maximum magnetisation as a function of temperature of heat treatment is given for the A series, separated as a function of substrate in Fig. 5.

As deposited films on all three substrates were paramagnetic. On Al$_2$O$_3$ and SiO$_2$ after heat-treating at 400 °C ferromagnetic behaviour develops and with further increase of the temperature of the heat treatment the coercivity as well as the saturation magnetisation increases (max. magnetisation after 700 °C treatment ~350 kA/m). The evolution of the B-series samples was similar, with a slightly larger spread in obtained magnitudes of magnetization for a given treatment temperature. The observed development of room temperature ferromagnetism is comparable to previous studies both in temperatures and magnitudes of magnetisation [8,37], where the necessity to heat films which were deposited at room temperature to obtain ferromagnetism was ascribed to diffusion controlled establishment of small scale structural and magnetic order only at elevated temperatures [8].

While the magnetic properties on Al$_2$O$_3$ and SiO$_2$ were comparable, Si as a substrate showed a different picture: Up to 400 °C the evolution of magnetization was similar as on Al$_2$O$_3$ and SiO$_2$ but at higher heating temperatures (550 °C and 700 °C) the maximum magnetisation dropped and the ferromagnetic behaviour vanished. This disappearance of ferromagnetism is ascribed to the diffusion process between Si and Ni$_5$MnGa proposed above and indicates that the phase(s) formed upon heating is paramagnetic. Similar behaviour on Si has already been reported for Pulsed Laser Deposited films which lost their ferromagnetism afterannealing at 800 °C or if deposited at substrate temperatures of more than 650 °C [17].

Low-temperature magnetic measurements on Al$_2$O$_3$ and Si were undertaken, in which the in-plane magnetisation at a constant applied
field of 160 kA/m was measured over a temperature range from 80 K to 473 K. As deposited films on both Al₂O₃ and Si showed paramagnetic behaviour over the entire temperature range from 80 K to 473 K with a constant magnetisation value (i.e. Pauli paramagnetism [30,53]). On Al₂O₃ all samples exhibit ferromagnetism after undergoing a heat treatment, however, with spreads in magnitude of magnetisation and Curie Temperatures in a range from (390 ± 50) K to (473 ± 50) K for A series and from (295 ± 50) K to (465 ± 50) K for B series. These variations are again ascribed to fluctuations in vacuum quality and thermal contact during heat treatment. On Si for the 400 °C treated samples the (ferro-)magnetic properties as a function of temperature range are similar to Al₂O₃, but after heat-treating samples on Si at or above 550 °C they remain paramagnetic over the entire temperature range measured, confirming the results from the room temperature measurements. XRD measurements showed that as deposited films on Al₂O₃, Si and SiO₂ are partially crystalline cubic austenite upon deposition (representative pattern in Fig. 6, peaks identified by [54]). The partial crystallinity of the film after sputtering is attributed to plasma induced heating up of the substrate in the course of sputtering [35]. Upon heating up to 400 °C the dominant (2 2 0) peak shifts slightly and increases in magnitude. This is attributed to further crystallisation in the cubic austenitic state [8]. This behaviour has been found in all 400 °C heated samples on all substrates. (To ensure that no structural change in the substrates upon heating is assigned to the film, bare substrates were heated at 700 °C. The bare substrates showed no structural changes upon heating at all, implying that the observed changes in structure are entirely happening in/in connection with the NiMnGa film.)

If heating at higher temperature different substrates show different structural evolution, corresponding well with the other information presented above: On Al₂O₃ and SiO₂ two different evolution patterns can be found: 1. The austenitic peak grows larger in size up to 700 °C (with a small shift in position), indicating that the material crystallizes further in the austenitic state (Fig. 6). 2. In other cases, which are not a function of whether the film is Mn-rich (A series) or near stoichiometric (B series), nor dependent upon Al₂O₃ or SiO₂ substrates, the austenitic peak splits into two peaks: one at a slightly smaller angle than the 400 °C austenite peak and one at a slightly larger angle. This is ascribed to the formation of martensite and its (2 2 0) and (2 0 2) reflections [28,39]. See Fig. 7. The coexistence of austenite and martensite cannot be ruled out, as the peaks are strongly overlapping and cannot be simply separated with respect to e.g. intensity ratios because of possible texture of the films [28]. This observed crystallisation behaviour is very similar to previous studies [8,34,37]. In addition, some manganese oxide was found in some samples of both A and B series which did not lead to any detectable degradation of the magnetic properties of the films. This again agrees with previously published reports [19,20,36].

Si, on the contrary, showed a different behaviour if heated at or above 550 °C: The martensite/austenite peak(s) completely disappeared and a new pattern of peaks evolved. See Fig. 8. This was accompanied by the vanishing of ferromagnetism and development of paramagnetism between 80 K and 473 K and also correlates with the change in surface appearance (Fig. 3) as well as the strong increase in Si signal in surface EDX spectra (Fig. 4). Therefore, it is confirmed that through a diffusional process Si and Ni₂MnGa form new phase(s) at these elevated temperatures. Comparison with [54] shows both Ni and Mn form silicides (NiSi₂ and Mn₁₅Si₂₆, respectively, with corresponding peaks labelled accordingly in Fig. 8). It was previously speculated that either formation of silicides or evaporation of Mn from the films leads to the vanishing of ferromagnetism in Ni₂MnGa on Si after heat treatments at elevated temperatures [17]. Our results confirm the former [55]. A previous study [39] reported similar behaviour and identified the formation of Mn₁₅Ni₃Si₁₅. However, neither the Mn₁₅Ni₃Si₁₅ pattern, nor any other Mn,Ni,Sn,Ge entry from [54], matches with our recorded patterns. There is no decrease in Ga content, according to EDX, and, despite identification of the

Fig. 3. SEM micrographs of A2 after heating at 700 °C on Al₂O₃ (left), SiO₂ (middle) and Si (right). Note the surface pattern with μm-sized features of darker contrast on Si in contrast to the featureless, smooth film surface on Al₂O₃ and SiO₂.

Fig. 4. Ratios of EDX intensities of Kα lines of substrate element (Si) over the sum of film elements (Ni + Mn + Ga) as a function of treatment temperature for SiO₂ and Si substrates.

mechanism of Ni$_2$MnGa–Si interaction, it is not clear where the Ga fits into the crystal structure present in the heat treated, silicized films.

4. Conclusions

Near-stoichiometric Ni$_2$MnGa thin films of different compositions were sputter deposited with a multi-gun sputter deposition system showing the flexibility of this setup. The effect of the substrate (Al$_2$O$_3$, SiO$_2$ and Si) on the film properties following heat treatments was studied: Al$_2$O$_3$ and SiO$_2$ provide a metallurgically inert substrate for Ni$_2$MnGa thin films with good obtainable magnetizations and an austenite/martensite structure upon vacuum heat treatment. While SiO$_2$ leads to cracking of the film upon heating, Al$_2$O$_3$ also provides mechanical stability. Si on the contrary leads to silicide formation with

![Fig. 5.](image1)

Fig. 5. Maximum room temperature magnetization as a function of heat treatment temperature for A series films on a) Al$_2$O$_3$, b) SiO$_2$ and c) Si. d) shows a typical magnetization vs. applied magnetic field measurement for A3 samples after heat treatments [Inset e.) shows a zoom-in into the low field region of d.].

![Fig. 6.](image2)

Fig. 6. XRD pattern of B3 on SiO$_2$ as deposited and after heat treatments at various temperatures (incl. a SiO$_2$ substrate as reference pattern).

![Fig. 7.](image3)

Fig. 7. XRD pattern of A3 on SiO$_2$ as deposited and after heat treatments at various temperatures (incl. a SiO$_2$ substrate as reference pattern).
the Ni$_2$MnGa at elevated temperatures which, in turn, leads to the loss of ferromagnetism and the austenite/martensite structure in the films.

Acknowledgements

A. F. Khan acknowledges the Higher Education Commission of Pakistan for providing a six months fellowship as a part of his PhD research at Cambridge University. This work was partially funded by the UK EPSRC.

References