Magnetic Properties, Structure and Shape-Memory Transitions in Ni–Mn–Ga Thin Films Grown by Ion-Beam Sputtering

Jae-Pyoung Ahn, Ning Cheng, Thomas Lograsso, and Kannan M. Krishnan

***Abstract*—$Ni_{1-2x}Mn_xGa_x$ ($x \sim 0.2$ and 0.25) alloys in thin film form were prepared by ion-beam sputtering from alloy targets. For Si(001) substrates the structure/texture of the films are a function of the growth temperature (T_g). The tetragonal martensite structure with a (220) texture was obtained for an optimal $T_g \sim 300$–350 °C. At higher temperatures a cubic silicide ($Mn_{12}Ni_4Si_3$) was obtained. At room temperature, optimal films with the stoichiometric composition $(x \sim 0.2)$ showed a ferromagnetic hysteresis behavior characterized by significant in-plane rotation. The coercivity of the films was 310 Oe and temperature-dependent measurements confirmed a Curie temperature, $T_c \sim 340$ K. At room temperature the films show a modulated 7M martensite structure which was observed in *in situ* heating experiments to transforms to the cubic austenite phase at 500 °C.**

***Index Terms*—Ion beam sputtering, magnetic actuation in MEMS, Ni–Mn–Ga, shape memory alloy thin films.**

I. Introduction

HEUSLER Ni–Mn–Ga alloys are known to exhibit a martensitic transition, T_M a magnetic Curie temperature, T_c and the shape-memory effect [1]. Both T_m and T_c are a function of the stoichiometry [2] and, for $x \sim 0.25$, are 202 K and 376 K, respectively in bulk alloys. Control of the composition can make the structural and magnetic transition temperatures to coincide offering the possibility of magnetically driving the shape memory transition. The associated strains have vast potential for magnetically actuating microelectromechanical (MEMS) systems provided the challenge of growing this material in thin film form [3], [4] with sufficient control of the stoichiometry and crystallography can be met.

In the bulk, stoichiometric Ni_2MnGa exists in two forms. The high temperature, austenite (γ) phase is a cubic ($L2_1$), Heusler alloy with a lattice parameter, $a_0 \sim 5.82$ Å. Below $T_M \sim 202$ K, it undergoes a martensitic or a diffusionless, displacive transformation to a tetragonal structure with $a_0 \sim b_0 \sim 5.92$ Å and $c_0 \sim 5.57$ Å. Moreover, in bulk single crystals, structural transitions as a result of $\langle 110 \rangle$ uniaxial compression of 1–2% yielded an orthorhombic (β'') phase with $a_0 \sim 6.12$ Å, $b_0 \sim 5.78$ Å and $c_0 \sim 5.54$ Å. [5]. Recent attempts [3] at epitaxially growing thin films of Ni_2MnGa on (001) GaAs by molecular beam epitaxy have yielded a biaxially compressed version of this β'' phase with $a_0 \sim b_0 \sim 5.65$ Å and $c_0 \sim 6.12$ Å. In this paper, we present our results of the growth, structural transitions and magnetic properties of Ni–Mn–Ga thin films deposited by ion-beam sputtering.

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II. Experimental Details

All depositions were carried out in a high-vacuum (base pressure $< 2 \times 10^{-9}$ torr) chamber using a Kauffman-type ion source with high purity Argon and optimized to yield a sputtering rate of $\sim$0.4 Å/sec. Ni–Mn–Ga films, $\sim$1000 Å thick, were deposited simultaneously on a variety of substrates ($NaCl_{(001)}$ and $MgO_{(001)}$ single crystals and $Si_{(001)}$ wafers pre-cleaned to remove the native oxide) and capped with a 40 Å layer of Pt. The substrate temperature was varied from room-temperature to 450 °C. In some cases, the films were grown at room temperature and subsequently annealed at elevated temperatures prior to removing the films from the vacuum chamber. The variation in the sputtering yields of Mn, Ni and Ga was accommodated by an appropriate adjustment of the target alloy composition. In general, compared to the target composition, in the film we found an increase of 5% for Ni and a decrease of 5% for Mn, whilst Ga remained unchanged. The films were characterized structurally by x-ray diffraction ($\theta - 2\theta$ scans), and selected area diffraction of plan view and cross-section samples in a transmission electron microscope (TEM). Samples for TEM measurements were prepared by conventional technique of mechanical polishing, dimpling and ion-milling using argon ions. The composition of the films was measured by x-ray emission spectroscopy using theoretical K-factors. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) over a range of temperatures. The structural transformation temperature, T_M was determined by electron diffraction combined with *in situ* heating in a TEM. A detailed comparison of the structure/properties of films grown on different substrates will be discussed separately in a future publication.

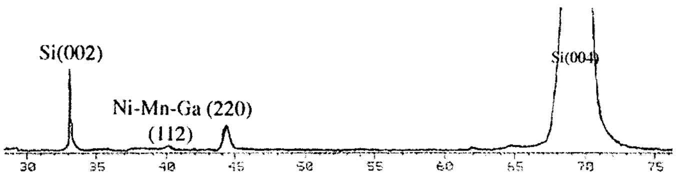

Fig. 1. X-ray $\theta - 2\theta$ scan confirming the presence of the $Ni_{50}Mn_{25}Ga_{25}$ phase. The martensite phase with a (220) texture is clearly evident but a very minor austenite (112) peak is also observed.

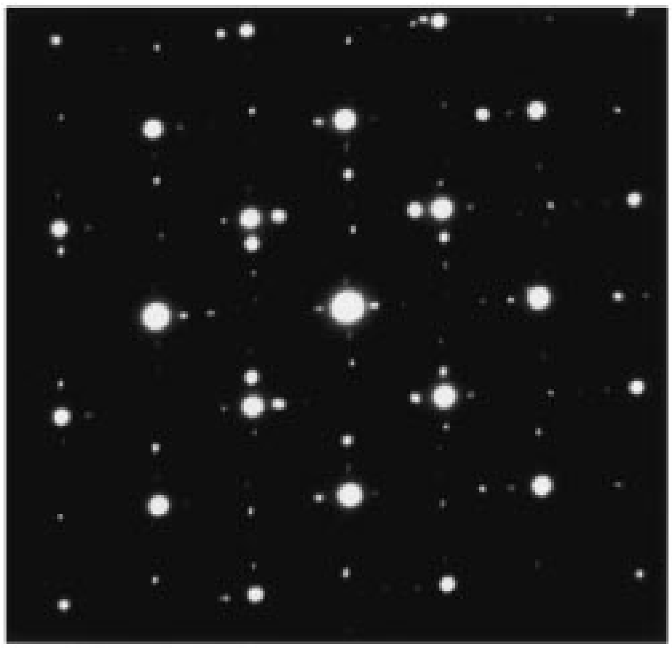

Fig. 2. A selected area diffraction pattern from a film with $x = 0.2$. The zone axis pattern taken at room temperature corresponds to [001] orientation. The modulation indicates a 7M martensite structure.

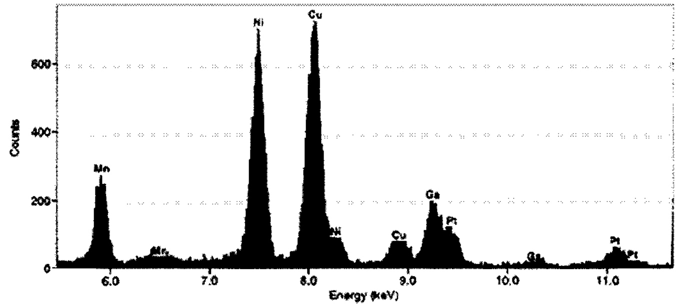

Fig. 3. XES Spectra of the thin film of Ni–Mn–Ga. Note that only the Ni–K, Mn–K, Ga–K and the Pt–L lines are observed. Using theoretical K-factors the composition of the film was determined from such spectra.

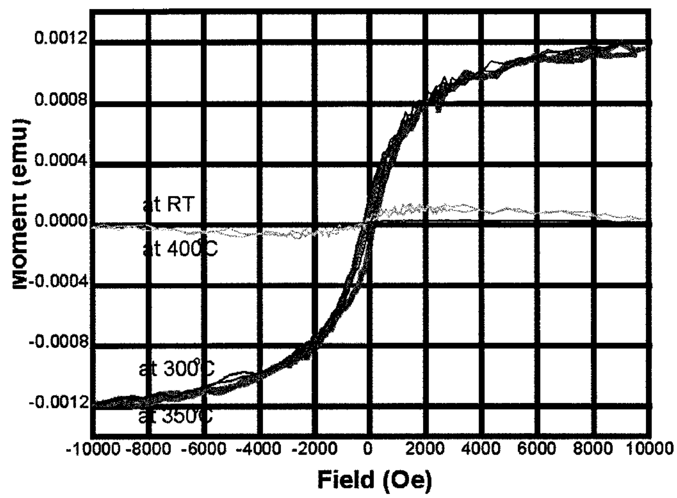

Fig. 4. Room temperature magnetic hysteresis loops (VSM) for an $x = 0.2$ sample measured as a function of growth temperature. At elevated growth temperatures the films become significantly nonmagnetic due to the formation of a silicide phase.

III. Results and Discussions

Two sets of $Ni_{1-2x}Mn_xGa_x$, $x = 0.2$ and 0.25, were grown on three different substrates over a range of growth temperatures (T_g). For Si substrates best results, in terms of crystallographic structure and magnetic properties were obtained for 300 °C $< T_g <$ 350 °C. For $T_g >$ 350 °C, considerable reaction between the deposited film and the Si substrate resulted in the formation of silicides. A representative x-ray $(\theta - 2\theta)$ scan for a film $(x = 0.25)$ grown at $T_g \sim 300$ °C is shown in Fig. 1. Apart from the Si (002) and (004) substrate peaks, the x-ray scan is characterized by a dominating peak corresponding to a lattice spacing of 2.05 Å. Clearly this film is single-phase for this peak can be indexed as the $\langle 220 \rangle$ reflection for the cubic, austenite (γ) phase with $a_0 \sim 5.82$ Å. On closer inspection this peak is observed to be split with peaks at 2.03 Å and 2.08 Å. The splitting corresponds to the (202) and (220) reflections of the tetragonal martensite phase with $a_0 \sim b_0 \sim 5.92$ Å and $c_0 \sim 5.57$ Å. In addition there is a very minor peak corresponding to the (112) austenite phase. All the other peaks in the complete x-ray scan $(20° < 2\theta < 80°)$ show negligible intensity confirming a strong (220) texture in the films.

Further proof for a (220) texture of the martensite film can be obtained from selected area diffraction (SAD) in a TEM using cross-section samples (Fig. 2). A [001] zone-axis pattern, normal to the (220) orientation is clearly observed. In addition, at room temperature, this SAD pattern is characterized by a modulation commensurate with periodic stacking sequences of seven $\{110\}$ planes along $\langle 110 \rangle$ directions as observed earlier in single crystals by Chernenko *et al.* [6].

Finally, the composition of the films was measured by x-ray emission spectroscopy using an energy-dispersive Si(Li) detector. A typical spectrum for a film with $x = 0.2$ is shown in Fig. 3. All the peaks can be identified as arising from either the film (Ni, Mn and Ga), the capping layer (Pt) or the TEM grid (Cu). Analysis of this spectra after background subtraction and deconvolution of overlapping peaks confirmed the composition of the film to be Mn $\sim$20.6 at%, Ni $\sim$59.51 at% and Ga $\sim$19.89 at%.

Fig. 4 shows M(H) measurements (VSM) with the field applied in-plane for $x = 0.2$ samples grown at $T_g \sim RT$, 300, 350, 400 °C. All measurements were made at room temperature. By normalizing with the weight of the film the saturation magnetization was calculated as ~42 emu/g. For samples grown at 400 °C, this drops to 2.80 emu/g. We attribute this to the formation of silicides at elevated temperatures; detailed structural work involving convergent beam electron diffraction and chemical microanalysis shows this silicide to be $Mn_{12}Ni_4Si_3$ with

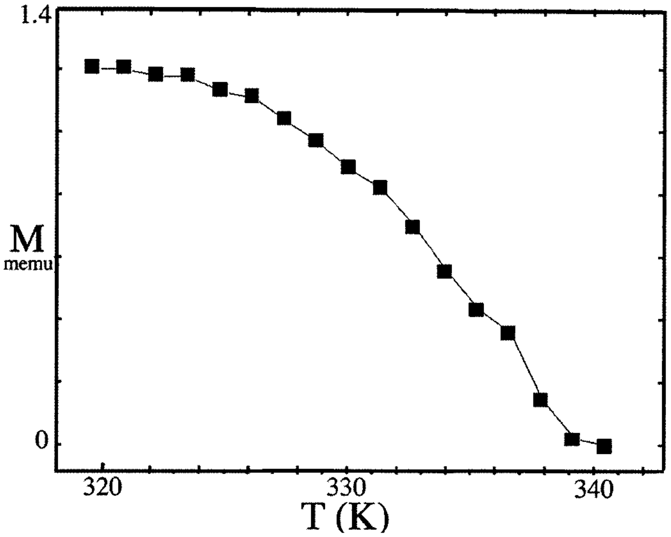

Fig. 5. Magnetic measurements as a function of temperature for $x = 0.2$ sample. There is a significant loss of magnetization with temperature. The Curie temperature of this film was observed at 340 K.

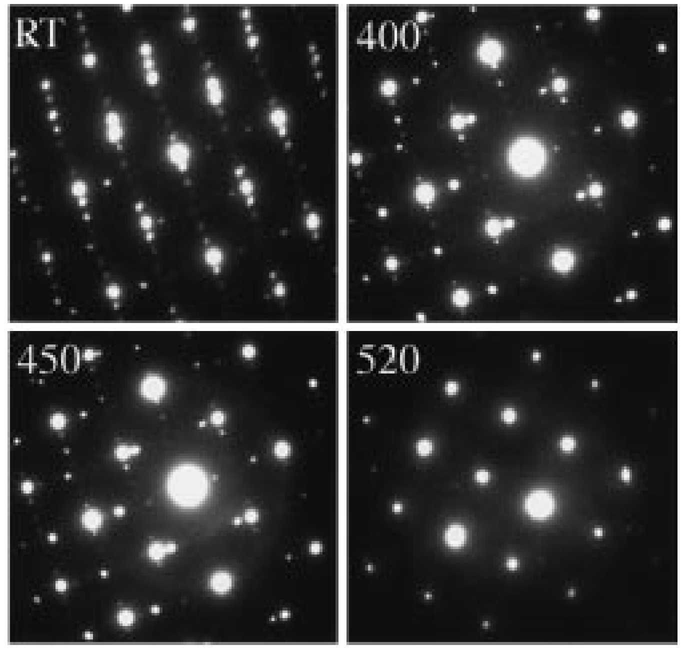

Fig. 6. *In situ* TEM heating experiments carried out to measure the martensitic transition temperature for the $x = 0.2$ sample. The room temperature modulated 7M diffraction pattern transforms to the cubic structure in the temperature range $T_M \sim 500$–520 °C.

a cubic structure and a primitive cell volume of 256 $Å^3$. The hysteresis loops, exhibiting a coercivity in the range of 310 Oe ($T_g \sim 300$ °C) to 210 Oe ($T_g \sim 400$ °C), are characterized by a significant in-plane rotation behavior. This is to be expected for a tetragonal structure with the magnetic easy direction (along the c-axis) randomly distributed in the plane of the film.

Fig. 5 shows the temperature dependence of the magnetization of the film for a field of 10 kOe applied in the plane of the film. For $x = 0.2$ samples, the data indicates a Curie temperature of 340 K.

Detailed measurements of the structural transformation of the films were carried out by *in situ* heating of cross-section samples in a TEM and simultaneously recording the selected area diffraction patterns as a function of temperature. A series of diffraction patterns as a function of temperature is shown in Fig. 6. The modulated structure observed in the SAD pattern at room temperature persists up to a temperature of 500 °C. However, at 520 °C, the SAD pattern corresponds to that of the cubic $L2_1$ structure. Within the accuracy of these heating measurements we can conclude that the martensitic transition temperature $T_M \sim 500$–520 °C.

In summary, we have successfully grown high quality thin films of the magnetic, Heusler Ni–Mn–Ga alloy by ion-beam sputtering. The properties of the films depend on the nature of the substrate and the growth temperature. For Si substrates, optimally grown films are ferromagnetic at room temperature. The Curie temperature of the films ($T_c \sim 340$ K) is significantly different from the martensitic transition temperature ($T_M \sim 500$–520 °C). The latter is also substantially higher than that observed in the bulk ($T_M \sim 202$ K) for similar compositions. We believe that this is due to clamping effects arising from the substrate. A systematic study of the role of the substrate, epitaxy, growth temperature and silicide formation is in progress and will be addressed in future publications.

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