Ni–Mn–Ga thin films produced by pulsed laser deposition

P. G. Tello, F. J. Castaño, R. C. O'Handley, and S. M. Allen
Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

M. Esteve and F. Castaño[a]
Departmento de Quimica-Fisica, Universidad del Pais Vasco, P.O. Box 644, 48080 Bilbao, Spain

A. Labarta and X. Batlle
Dpt. Fisica Fonamental, Facultat de Fisica, Universitat de Barcelona, Diagonal 647, Barcelona 08028, Spain

Polycrystalline Ni–Mn–Ga thin films have been deposited by the pulsed laser deposition (PLD) technique, using slices of a Ni–Mn–Ga single crystal as targets and onto Si (100) substrates at temperatures ranging from 673 K up to 973 K. Off-stoichiometry thin films were deposited at a base pressure of 1×10^{-6} Torr or in a 5 mTorr Ar atmosphere. Samples deposited in vacuum and temperatures above 823 K are magnetic at room temperature and show the austenitic {220} reflection in their x-ray diffraction patterns. The temperature dependences of both electrical resistance and magnetic susceptibility suggest that these samples exhibit a structural martensitic transition at around 260 K. The magnetoresistance ratio at low temperature can be as high as 1.3%, suggesting the existence of a granular structure in the films.
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I. INTRODUCTION

In recent years considerable attention has been devoted to the Ni–Mn–Ga alloy system as a new material for actuating devices.[1,2] A magnetic-field-induced strain of up to 6% has been reported in selected compositions of the Ni–Mn–Ga alloy system.[3] These large field-induced strains have provided the possibility of using thin films of Ni–Mn–Ga as new materials for shape memory components in microelectromechanical systems (MEMS), as some reports have pointed out.[4,5]

The present work aims to contribute to this emerging field by reporting initial results concerning magnetic Ni–Mn–Ga thin films deposited by the pulsed laser deposition (PLD) technique.

II. EXPERIMENT

Ni–Mn–Ga thin films were deposited using a custom built vacuum chamber with a Nd-YAG laser, operating at 355 nm. The targets were sections of a Ni–Mn–Ga single crystal and were rotated during the ablation process. Substrates consisted in pieces of a 4 in. Si (100) wafer and were attached to a plate that could be heated up to 973 K. Samples were deposited at substrate temperatures ranging from 673 K up to 973 K. Depositions were undertaken at a base pressure of 1×10^{-6} Torr or in a 5 mTorr Ar atmosphere. Films were deposited during times varying between 1 and 3 h, yielding thicknesses between 0.5 and 2.5 μm. The microstructure and composition of the films were checked using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) measurements.

Magnetotransport measurements were made, using the conventional four-point probe method, in fields up to 1 T and temperatures ranging from room temperature to 4.2 K. Hysteresis loops and thermomagnetization measurements were performed, in fields up to 5 T and temperatures ranging from 120 K to 350 K, using a Quantum Design MPMS SQUID magnetometer.

III. RESULTS AND DISCUSSION

Figure 1 shows x-ray diffraction patterns corresponding to two Ni–Mn–Ga thin films deposited in vacuum and in a 5 mTorr Ar atmosphere, respectively. The austenitic {220} peak dominates the polycrystalline diffraction pattern of the films suggesting a strong texture, perhaps due a (110) growth

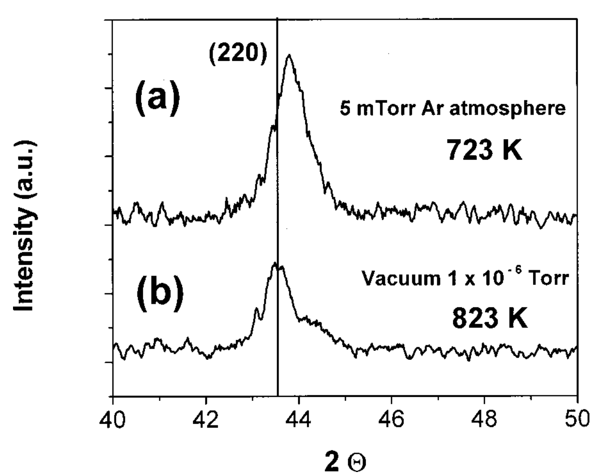

FIG. 1. XRD measurements corresponding to Ni–Mn–Ga thin film samples deposited at 723 K and 5 mTorr of Ar (a), and 823 K and 1×10^{-6} Torr (b), respectively. Each sample was grown during 3 h.

[a]Author to whom correspondence should be addressed; electronic mail: gfpcaalf@lg.ehu.es

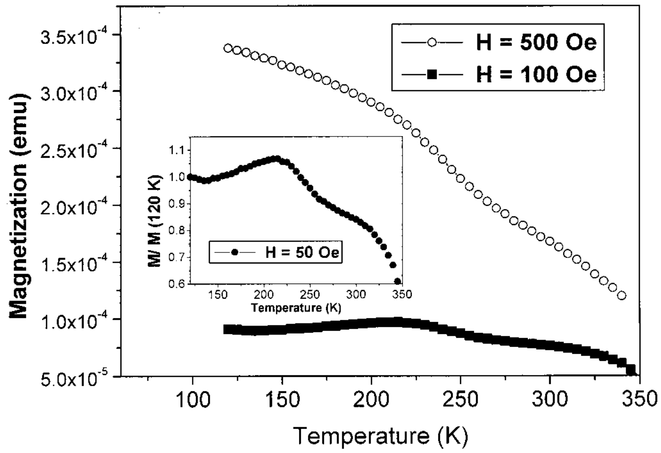

FIG. 2. Thermomagnetic measurements corresponding to the Ni–Mn–Ga thin film deposited at 823 K and 1×10^{-6} Torr. Measurements presented were performed on heating and under applied fields of 500 Oe and 100 Oe, respectively. The inset shows the normalized thermal dependence of the magnetization for an in-plane applied field of 50 Oe. Solid lines are shown as a guide to the eye.

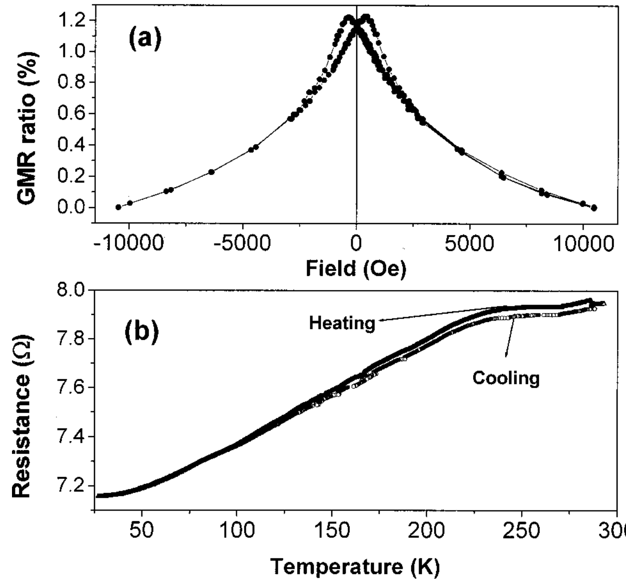

FIG. 3. (a) In-plane field magnetoresistance measurements performed at 23 K and corresponding to the Ni–Mn–Ga thin film deposited at 823 K and 1×10^{-6} Torr. (b) Thermal dependence of the resistance measured on heating and cooling the sample.

mode. The {220} peak appeared only for samples deposited above 723 K (in Ar) and 823 K (in vacuum). Nevertheless only those samples produced in vacuum and at substrates temperature above 823 K were magnetic at room temperature. In the present work we will focus on a Ni–Mn–Ga thin film produced in vacuum and at a substrate temperature of 823 K. The diffraction pattern of this film [Fig. 1(b)] shows a main peak at $2\theta=43.6°$ and what might be regarded as a shoulder at $2\theta=44.2°$. The peak width suggests a polycrystalline structure with a grain size of about 12 nm, as estimated using the Scherrer formula. The shoulder is either due to the {202} reflection of untransformed (retained) martensite or a second unidentified phase. Ni–Mn–Ga thin films of coexisting austenite/martensite phases have been reported elsewhere.[5]

Figure 2 shows three thermomagnetization zero field cooled (ZFC) measurements, performed at 50 Oe, 100 Oe, and 500 Oe, respectively. The appearance of a different magnetic phase below 260 K is evident in these measurements at applied fields below 1000 Oe. For temperature values around 260 K and low applied fields, the thermal dependence of the susceptibility differs considerably from that obtained on superimposing a Bloch law term $[M(T)=M(0)(1-BT^{-3/2})]$ to the susceptibility curve of a magnetic phase with Curie temperature above 350 K. Nevertheless the susceptibility shoulder, manifested at low applied fields, might be regarded to the onset of ferromagnetism in a phase that would be paramagnetic at room temperature or to the transformation of some of the Ni–Mn–Ga austenite into martensite beginning at $T_{mart}\sim260$ K.

In order to further discuss this issue, Fig. 3 shows highlights of the magnetotransport properties of the Ni–Mn–Ga thin film investigated in the present work. Figure 3(a) shows clear spin-dependent magnetoresistance, which may be ascribed to an inhomogeneous or granular structure.[6] Figure 3(b) shows that as temperature and resistivity decrease, an additional source of scattering appears below a T_C of about 270 K, presumably due to spin scattering from the large moments on the randomly oriented grains. The experimental $\rho(T)$ curve shown here is in excellent agreement with those reported earlier,[7] for Ni–Mn–Ga martensites which had electron/atom ratios between 7.55 and 7.7 e/a and T_{mart} below room temperature. The aforementioned experimental results (especially the broad XRD peaks and the large, granularlike MR ratio) strongly support the coexistence of granular phases and a martensitic transition starting around 260 K for the sample investigated.

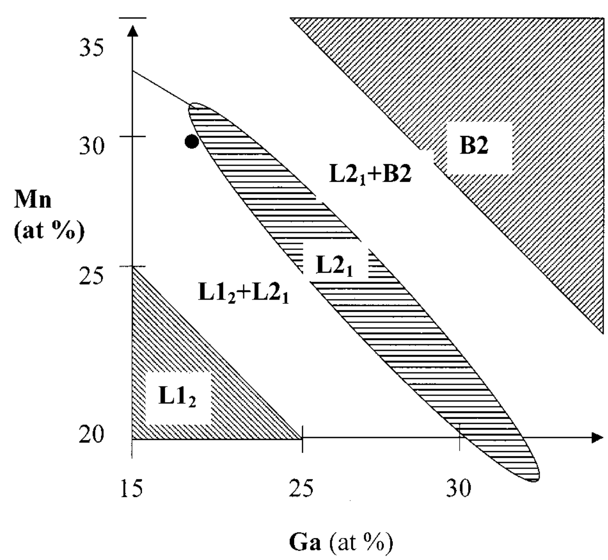

FIG. 4. Hypothetic phase diagram of the Ni–Mn–Ga alloy based on a database of Ni–Ti–Al at 1000 °C using Thermo-calc®. The black dot indicates the location of the thin film sample investigated in the present work.

Recently performed energy dispersive spectroscopy (EDS) measurements revealed that the average composition of the film analyzed was $Ni_{50.99}Mn_{29.28}Ga_{19.72}$ (atomic %). It is interesting to locate this composition on a phase diagram corresponding to a Heusler alloy system. In the absence of published phase diagrams for Ni–Mn–Ga, here we refer to a Ni–Ti–Al phase diagram generated by Thermo-calc®[8] (this is the Heusler system for which the most complete set of experimental thermal data is available). Figure 4 shows this phase diagram. In this alloy system the $L2_1$ phase is clearly more stable than in Ni–Mn–Ga where it only appears below 1073 K. The extent of the $L2_1$ phase field shown here corresponds to the stable range of the Ni_2MnGa Heusler phase at room temperature. The investigated film lies on the two-phase region of this diagram.

In summary, we have shown that thin films of Ni–Mn–Ga can be produced on top of Si-(100) substrate using pulsed laser deposition. According to our results, only those films produced in vacuum and at a substrate temperature above 823 K were magnetic at room temperature. Measurements of M (T) and ρ (T) on one of these samples indicate the presence of a martensitic phase below 260 K. The film that shows a martensitic transition has an average composition of $Ni_{50.99}Mn_{29.28}Ga_{19.72}$ (at. %). Data presented suggest a film in which two granular phases coexist at room temperature.

[1] K. Ulakko, J. K. Huang, C. Kantner, V. V. Kokorin, and R. C. O'Handley, Appl. Phys. Lett. **69**, 1966 (1996).

[2] R. C. O'Handley, J. Appl. Phys. **83**, 3263 (1998).

[3] S. J. Murray, M. Marioni, P. G. Tello, S. M. Allen, and R. C. O'Handley, J. Magn. Magn. Mater. **226**, 945 (2001).

[4] J. W. Dong, L. C. Chen, C. J. Palmstrom, R. D. James, and S. McKerman, Appl. Phys. Lett. **75**, 1443 (1999).

[5] M. Wuttig, C. Craciunescu, and Jian Li, Mater. Trans., JIM **41**, 933 (2000).

[6] A. E. Berkowitz, J. R. Mitchell, M. J. Carey, A. P. Young, S. Zhang, F. E. Spada, F. T. Parker, A. Hutten, and G. Thomas, Phys. Rev. Lett. **68**, 3745 (1992); C. L. Chien, J. Q. Xiao, and J. S. Jiang, J. Appl. Phys. **73**, 5309 (1993).

[7] V. A. Chernenko, Scr. Mater. **40**, 523 (1999).

[8] M. J. Farinelli, S. Murray, and L. Kauffman (unpublished).