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Evidence of martensitic phase transitions in magnetic Ni-Mn-In thin films

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$Ni_{50}Mn_{35}In_{15}$ Heusler alloy thin films (with thicknesses of about 10 nm) have been grown on single crystal MgO and $SrTiO_3$ (STO) (100) substrates using a laser-assisted molecular beam epitaxy method. Films of mixed austenitic and martensitic phases and of pure martensitic phase have been detected for those grown on MgO and STO substrates, respectively. Thermomagnetic curves were measured using a SQUID magnetometer and are consistent with those of off-stoichiometric In-based bulk Heusler alloys, including a martensitic transition at T = 315 K for films grown on MgO. The differences in the properties of the films grown on MgO and STO are discussed. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4793421]

Heusler alloys are receiving increasing attention from both the magnetism and material science communities due to their large variety of magnetoresponsive effects,[1,2] such as magnetic shape memory/strain,[3,4] large magnetoresistance,[5,6] anomalous Hall,[7] and magnetocaloric effects.[8–10] This interest has been stimulated by their potential technological applications in the field of magnetic actuators,[11] sensors,[12] energy-harvesting devices,[13] and solid-state magnetic refrigeration.[14] The broad spectrum of properties of these materials is mainly attributed to the specific type of structural instability known as a martensitic transformation observed in these compounds. This instability is described as a temperature-induced first-order structural phase transition from a high-temperature austenitic phase (AP: cubic $L2_1$ or B2 crystal structure) to a low-temperature martensitic phase (MP) and characterized by a crystal cell of lower symmetry (tetragonal, modulated orthorhombic, or monoclinic).[15] While a vast majority of reported results have dealt with bulk shape-memory Ni-Mn-Ga or Ni-Mn-In alloys, for many electronic applications, it would be extremely desirable to synthesize such materials (with corresponding properties) in thin film form. Various approaches have been undertaken in an attempt to fabricate films: flash-evaporation of alloy powders,[16] thermal co-evaporation,[17] molecular beam epitaxy (MBE),[18] and pulsed laser deposition (PLD).[19,20] However, the fabrication of films with desirable characteristics remains a technological challenge. The successful synthesis of epitaxial Ni-Co-Mn-In Heusler alloy with the characteristic behavior of bulk alloys has been recently reported by Niemann *et al.*[21,22] The result was obtained by sputtering from a pre-synthesized target onto a MgO substrate with an epitaxial chromium seed layer. It has been shown that a relatively high substrate temperature (~400 °C) is required for proper chemical order formation of the Heusler alloy. However, argon bombardment of the target resulted in differing sputtering rates of constituent materials (i.e., non-congruent transfer) and the evidence of composition deviation with time were reported. On the other hand, while a Cr seed layer apparently promotes epitaxial growth on MgO substrates, for many applications, which take advantage of unique transport properties of Heusler alloys, the use of metallic buffer layer should be avoided. In order to provide high quality growth with low defect density, the identification of a suitable substrate material is critical. One of the decisive parameters is the lattice constant of the substrate, which should closely match the parameters of the film. However, since the structural martensitic transition is accompanied by a drastic change in lattice parameters, as-grown films may experience a kinetic arrest,[23] where the martensitic transformation is interrupted. Thus, the impact of the substrate on the martensite transformation should be clarified.

In this Letter, we report on the growth and characterization of compressive and nearly zero strained Ni-Mn-In thin films grown on $SrTiO_3$ (STO) and MgO single crystal substrates from a $Ni_{50}Mn_{35}In_{15}$ target of nominal composition. The off-stoichiometric $Ni_{50}Mn_{35}In_{15}$ alloy has been selected as a target since the martensitic transition observed in the bulk material is very close to ambient temperature and is therefore of practical importance.[9,10] The effect of induced strain on the resulting crystal structures and magnetic properties is discussed.

We employed a laser-assisted molecular beam epitaxy (LMBE) method as the most reliable for the congruent transfer of the target constituents. The $Ni_{50}Mn_{35}In_{15}$target was fabricated by conventional arc-melting in a high-purity argon atmosphere using 4N purity elements and was annealed in high vacuum (≈10^{-4} Torr) for 24 h at 850 °C. Laser ablation was performed using KrF excimer laser (248 nm) with an energy density of 4 J/cm^2 under high vacuum conditions (better then 10^{-8} Torr) and a 10 Hz repetition rate. The substrate temperature was held at 150 °C for the STO substrate and at ambient temperature for the MgO substrate. Film thicknesses were calibrated per laser pulse by an x-ray reflectivity method. The resulting phase compositions and unit cell parameters of the samples were determined by x-ray powder diffraction using the single crystal substrates as an internal standard. Thermomagnetic curves M(H,T) were measured using a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design). The temperature dependencies of M(T) have been obtained during heating at H = 500 Oe after the samples were cooled to 5 K in zero magnetic field (FC) and during cooling from T = 380 K at H = 500 Oe (FCC).

A typical AFM image of the film surface with up to 10 nm thickness is shown in Fig. 1 for the case of the STO

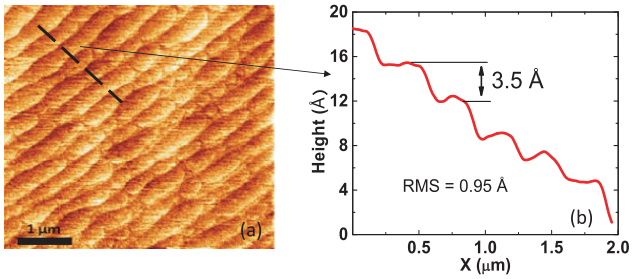

FIG. 1. AFM image (a) and line scan profile (b) of a 10 nm $Ni_{50}Mn_{35}In_{15}$ thin film on a $SrTiO_3$ ⟨100⟩ single crystal substrate. Estimated roughness on the terrace surfaces is about 95 pm, and the step heights close to that of the STO unit cell parameter (0.3905 nm).

substrate. As clearly seen, the step structure of the substrate is still preserved for this film thickness, with typical step heights corresponding to the STO unit cell parameter of 0.39 nm. The roughness on the terrace surfaces is limited to 0.15 nm, indicating an atomically smooth layer, hence suggesting a Frank-van der Merwe (FM: layer-by-layer) initial growth mode. As the thickness increases, the topography profile becomes rougher and grain formation becomes evident. AFM topography analysis of different film thickness suggests that growth dynamics changes from FM to a Stranski-Krastanov mode (SK: layer-plus-island) and finally to a 3-d island growth regime. The relatively quick transformation from a strained to nearly no strained form of thin film growth is apparently induced by the relatively large mismatch of the STO and NiMnIn unit cell parameters. In spite of the lower lattice mismatch, films grown on the MgO substrate tend to form 3d-islands noticeably sooner. This may be due to a different surface-ad-atom interaction potential, but the possibility of random nucleation due to the higher defect density of the MgO substrate cannot be excluded. For both substrates, an increase of temperature leads to rougher films. While this is an indicator that the growth parameters, such as growth rate and substrate temperatures should be further optimized for thicker film synthesis, we will focus our attention on the films with thicknesses less than 10 nm, where we can safely assume the domination of substrate-induced strained films in the magnetic response.

The room temperature XRD analysis clearly indicates the presence of Ni-Mn-In phases for films grown on both the STO and MgO substrates (Fig. 2). In both cases, the films were found to be textured along the ⟨220⟩ directions. X-ray patterns identify the structures of the MgO-grown Heusler alloys as cubic (austenitic) and tetragonal (martensitic) mixed phases that can be described by the cell parameters $a_C = 5.96$ Å, and $a_T = 5.82$ Å, and $c_T = 6.74$ Å for cubic and tetragonal phases, respectively. It is interesting to note that, while the cubic parameter a_C is slightly larger than $\sqrt{2} \times$ MgO cell parameter, the tetragonal parameter a_T is smaller. Therefore, in the case of MgO, it seems that it is energetically favorable for the mixed phase lattice parameters to have values close to those of the substrate.

In contrast, peaks from the cubic phase have not been detected in the case of the STO-grown films; the observed XRD patterns (see Figure 2) suggest the presence of a single tetragonal phase at ambient temperature with unit cell parameters $a_T = 5.48$ Å and $c_T = 6.14$ Å. In this case, a_T deviated

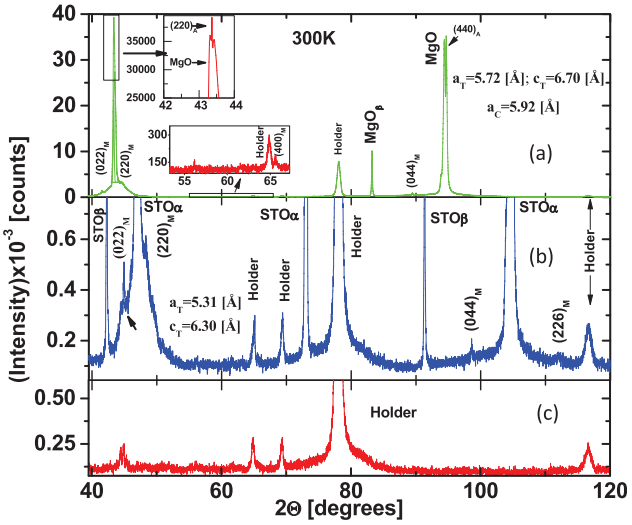

FIG. 2. Room temperature XRD patterns of $Ni_{50}Mn_{35}In_{15}$ thin films grown on (a) MgO and (b) $SrTiO_3$ substrates, and (c) the sample holder. The peaks can be identified as being from a cubic/austenitic Heusler alloy structure ((hkl) marked by index "A"), plus a tetragonal/martensitic phase ((hkl) marked by index "M") for films grown on MgO. Only a martensitic phase was observed for films grown on STO.

from $\sqrt{2} \times$ STO cell parameter by 0.7%. Obtained lattice parameters are significantly smaller when compared to those observed in the MgO and bulk compounds, confirming the formation of compressively strained film induced by corresponding lattice mismatch.

The coexistence of the high- and low-temperature crystal phases for films grown on the MgO substrate is evidence of the presence of a temperature-induced first order structural transition close to 300 K. Indeed, we found (see Fig. 3) that the M(T) curve of the tensile-strained MgO-grown film is very similar to those observed for bulk off-stoichiometric NiMnIn alloys.[9] As the temperature increases, the first sharp magnetization decrease is observed at $T_{CM} = 286$ K, indicating a magnetic second order phase transition in the martensitic phase. At $T_A = 321$ K, a first order phase transition associated with the onset of the austenite phase is observed. At this temperature, the magnetization sharply increases and then falls again at the Curie temperature in the vicinity of

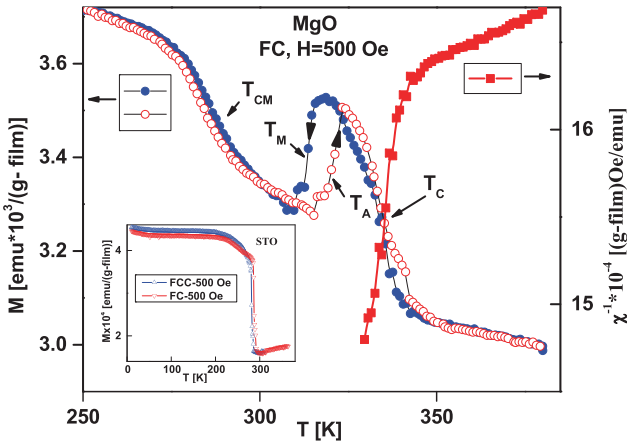

FIG. 3. (Left panel) Magnetization vs. temperature for $Ni_{50}Mn_{35}In_{15}$ 10 nm thin films grown on MgO and STO (inset) single crystal substrates. (Right panel) Temperature dependence of the inverse susceptibility for the film grown on MgO.

$T_C = 334$ K. While the cooling cycle repeats, the martensitic phase re-establishes at $T_M = 313$ K, yielding a 8 K temperature hysteresis, confirming that the phase transition is of first order. The inverse susceptibility increases linearly with increasing temperature in interval $T > 334$ K (Fig. 3), confirming the paramagnetic state of the sample above 334 K.

A different M(T) scenario was observed for compressively strained STO-grown films. Only one sharp magnetization drop was observed near 300 K. Taking into account the presence of a low-symmetry phase from X-ray analysis, we can conclude that this magnetization drop originates from a magnetic transformation inside the martensitic phase. We did not observe an indication of a first order magnetic phase transition with large hysteresis—a characteristic signature of an austenitic transformation in NiMnIn Heusler alloys. It is likely that T_M and T_C are higher than 400 K (upper limit of the measured temperature interval) in our compressively strained films. If we consider the martensitic transformation as a tetragonal distortion of the cubic-phase film, then it is possible to assume that the preferential axis of such a deformation would be sensitive to the strain induced on the basal plane. The difference between the preferred distortion axes of films grown on MgO and STO can be easily inferred from the magnetization curves taken in the martensitic phase (Fig. 4). It is clearly seen that the MgO-based nearly relaxed film results in out-of plane anisotropy, while the STO-grown samples have a slight in-plane anisotropy. Such a drastic anisotropy change is striking enough but could be understood considering the extreme sensitivity of off-stochiometric Heusler alloys to changes in electronic structure, ionic microstructure, and strain distribution.[24]

In conclusion, we have successfully synthesized high quality thin films from a $Ni_{50}Mn_{35}In_{15}$ Heusler alloy target using pulsed laser deposition. Nearly relaxed thin films consisting of a cubic and tetragonal phase mixture were grown on MgO ⟨001⟩ single crystal substrates, and compressively strained epitaxial-like films were grown on $SrTiO_3$⟨001⟩. X-ray and thermomagnetic measurements indicated the presence of a martensitic-like transition in the case of MgO at about 315 K, between the ferromagnetic austenitic and low magnetization state of the martensitic phase, similar to that observed in off-stoichiometric bulk Ni-Mn-In Heusler alloys with approximately 15 at. % In concentration. Finally, we have found that compressive strain from growth on STO stabilizes the martensitic phase.

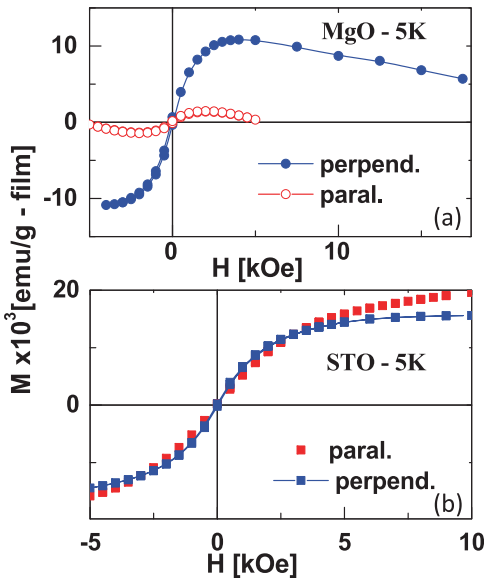

FIG. 4. Magnetization vs. applied field at T = 5 K (see text). MgO-grown films show out-of-plane anisotropy, whereas STO-grown films reveal a slight in-plane anisotropy.

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[1]I. Dubenko, T. Samanta, A. Kumar Pathak, A. Kazakov, V. Prudnikov, S. Stadler, A. Granovsky, A. Zhukov, and N. Ali, J. Magn. Magn. Mater. **324**, 3530 (2012).
[2]E. Liu, W. Wang, L. Feng, W. Zhu, G. Li, J. Chen, H. Zhang, G. Wu, C. Jiang, H. Xu, and F. de Boer, Nat. Commun. **3**, 873 (2012).
[3]C. H. Yu, L. Q. Meng, J. L. Chen, F. M. Yang, S. R. Qi, W. S. Zhan, Z. Wang, Y. F. Zheng, and L. C. Zhao, Appl. Phys. Lett. **75**, 2990 (1999).
[4]R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, O. Kitakami, K. Oikawa, A. Fujita, T. Kanomata, and K. Ishida, Nature **439**, 957 (2006).
[5]M. Khan, I. Dubenko, S. Stadler, and N. Ali, J. Phys.: Condens. Matter **20**, 235204 (2008).
[6]A. K. Pathak, I. Dubenko, Y. Xiong, P. W. Adams, S. Stadler, and N. Ali, IEEE Trans. Magn. **46**, 1444 (2010).
[7]I. Dubenko, A. K. Pathak, S. Stadler, N. Ali, Ya. Kovarskii, V. N. Prudnikov, N. S. Perov, and A. B. Granovsky, Phys. Rev. B **80**, 092408 (2009).
[8]T. Krenke, E. Duman, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, "Inverse magnetocaloric effect in ferromagnetic Ni-Mn-Sn alloys," Nature Mater. **4**, 450 (2005).
[9]A. K. Pathak, M. Khan, I. Dubenko, S. Stadler, and N. Ali, Appl. Phys. Lett. **90**, 262504 (2007).
[10]I. Dubenko, M. Khan, A. K. Pathak, B. R. Gautam, S. Stadler, and N. Ali, J. Magn. Magn. Mater. **321**, 754 (2009).
[11]H. E. Karaca, I. Karaman, B. Basaran, Y. Ren, Y. I. Chumlyakov, and H. J. Maier, Adv. Funct. Mater. **19**, 983 (2009).
[12]N. Sarawate and M. Dapino, Appl. Phys. Lett. **88**, 121923 (2006).
[13]I. Karaman, B. Basaran, H. E. Karaca, A. I. Karsilayan, and Y. I. Chumlyakov, Appl. Phys. Lett. **90**, 172505 (2007).
[14]K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, Rep. Prog. Phys. **68**, 1479 (2005).
[15]T. Krenke, M. Acet, E. F. Wassermann, X. Moya, L. Mañosa, and A. Planes, "Ferromagnetism in the austenitic and martensitic states of Ni-Mn-In alloys," Phys. Rev. B **73**, 174413 (2006).
[16]J. Dubowik, Y. Kudryavtsev, Y. P. Lee, N. N. Lee, and B. S. Hong, Mol. Phys. Rep. **40**, 55 (2004).
[17]M. Kurfi, B. Schultz, R. Anton, G. Meier, L. Sawilski, and J. Kotzler, J. Magn. Magn. Mater. **290–291**, 591 (2005).
[18]B. Bohse, A. Zolotaryov, W. Kreuzpaintner, D. Lott, A. Kornowski, A. Stemmann, Ch. Heyn, and W. Hansen, J. Cryst. Growth **323**, 368 (2011).
[19]A. Grunin, A. Goikhman, and V. Rodionova, Solid State Phenom. **190**, 311 (2012).
[20]A. Hakola, O. Heczko, A. Jaakkola, T. Kajava, and K. Ullakko, Appl. Phys. A **79**, 1505 (2004).
[21]R. Niemann, O. Heczko, L. Schultz, and S. Fähler, Appl. Phys. Lett. **97**, 222507 (2010).
[22]R. Niemann, L. Schultz, and S. Fähler, J. Appl. Phys. **111**, 093909 (2012).
[23]W. Ito, K. Ito, R. Y. Umetsu, R. Kainuma, K. Koyama, K. Watanabe, A. Fujita, K. Oikawa, K. Ishida, and T. Kanomata, Appl. Phys. Lett. **92**, 021908 (2008).
[24]S. Roy, E. Blackburn, S. M. Valvidares, M. R. Fitzsimmons, S. C. Vogel, M. Khan, I. Dubenko, S. Stadler, N. Ali, S. K. Sinha, and J. B. Kortright, Phys. Rev. B **79**, 235127 (2009).