2016

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Sokolov, Andrei; Kirianov, Eugene; Zlenko, Albina; Quetz, Abdiel; Aryal, Anil; Pandey, Sudip; Dubenko, Igor; Stadler, Shane; Ali, Naushad; Al-Aqtash, Nabil M.; and Sabirianov, Renat F., "Magnetic and magneto-transport studies of substrate effect on the martensitic transformation in a NiMnIn shape memory alloy" (2016). *Faculty Publications, Department of Physics and Astronomy*. 162.
http://digitalcommons.unl.edu/physicsfacpub/162

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AIP ADVANCES **6**, 056211 (2016)

Magnetic and magneto-transport studies of substrate effect on the martensitic transformation in a NiMnIn shape memory alloy

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(Presented 13 January 2016; received 6 November 2015; accepted 22 December 2015; published online 3 March 2016)

The effect of substrates on the magnetic and transport properties of $Ni_2Mn_{1.5}In_{0.5}$ ultra-thin films were studied theoretically and experimentally. High quality 8-nm films were grown by laser-assisted molecular beam epitaxy deposition. Magneto-transport measurements revealed that the films undergo electronic structure transformation similar to those of bulk materials at the martensitic transformation. The temperature of the transformation depends strongly on lattice parameters of the substrate. To explain this behavior, we performed DFT calculations on the system and found that different substrates change the relative stability of the ferromagnetic (FM) austenite and ferrimagnetic (FiM) martensite states. We conclude that the energy difference between the FM austenite and FiM martensite states in $Ni_2Mn_{1.5}In_{0.5}$ films grown on MgO (001) substrates is $\Delta E = 0.20$ eV per NiMnIn f.u, somewhat lower compared to $\Delta E = 0.24$ eV in the bulk material with the same lattice parameters. When the lattice parameters of $Ni_2Mn_{1.5}In_{0.5}$ film have values close to those of the MgO substrate, the energy difference becomes $\Delta E = 0.08$ eV per NiMnIn f.u. These results suggest the possibility to control the martensitic transition in thin films through substrate engineering.

INTRODUCTION

The off-stoichiometric Ni-Mn-In based Heusler alloys attract tremendous research attention due to their wide variety of magnetoresponsive effects[1,2] such as magnetic shape memory/strain[3,4] large magnetoresistance[5,6] anomalous Hall effect,[7] and magnetocaloric effects.[8–10] Such a variety of coupled magnetic, structural, and elastic properties make Ni-Mn-In alloys excellent candidates for multifunctional applications. Systematic theoretical[11] and experimental studies of the intrinsic properties of bulk Heusler alloy compounds[12] show that their broad spectrum of properties is attributed to a specific type of structural instability known as a martensitic transformation, which is accompanied by a change in the electronic structure. Such modifications are manifested in their transport and thermopower[13] properties and have been confirmed by photoelectron spectroscopy experiments and *ab initio* calculations of the electronic structure.[14]

While a vast majority of reported results have dealt with bulk shape-memory Ni-Mn-Ga or Ni-Mn-In alloys, the range of potential applications may be greatly extended by extrapolating their properties in thin films. Various approaches have been undertaken to meet this goal: flash-evaporation of alloy powders,[15] thermal co-evaporation,[16] molecular beam epitaxy (MBE),[17] sputtering,[18] and pulsed laser deposition (PLD).[19,20] It has been emphasized that the growth temperature[21] and film thickness[22] play crucial roles in obtaining the desired mixture of phases. The importance of substrate engineering on the initial growth conditions, and the possibility of metamagnetic transformations for thickness as low as 10 nm, was reported for films grown on MgO substrates using laser MBE,[23] but the impact of strain on thin and ultra-thin films has not been investigated systematically. On the other hand, XRD measurements showing the temperature-dependent residual strain on the substrate[24] emphasize that thin film-substrate coupling may play an important role in their behavior.

In this paper we report our study of the impact of substrates on the magnetic and magneto-transport properties of martensitic transformation in 8-nm thick $Ni_{50}Mn_{35}In_{15}$ shape memory alloy thin films.

SAMPLE PREPARATION

The films were grown on STO (001), MgO (001), and MgO (111) substrates using a Surelite II Nd:YAG pulsed laser with a fluence of 1.1 J/cm^2. Substrates were placed at a distance of 4 cm from the target and were held at 350 C° in vacuum at pressures lower than 10^{-8} Torr. Film thicknesses and phase compositions were determined using an X-ray reflectivity method and X-ray spectroscopy (EDS), respectively.

RESULTS AND DISCUSSION

The XRD patterns (Figures 1(a) – 1(c)) reveal distinct changes in the peak positions when the films are grow on substrates with different lattice parameters. The limited number of reflections makes it difficult to unambiguously describe the crystal structures as either $L2_1$ (austenite phase) or as pure tetragonal $L1_0$ martensite phase. In the case of MgO (111) and STO (001), only one peak at $2\theta = 42°$ was observed. Its intensity is much stronger in the MgO case and nearly at the noise level for STO. We tentatively indexed them as the (220) peak in the $L2_1$ cubic crystal structure, keeping in mind that its relative width (in the MgO (111) case) may suggest some degree of splitting due to the cubic and 10M modulated martensitic structures.[25] In contrast, the two strong peaks in the case of MgO (001) can be identified as an unmodulated, double-tetragonal $L1_0$ structure. These data suggest that all three films most likely contain a mixture of modulated, pure tetragonal, and cubic phases with different relative concentrations.

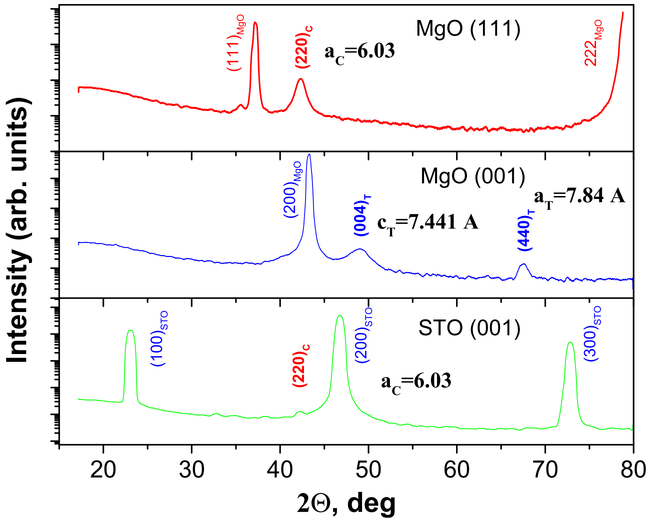

FIG. 1. The X-ray diffraction pattern obtained on 8-nm thick $Ni_{50}Mn_{35}In_{15}$ thin films grown on MgO 111, MgO 001, and STO 001 substrates. The indices and corresponding cubic and tetragonal lattice parameters are presented.

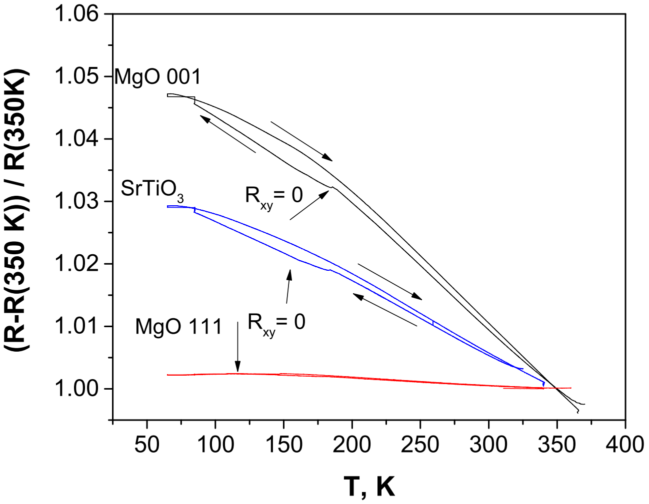

FIG. 2. The temperature dependencies of the resistivity ρ(T), normalized to ρ(350K). The arrows indicate the temperatures where the AHE (R_{xy}) is zeroed-in (see the text).

In order to study how the electronic structure changes with temperature, we measured the electronic transport properties of the samples. The temperature dependencies of resistivity ρ(T), normalized to ρ(350K) are presented in Figure 2. The absolute values for resistivity at 350 K are 320, 280, and 80μΩ·cm for STO (001), MgO (001), and MgO (111) substrates, respectively. While the first two cases match well to the data for the bulk material in the martensitic phase as reported in Ref. 26 the resistivity of the latter one is approximately 3 times smaller, and corresponds to the austenite phase bulk samples.

On the other hand, all samples display a negative temperature coefficient of resistivity (TCR), typical for bulk samples in the martensitic phase. This TCR behavior is justified by the Mooji criteria[27] for STO 001 and MgO 001 films, whose resistivity is 3 times larger than the threshold value. In contrast, the resistivity of the MgO (111) film is slightly lower than the Mooji threshold value. The observed TCR is indeed much weaker but positive as expected at lower temperature, and still negative for $T > 120$ K. This data may reflect that the scattering is not dominated by the phonon mechanism, but that the temperature-induced structural disorder may play an important role.

The results of Hall effect measurements are depicted in figure 3. All of the samples display similar qualitative temperature dependencies of the anomalous (AHE) and ordinary contributions (OHE) to the Hall resistivity. Both AHE and OHE coefficients are positive at low temperatures, but gradually change their sign as the temperature increases. The sign change of the OHE was previously documented[7,26] and attributed to a change in electronic structure associated with a first order martensitic phase transition. Our data indicate that the AHE also undergoes a sign change. The critical temperatures, where the AHE were zeroed are 150°K, 170°K, and 120°K for STO (001), MgO (001), and MgO (111) substrates, respectively. Contrary to the bulk NiMnIn Hall resistivity as function of temperature does not show significant hysteresis, but we note that the AHE sign change coincides with a hysteresis – like loop in the ρ (T) data for all 3 samples.

The absence of hysteris behavior may indicate a suppression of the first order phase transition by a substrate-film elastic interaction. This is confirmed by the detection of a mutually induced strain, observed in similar epitaxial films through a temperature dependent analysis of the width of the substrate XRD peak.[24] Since the initial epitaxial strain changes with the choice of substrate, it is not surprising that the actual temperature of the phase transformation correlates with the substrate/thin film lattice mismatch.

In order to elucidate the effect of the substrate and interfacial strain, we studied $Ni_2Mn_{1.5}In_{0.5}$ thin films deposited on MgO (001) substrates using density-functional theory (DFT) as implemented in VASP.[28] The calculated total energy difference between the FM austenite and FiM martensite states (assuming a Ni/MgO interface) is $\Delta E = 0.20$ eV per NiMnIn f.u, while $\Delta E = 0.24$ eV in the bulk

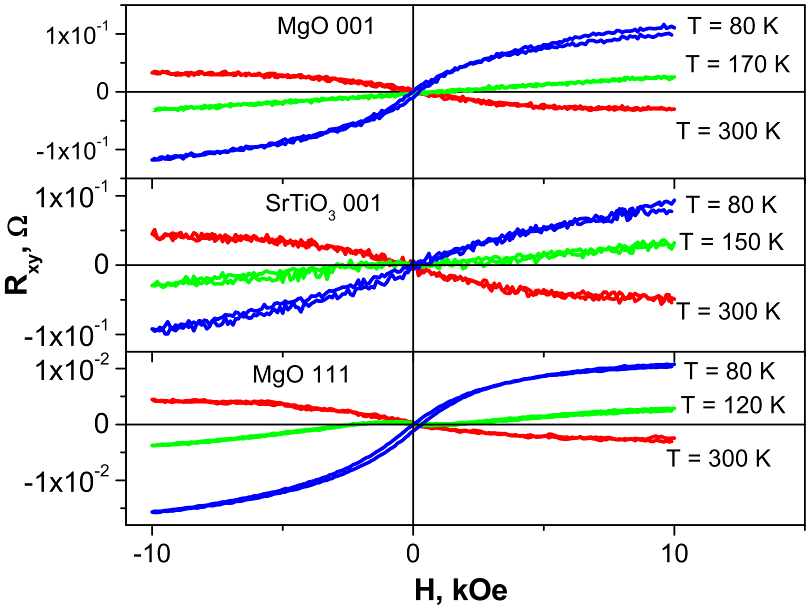

FIG. 3. The Hall resistivity of 8-nm thick $Ni_{50}Mn_{35}In_{15}$ thin films on different substrates at different temperatures.

material with the same (equilibrium) lattice parameters, i.e., when the film is "unstrained". When the lattice parameters of $Ni_2Mn_{1.5}In_{0.5}$ on MgO are of those of MgO substrate, i.e. when the film experiences a strong bi-axial tensile strain of $\Delta a/a = 2.4\%$, the energy difference is $\Delta E = 0.08$ eV per NiMnIn f.u. These results clearly indicate a strong interplay between the lattice strain/stress and the relative stability of the martensite and austenite phases, thus affecting the martensitic transition in the thin films.

We have found a considerable variation of the degree of local deformations in the NiMnIn film at two different lattice parameters. These variations are present in both the FM and FiM states of the film but are considerably larger in the FiM state. The densities of states of the NiMnIn film at two different lattice parameters are different as well, as shown in Figure 4. Because the Fermi velocity is much larger in the majority spin channel, it creates a substantial difference in the conducting properties of the films at temperatures below and above the martensitic transition, and are reflected in experimental observations.

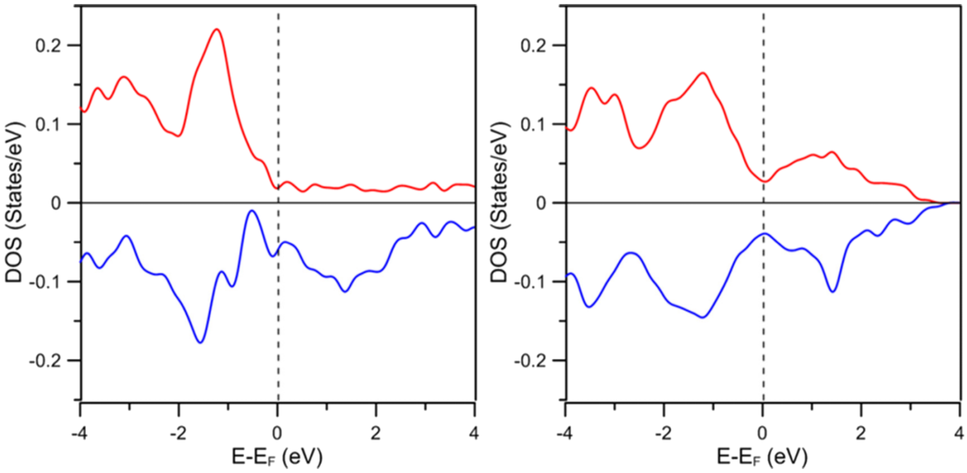

FIG. 4. Local densities of states of the Ni interfacial layer of $Ni_2Mn_{1.5}In_{0.5}$ films deposited on MgO (001) substrates with two in-plane lattice parameters: 4.21Å (left), in the FM state, and 4.312Å (right), in the FiM state.

CONCLUSIONS

In conclusion, we have demonstrated the synthesis of high-quality thin films of $Ni_{50}Mn_{35}In_{15}$, a shape memory alloy, on substrates with different lattice parameters. As revealed by magneto-transport measurements, all films undergo a transformation of electronic structure similar to that of the bulk materials at the martensitic transformation. However, the substrate-film interaction significantly suppresses the first-order phase transition and shifts its temperature in response to epitaxial strain. Therefore, the epitaxial strain induced by substrate can be a mechanism to potentially control the behavior of shape memory alloys.

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation (NSF) through NSF DMR-1310542 grant and the Nebraska Materials Research Science and Engineering Center (MRSEC) under Grant No DMR-1420645, and by the Office of Basic Energy Sciences, Material Science Division of the U.S. Department of Energy (DOE Grant No. DE-FG02-06ER46291 (SIU), and DE-FG02-13ER46946 (LSU)).

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