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Short communication

Improved magnetocaloric effect in magnetron sputtered Ni–Mn–Sb–Al ferromagnetic shape memory alloy thin films

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ABSTRACT

The present study systematically explored the effect of Aluminium (Al) addition on the martensitic phase transformation, magnetocaloric effect (MCE) and mechanical properties in Ni–Mn–Sb ferromagnetic shape memory alloy (FSMA) thin films. From the isothermal magnetization (M–H) curves, a large entropy change $\Delta S = 15.2$ mJ/cm^3 K at 272 K was found in $Ni_{50}Mn_{36.3}Sb_{10.4}Al_{3.3}$ thin film. The refrigeration capacity (RC) was also calculated for all the thin films in an applied magnetic field of 2 T. Further, the room temperature nanoindentation measurements have performed for all these thin films and it reveals the higher values of hardness and elastic modulus of about 12.6 ± 2.2 and 280 ± 2.3 GPa in $Ni_{49.7}Mn_{36.4}Sb_{8.3}Al_{5.6}$ thin film. Hence, the appropriate addition of Al significantly improves the mechanical properties as well as MCE of Ni–Mn–Sb thin films. These findings indicate Ni–Mn–Sb–Al thin films are potential candidates for micro-length scale magnetic refrigeration applications.

The magnetocaloric effect (MCE) phenomenon was first observed by E. Warburg [1], in which an entropy or temperature were changed when a magnetic material subjected to a variation of magnetic field. In this process decrease in entropy under isothermal application of field and increase in temperature under adiabatic application of field in magnetic material, are designated as conventional MCE. This MCE phenomenon is often used in refrigeration cycles where low temperatures are achieved in a process of adiabatic demagnetization [2]. However, magnetocaloric cooling process has been restricted to low temperature cryogenic applications for many decades. Recent discoveries of giant magnetocaloric effect in $Gd_5(Si_XGe_{1-X})_4$ near room temperature can be the potential candidate as room temperature magnetic refrigerants [3]. Following this discovery, a few other systems such as Mn–Fe–As and La(Fe,Si)$_{13}$ were found to exhibit gaint MCE [4,5].

Among these materials, ferromagnetic shape memory alloys (FSMA) based on Heusler compounds show large values of MCE at the martensitic transformation (MT). The different ferromagnetic exchange interaction in each phase promotes a discontinuous magnetization and consequently a magnetic entropy change at the MT temperature [6]. However, the value of magnetic entropy change ΔS (−20.7 J/kg K) in Ni–Mn–Ga alloys is greater than (−18.5 J/Kg K) $Gd_5Si_2Ge_2$ alloys under same condition leads to special attention. The factor responsible for this large entropy change is the first order structural and concomitant magnetic transition. Several authors, like Khan et al. have reported that the maximum entropy change $\Delta S = 19$ J/kg K was observed at 297 K for $Ni_{50}Mn_{37+x}Sb_{13-x}$ alloy [7–9]. This value is remarkably high comparable to that of $Ni_{45}Mn_{44}Sn_{11}$ [10], $Ni_{45.4}Mn_{41.5}In_{13.1}$ [11], $Ni_{46}Mn_{42}In_{12}$ [12], in which ΔS is 6.8 J/kg K at 270 K, 8 J/kg K at 250 K and 5.0 J/kg K at 318 K, respectively. Consequently the MCE is already well investigated in bulk FSMA, information on thin films is still a novel effort. The thin film technology arises as a promising technique for implementation of these features in (nano) micro-systems, which have received much attention during last few years. In addition, from the perspective of micro-devices large magnetic field is undesirable because it can interfere with the electronics of the device and significant power is required to generate the fields. Therefore, the study of MCE in FSMA thin films is of great interest for testing the viability of FSMA as nucleus of refrigeration systems at (nano) microscale [13–16]. In the present study, we have systematically investigated the effect of Al content on magnetocaloric effect of Ni–Mn–Sb–Al thin films synthesised by co-sputtering of Ni–Mn–Sb with Al target on Si (100) substrate.

$Ni_{50.3}Mn_{36.9}Sb_{12.8}$ (S1), $Ni_{50.2}Mn_{36.7}Sb_{11.9}Al_{1.2}$ (S2), $Ni_{50}Mn_{36.3}Sb_{10.4}Al_{3.3}$ (S3), and $Ni_{49.7}Mn_{36.4}Sb_{8.3}Al_{5.6}$ (S4) thin films

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were prepared by co-sputtering of Ni–Mn–Sb and Al targets on Si(100) substrates using dc magnetron sputtering. Depositions were performed at a substrate temperature of 823 K in Ar atmosphere at a working pressure of 10 mTorr. Details on the growing procedure, structural characterization and how to adjust the film composition were published elsewhere [17]. The surface topography was studied using atomic force microscope (AFM) NT-MDT: NTEGRA Model. The average roughness (R_{avg}) of the surface of films was calculated from AFM scans over substrate areas of 1 × 1 μm, performed five times at different spots for each sample. The temperature dependent magnetization (M–T) measurement procedure has been described in Ritu et al. [18]. For the isothermal *M–H* measurements, initially the thin films were prepared by cooling it unidirectionally from 300 K down to the target temperature 10 K. The isothermal *M–H* measurements were then performed at close temperature interval of 3 K by varying magnetic field (*H*) from 0 to 2 T. The mechanical properties of the films were examined using depth sensing Nanoindentation equipped with a diamond Berkovich indenter at room temperature. In order to avoid the influence of substrate on the indentation response of the films, the maximum load is chosen such that the indentation depth does not exceed 10% of the film thickness. Since we are doing a comparative study for the S1, S2, S3 and S4 thin films, the same load was applied for the measurements of all thin films. Thus, the maximum load was set at 2 mN and was kept same for all the films to compare their mechanical properties.

Fig. 1(a)–(d) shows the AFM micrographs for S1, S2, S3, and S4 thin films. These micrographs clearly show the change of microstructure of these films with the change in Al content of these films. The grain size and surface roughness have been calculated from AFM and corresponding values are given in Table 1. It can be seen that the grain size deceased with the increase of Al content in the Ni–Mn–Sb–Al alloy thin film. In pure $Ni_{50.3}Mn_{36.9}Sb_{12.8}$ (S1) thin film, larger grain size 180 nm was observed, where as in S4 thin film with highest Al content having lower grain size 99 nm. The average roughness (R_{avg}) is defined from the following relation [19]:

$$R_{avg} = \frac{1}{N}\sum_{i=1}^{N}|Z_i - \overline{Z}| \quad (1)$$

where, N is the number of surface height data and $\overline{Z}$ is the mean-height distance. It was observed that the R_{avg} of the film decreases with the increase of Al content in Ni–Mn–Sb–Al thin films. The thin film S1 shows R_{avg} of 44.6 nm, while the films S2–S4, which show $R_{avg} \leq 40$ nm.

In order to determine the magnetic properties of Ni–Mn–Sb–Al thin films, we have measured the temperature dependent of magnetization M (T) in field cooling (FC) and field heating (FH) cycles with an applied field of 1 T, as shown in Fig. 2(a–d). The magnetization data for all the films were corrected to account for the diamagnetic contribution of the Si (100) substrate [20]. In S1 thin film during FC cooling cycle, initially at $M_S = 322$ K magnetization starts decreasing sharply, during this twinning of martensitic variants take place. It could be due to the change in exchange interaction across the martensitic transition, which is attributed to different lattice parameters coexistence in austenite and martensite phases [21]. As temperature decreases to 272 K (M_f) the austenite phase of S1 thin film gets completely converted to a twinned martensite phase. In a similar manner, in FH curve reverse martisitic transformation was observed followed by $A_S = 305$ K and $A_f = 348$ K. Although, FH curve in S1 film do not retrace the FC curve but show hysteresis, indicating the presence of first-order

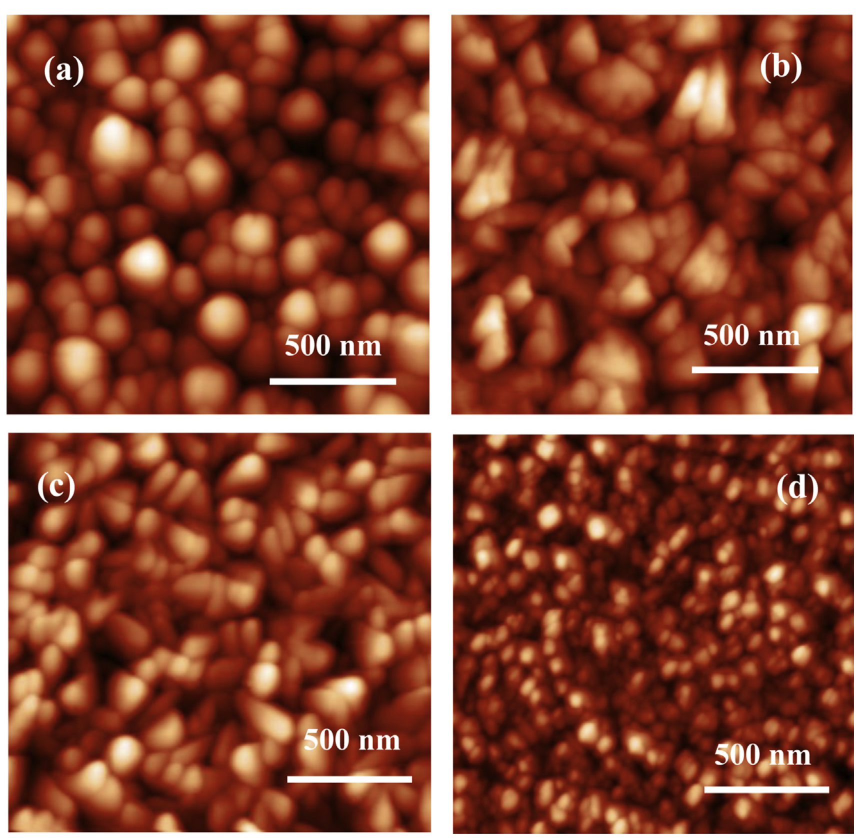

Fig. 1. AFM images of Ni–Mn–Sb–Al thin films with compositions of (a) $Ni_{50.3}Mn_{36.9}Sb_{12.8}$ (S1), (b) $Ni_{50.2}Mn_{36.7}Sb_{11.9}Al_{1.2}$ (S2), (c) $Ni_{50}Mn_{36.3}Sb_{10.4}Al_{3.3}$ (S3), and (d) $Ni_{49.7}Mn_{36.4}Sb_{8.3}Al_{5.6}$ (S4).