Vacuum 89 (2013) 215–219

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Electronic excitation induced phase transformation in FSMA thin film

R. Singhal [a,*], R. Vishnoi [b], K. Asokan [a], D. Kanjilal [a], D. Kaur [b]

[a] Inter University Accelerator Centre, Aruna Asaf Ali Marg, Post Box No. 10502, New Delhi 110067, India
[b] Functional Nanomaterials Research Laboratory, Department of Physics and Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India

ARTICLE INFO

Article history:
Received 24 September 2011
Received in revised form
15 May 2012
Accepted 16 May 2012

Keywords:
Ferromagnetic shape memory alloys
Ion irradiation
Phase transformation

ABSTRACT

The influence of 120 MeV Ag ion irradiation on the structural and magnetic properties of Ni–Mn–Sn ferromagnetic shape memory alloy thin film is investigated. X-ray diffraction data confirms the phase transformation from martensite to austenite phase at a fluence of 1×10^{13} ions/cm^2, which is further supported by the change in surface morphology of the film with increasing fluence as evidenced by field emission scanning electron microscopy. Thermo-magnetic measurements reveal the increase in magnetization and decrease in phase transformation temperatures with increasing fluence. The maximum value of magnetization is $\sim 2.9 \times 10^5$ Amp/meter for the film irradiated at a fluence of 1×10^{13} ions/cm^2. The results are explained on the basis of thermal spike model considering the core and halo regions of ion tracks in FSMA materials.

1. Introduction

Ferromagnetic shape memory alloys (FSMAs) are of increasing scientific attention over the conventional shape memory alloys because they can be controlled not only by temperature and stress but also by applying magnetic field. After the extensive study on Ni–Mn–Ga FSMA system, the second most studied magnetic ternary Heusler alloy system exhibiting magnetic shape memory effect is intermetallic Ni–Mn–Z (Z = Sn, Sb or In) system. Apart from the replacement of very costly Ga element, Ni–Mn–Z system is interesting because it shows the martensitic transformation from the cubic $L2_1$-type structure to an orthorhombic four-layered/monoclinic structure [1,2], which is accompanied by the magnetic transformation from the ferromagnetic austenitic phase to the ferrimagnetic-like martensitic phase [2,3]. In these alloys, large strains can be induced by an external magnetic field, when applied in the martensitic state. These strains can be as large as 10% in a field of about 1 T. The field-induced strain is due to the reorientation of the martensite variants by twin boundary motion. The driving force for the reorientation is provided by the difference in the Zeeman energy ($\mathbf{M}\cdot\mathbf{H}$) of neighbouring variants. In stoichiometric $Ni_{50}Mn_{25}Sn_{25}$ alloy, the magnetic state in the martensitic phase has a lower magnetization than in the austenitic phase [2,3]. Off-stoichiometric $Ni_{50}Mn_{50-x}Sn_x$ ($10 \leq x \leq 16.5$) is another worth studying system and martensitic transformation from cubic $L2_1$-type crystal structure to orthorhombic four-layered martensite structure in $Ni_{50}Mn_{50-x}Sn_x$ was first reported by Sutou et al. [1]. After this report, there is an exponential increase in the work on off-stoichiometric $Ni_{50}Mn_{50-x}Sn_x$ system. Krenke et al. studied phase transformation, magnetic and magnetocaloric properties of the Heusler $Ni_{50}Mn_{50-x}Sn_x$ alloy [4,5]. Brown et al. [3] and Koyama et al. [6] reported on the structural and magnetoelastic behaviour of $Ni_{50}Mn_{36}Sn_{14}$ alloy. The Ni–Mn–Sn system is therefore of prospective importance as FSMA.

The increasing demand for miniaturization of electronic and optical devices has simulated an intense research on materials in form of thin films. Numerous applications from these materials can be generated if the properties of FSMA can be controlled when they are in the form of thin films. Synthesis of FSMA in the form of thin films also provides many ways to control and engineer the properties of these interesting materials such as deposition technique, deposition parameters, thickness of film, choice of substrate etc. We reported the effect of composition [7], substrate temperature [8] and thickness [9] on the structural, electrical, magnetic and mechanical properties of Ni–Mn–Sn thin films and found that martensitic transformation temperature depends significantly on these parameters. Another interest is to investigate the influence of different type of perturbation such as very high temperature, pressure, laser irradiation and different energetic ion irradiation on the properties of FSMA thin films.

Recently, we have studied the low energy (450 keV Ar) ion irradiation induced modifications on structural, electrical and magnetic properties of Ni–Mn–Sn thin films [10]. In the present study, we report the effect of high energy ion irradiation (120 MeV Ag) on the structural and magnetic properties of Ni–Mn–Sn thin film when it is crystallized in martensite phase by appropriately

* Corresponding author. Tel.: +91 9311827207; fax: +91 1126893666.
E-mail address: rahuliuac@gmail.com (R. Singhal).

0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.vacuum.2012.05.017

choosing the composition of the film. When a swift heavy ion passes through the film, it loses its energy mainly via two processes: (i) collisions with the electrons of target atoms which is called electronic energy loss (S_e) and (ii) collisions with the nuclei of target atoms which is known as nuclear energy loss (S_n). For swift heavy ions (ions having velocity comparable to Bohr velocity of electron), S_n is negligible in comparison to S_e and the modifications produced in target material are mainly due to the electronic energy deposition into the film by incoming ions. Ni–Mn–Sn FSMA is an intermetallic system and it is difficult to make significant modifications in metallic system with swift heavy ion irradiation due to the presence of large number of free mobile electrons. Although in some metals, ion tracks have been reported such as $NiZr_2$ and Ni_3B [11–16] and specially in NiTi shape memory alloy, where Barbu et al. [17] showed the formation of ion tracks for $S_e \geq 46$ keV/nm. In the present study, we chose 120 MeV Ag ions beam for bombarding the Ni–Mn–Sn film so that a very high electronic energy (~28 keV/nm) can be deposited into the films without compromising much with the beam current.

This study is also important in order to make a basic understanding on how the swift heavy ions interact with shape memory alloys when it also possesses magnetism. This type of study also throws light on the applications of these FSMA materials in radiation zones such as in space or nuclear reactors.

2. Experimental plan

Thin films of Ni–Mn–Sn FSMA were deposited on Si (100) substrate by DC magnetron sputtering using $Ni_{50}Mn_{37}Sn_{13}$ sputtering target of 25.4 mm diameter and 3 mm thickness. The substrates were initially cleaned thoroughly in an ultrasonic bath with a mixture of distilled water and trichloroethylene in 4:1 ratio and then washed with boiled acetone. During sputtering, the substrate holder was rotated at a speed of 20 rpm in horizontal plane to achieve uniform film composition. Before deposition, the chamber was evacuated to a base pressure of the order of 1.3×10^{-5} Pa and then backfilled with Ar gas to desired pressure of 2.6 Pa. The target to substrate distance was fixed at 5 cm. The Ni–Mn–Sn films of ~750 nm thickness were deposited at substrate temperature of 550 °C and fixed sputtering power of 100 W. No post-annealing was performed after deposition. The composition of the film, determined by energy dispersive X-ray analysis (EDAX), was found to be $Ni_{50}Mn_{36.5}Sn_{13.5}$ and a typical EDAX spectrum is shown in Fig. 1. All the peaks can be identified as arising from the film (Ni, Mn and Sn). Analysis of the spectra after background subtraction and de-convolution of peaks confirm the composition of the Ni–Mn–Sn film to be close to the nominal composition of the target. There is no contamination from remaining water and hydrogen.

These Ni–Mn–Sn FSMA films on Si substrate were irradiated with 120 MeV Ag ions provided by the 15 UD Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi. The vacuum in the chamber during the irradiation was $\sim 4.5 \times 10^{-4}$ Pa. Ion fluence was varied from 1×10^{12} to 1×10^{13} ions/cm^2. In the case of 120 MeV Ag ions, the S_e and S_n in Ni–Mn–Sn FSMA are $\sim 2.8 \times 10^3$ and 1.4×10^1 eV/Å respectively and the range of Ag ions in Ni–Mn–Sn is ~9.1 μm as calculated by SRIM (The stopping and range of ions in matter) programme [18], which is much higher than the thickness of film so most of the ions are buried in the Si substrate. The orientation and crystallinity of the films were studied using a Bruker AXS D8 advanced diffractometer of CuK_α (1.54 Å) radiations in θ–2θ geometry. The measurements were recorded at a step size of 0.02° with a speed of 1.2 s/step. The surface topography and microstructure were studied using field emission scanning electron microscope (FESEM)- FEI Quanta 200F

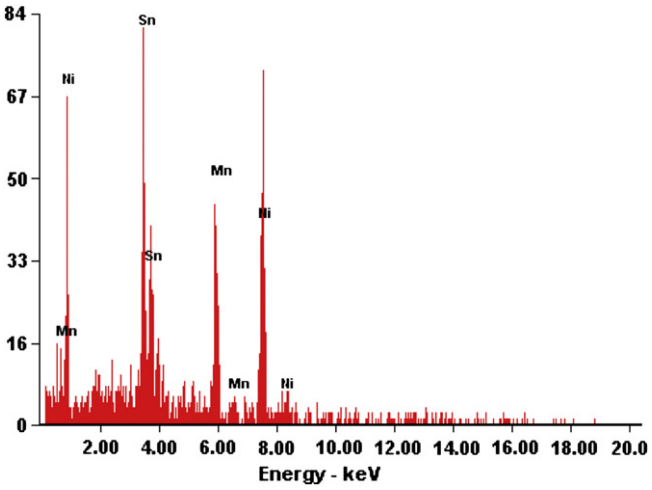

Fig. 1. Energy dispersive X-ray analysis spectrum of Ni–Mn–Sn film.

model. The film thickness was measured using cross sectional FESEM and found to be ~800 nm. The temperature dependence of magnetization $M(T)$ of the films was measured in an external magnetic field ($H = \sim 8000$ Amp/meter) in the temperature range $5\ K \leq T \leq 300\ K$ using superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) under zero field cooled (ZFC), field cooled cooling (FC) and field cooled heating (FH) modes. The measurements in ZFC mode were taken by first cooling the film from 300 to 5 K in the absence of field and then applying the field and recording the data upto 300 K. Then the film was again cooled to 5 K but this time in the presence of field and the data recorded was in FC mode. Finally, the temperature was increased to 300 K in the presence of field and measurement obtained was in FH mode.

3. Results and discussion

3.1. Structural properties

The X-ray diffraction (XRD) patterns of the Ni–Mn–Sn pristine film and also of those irradiated by 120 MeV Ag ions at different fluences ranging from 1×10^{12} to 1×10^{13} ions/cm^2 are shown in Fig. 2. XRD analysis reveals the formation of 14 M modulated monoclinic martensitic phase in pristine film and the planes corresponding to martensitic structure are marked by their Miller indices. The lattice constants a, b, and c are estimated to be about 0.47 nm, 0.51 nm, and 2.95 nm, respectively. For the film irradiated at a fluence of 1×10^{12} ions/cm^2, the intensity of XRD peaks decreases and peaks become broad. It indicates the damage of martensitic structure in the film with ion irradiation. Due to the impact of energetic 120 MeV Ag ions, the modulated monoclinic structure of martensite phase is destroyed at the ion impact site and amorphization occurs to some extent in the film. The mean crystallographic particle sizes of the films were calculated from the XRD data using (1 2 7) peak and applying the Scherrer formula. The average values of calculated crystallite sizes were 21.8 nm for pristine film and 18.5 nm for film irradiated at a fluence of 1×10^{12} ions/cm^2. With further increase in the fluence (3×10^{12} ions/cm^2), the intensity of peaks further decreases and some new peaks appear at around 25.8, 42.7 and 61.7°. For the film irradiated at a fluence of 1×10^{13} ions/cm^2, all the peaks corresponding to the martensite structure disappears and the XRD pattern shows only the (111), (220) and (400) peaks corresponding to cubic $L2_1$ austenite structure. In general, the peaks in XRD