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Energetic ion irradiation induced crystallization of Ni–Mn–Sn ferromagnetic shape memory alloy thin film

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ABSTRACT

The ion irradiation induced crystallization of Ni–Mn–Sn ferromagnetic shape memory alloy (FSMA) thin film is investigated. Thin films of Ni–Mn–Sn FSMA synthesized by DC magnetron sputtering on Si substrate at 200 °C are irradiated by a beam of 120 MeV Ag ions at different fluence varying from 1×10^{12} to 6×10^{12} ions/cm^2. X-ray diffraction pattern reveals that the pristine film grows in $L2_1$ cubic austenite phase with poor crystallinity and crystallinity of the film improves with increasing ion fluence, which is attributed to the strain relaxation by the energy deposited by incoming ions and promotes the grain growth. Grain growth is further confirmed by Atomic force microscopy. The temperature dependent magnetization measurements show improvement in the magnetic and shape memory properties of the films with increasing fluence, which is ascribed to the ordering of austenite phase. Nanoindentation measurements show that with increasing fluence of 120 MeV Ag ions, films exhibit a greater stiffness and smaller tendency towards plastic deformation.

1. Introduction

The properties of ferromagnetic shape memory alloys (FSMAs) have been intensively investigated in the past decade due to their extraordinary properties which combine ferromagnetism together with a shape memory effect associated with reversible martensitic transformation [1–4]. In FSMA, shape memory effect can be controlled not only by temperature and stress, but also by magnetic field, due to which their response is very fast [5–7]. The characteristic martensitic phase transformation in shape memory alloys is a first order solid–solid phase transition which takes place by the diffusionless shearing of the parent austenitic phase. By lowering the temperature, high temperature parent cubic austenite phase transforms into a tetragonal, orthorhombic, or monoclinic martensite phase depending on the composition of the alloy. Due to these extraordinary functional properties such as magnetic superelasticity, large inverse magnetocaloric effect, large magnetoresistance change, shape memory effect etc, FSMAs are interesting materials for developing new thermal or magnetically driven actuators, sensors, and magnetic coolant for magnetic refrigeration.

In order to utilize the ferromagnetic shape memory effect in devices at room temperature, the martensitic phase transformation temperature must be raised near to room temperature. Also, in order to realize these microscopic structures in a small volume, FSMAs must be used in the form of thin films, in which tuning of martensitic transformation temperature is also possible by varying deposition parameters and thus the applicability of these materials can be enhanced. Shape memory alloys in form of thin films will benefit applications, such as microvalves, micropumps and micromanipulators, where large displacement forces are required [8,9]. Several techniques have been successfully employed to deposit thin films of FSMA such as electron-beam evaporation, sputtering or pulsed laser ablation. Since the shape memory effect arises from a characteristic martensitic phase transformation between the high temperature austenite phase and the low temperature martensite phase, the film has to be crystallized for the occurrence of shape memory behaviour. The crystallization of sputtered FSMA thin film has been usually obtained by high temperature (~550 °C) annealing process during and/or after the film deposition [10,11]. High temperature treatment, during or after the film deposition, requires special attention such as need of special substrate which can sustain high temperatures and extra precautions during and after the film deposition to avoid the possibility of oxidation of the samples. Therefore, researchers are trying other methods to lower the crystallization temperature for the growth of FSMA films such

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as by utilizing high-energy sputtered particles with a single-target sputtering deposition [12–15].

In this paper, we report the energetic ion irradiation induced crystallization of Ni–Mn–Sn thin film deposited by DC magnetron sputtering at a substrate temperature of 200 °C. The Ni–Mn–Sn thin films were irradiated by 120 MeV Ag ions using an electromagnetic scanner in the path of beam to scan complete 1×1 cm^2 area of the films. This study is also important in order to make a basic understanding on how the swift heavy ions (SHI) interact with shape memory alloy when it also possesses magnetism and up to what extent it is possible to control their magnetic and structural transformation temperatures by irradiation. This type of study also throws light on the applications of these FSMA materials in radiation environment such as in space or nuclear reactors.

2. Experimental plan

Thin films of $Ni_{50}Mn_{35.8}Sn_{14.2}$ FSMA were deposited on Si (100) substrate by DC magnetron sputtering using $Ni_{50}Mn_{36}Sn_{14}$ sputtering target of 1 inch 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 1.33×10^{-5} Pa and then backfilled with Ar gas to desired pressure of 2.66 Pa. The target to substrate distance was fixed at 5 cm. The Ni–Mn–Sn films of ~900 nm thickness were deposited at substrate temperature of 200 °C and fixed sputtering power of 100 W. No post-annealing was performed after deposition. The composition of the as deposited films in austenite phase determined by energy dispersive X-ray analysis (EDAX) is found to be $Ni_{50}Mn_{35.8}Sn_{14.2}$. 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 $\sim 5 \times 10^{-4}$ Pa. Ion fluence was varied from 1×10^{12} to 6×10^{12} 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 programme [16], which is much higher than the film thickness so most of the ions are buried in the Si substrate after passing through the film. 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 at a scan speed of 1°/min. The surface topography and microstructure were studied using atomic force microscope (AFM)-NTMDT-NTEGRA model. The temperature dependence of magnetization $M(T)$ of the films was measured in an external magnetic field ($H = \sim 8000$ A/m) 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 (ZFC measurements). Then the film was again cooled to 5 K but this time applying the low field of ~8000 A/m and data was recorded (FC measurements). Film was again heated in the presence of field and simultaneously data was recorded (FH measurements). The mechanical properties of the films were measured using IBIS Nanoindentation instrument equipped with Berkovich indenter. 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.

3. Results and discussion

3.1. Structural properties

3.1.1. X-ray diffraction studies

The X-ray diffraction (XRD) patterns of the Ni–Mn–Sn pristine film and also of those irradiated by 120 MeV Ag ions at fluences of 1×10^{12}, 3×10^{12} and 6×10^{12} ions/cm^2 are shown in Fig. 1. XRD pattern confirms that the dominant phase of pristine film at room temperature is austenite and the reflections are indexed to the cubic $L2_1$ structure. In general, the peaks in XRD diffraction pattern corresponding to the $L2_1$ structure should have two types of superlattice reflections in addition to fundamental reflections. One type of superlattice reflections appears, when h, k, and l are all odd (h, k, and l are Miller indices and n is an integer), and satisfies the condition $h + k + l = 2n + 1$, while another appears, when h, k, and l are all even and satisfies the condition $h + k + l = 2n$. For the fundamental reflections, h, k, l are all even and satisfies the condition $h + k + l = 4n$. In the spectrum of XRD pattern of pristine film, (111) and (311) peaks at 25.5 and 50.1° are odd superlattice reflections, (220) and (422) are the fundamental reflections. The presence of these peaks confirms the $L2_1$ austenite phase in pristine sample. In case of the pristine film, the little intensity and noticeable width of the peaks show that the film is poorly crystallized when deposited at a substrate temperature of 200 °C. With increase in ion fluence, an increase in the intensity of all peaks along with the evolution of (200) even superlattice reflection and (400) fundamental reflection can be observed which indicates the increase in the ordering of $L2_1$ crystal structure with ion irradiation. The mean crystallite size is measured by Scherrer relation using the full width at half maxima (FWHM) of (220) fundamental peak and the values are reported in Table 1. It is clear that mean crystallite size increases with increase in ion fluence. Initially for the pristine film, the film–substrate interfacial strain is higher resulting in very small grain size and large number of grain boundaries which

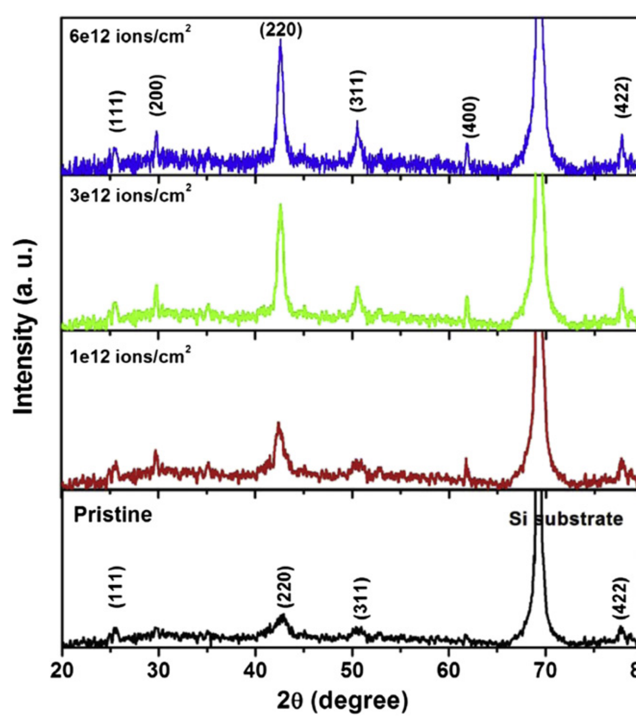

Fig. 1. X-ray diffraction spectra of pristine and irradiated thin films of Ni–Mn–Sn at different fluences of 120 MeV Ag ions.