Materials Research Bulletin 61 (2015) 95–100

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Phase structure and magnetic properties of the annealed Mn-rich Ni–Mn–Ga ferromagnetic shape memory thin films

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ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form 26 September 2014
Accepted 1 October 2014
Available online 5 October 2014

Keywords:
Ferromagnetic shape memory alloy
Thin films
Magnetic properties
TEM

ABSTRACT

The phase structure and magnetic behavior of sputter deposited and annealed Ni–Mn–Ga thin films of varying thickness have been studied. The as-deposited films exhibited quasi-amorphous structure having paramagnetic nature at room temperature. After annealing at 873 K for 30 min ferromagnetic ordering is recovered and the quasi-amorphous structure has changed to nanocrystalline structure. At low film thickness (<300 nm), the annealed films exhibited a mixture of cubic austenite ($L2_1$) and martensite phases while at thickness greater than 1000 nm ordered $L1_2$ phase was observed. The magnetic properties were found to strongly depend on the structure of the constituent phases in the films.

1. Introduction

Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) are technologically important class of materials due to their large recoverable strain at frequency (~1 kHz) greater than that of the conventional shape memory alloys [1]. The large value of magnetic field induced strain (MFIS) is attributed to the reorientation of twin variants in martensite phase by an external magnetic field. The main requirements for the occurrence of FSMA phenomenon are the low de-twinning stresses and high magnetocrystalline anisotropy of the martensite phase [2]. This combination of structural and magnetic properties is generally observed in the modulated martensite phase of the single crystalline Ni–Mn–Ga alloys [3]. While single crystals exhibit large MFIS, different processing routes such as melt spinning [4], powder metallurgy [5], composites [6], Ni–Mn–Ga foam [7], and thin film [8] have also been explored to improve MFIS, ductility, and cost effectiveness of polycrystalline Ni–Mn–Ga alloy. From the view point of micromechanical miniaturized systems, the Ni–Mn–Ga thin films are considered as a promising candidate since it can deliver larger stroke than the conventional piezoelectric [9] and magnetostrictive thin films [10]. Micro-devices such as microactuator, microvalves, and micro scanner have been developed based on Ni–Mn–Ga thin films [11,12]. In addition, Ni–Mn–Ga alloys have advantages over other ferromagnetic shape memory Fe–Pd [13] and Fe–Pt [14] alloys due to their low cost and availability of raw materials.

Recently, considerable effort has been expended in optimizing the growth parameters of Ni–Mn–Ga thin films to achieve desired phase structure and magnetic properties [8,15]. The characteristics of sputter deposited films can be changed by many parameters such as sputtering power, pressure, substrate temperature, and sputtering time. Particularly, thickness of the film is one of the key factors which affect the microstructure, magnetic, and magneto transport properties and predominantly shape memory behavior of FSMA thin films [16,17]. The key requirements for micro-electro mechanical system (MEMS) are the film thickness in the range of 100 nm–1 μm with a fast response and a large recovery strain [18]. Therefore, it is important to study the effect of film thickness in nanometer range on the structural and magnetic properties of Ni–Mn–Ga films. In the present work, polycrystalline Ni–Mn–Ga films with varying thickness were deposited on to Si(100) substrate using DC magnetron sputtering. The as-deposited films were then annealed at 873 K, and characterized to study the phase structure and associated magnetic properties.

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http://dx.doi.org/10.1016/j.materresbull.2014.10.008
0025-5408/

Table 1
Composition and *e/a* ratio of annealed Ni–Mn–Ga thin films.

Film ID	Thickness (nm)	Ni (at%)	Mn (at%)	Ga (at%)	*e/a* Ratio
NMG1	135	49.2	29.9	20.9	7.64
NMG2	260	48.6	31.2	20.2	7.65
NMG3	595	49.1	30.4	20.5	7.65
NMG4	1020	50.7	28.6	20.7	7.69

2. Experimental details

A 500 g pancake of Mn-rich off-stoichiometric polycrystalline $Ni_{50}Mn_{30}Ga_{20}$ alloy 90 mm diameter and 12 mm thickness was prepared using high purity raw elements nickel (99.95%), manganese (99.9%), and gallium (99.99%) in a vacuum arc-melting furnace. To ensure chemical homogeneity, the pancake was reverted and re-melted four times under the protective atmosphere of argon gas. The sputtering targets of 75 mm diameter and 1 mm thickness were wire-cut from the pancake alloy. The composition of the sputtering target was found to be $Ni_{49.6}Mn_{30.6}Ga_{19.8}$ using inductively coupled plasma – optical emission spectroscopy (ICP-OES–PerkinElmer Optima 5300 DV).

The Ni–Mn–Ga thin films were deposited using DC magnetron sputtering on well cleaned Si(100) substrates under high purity argon atmosphere at room temperature. The substrates were cleaned thoroughly in an ultrasonic bath with a mixture of distilled water, acetone, and trichloroethylene for 15 min each and then dried in hot air blower. The sputtering experiments were performed at a constant power of 100 W. The sputtering pressure was maintained at a constant value of 10 mTorr during deposition. The distance between the substrate and target was fixed at 100 mm for all experiments. High purity of argon gas was used as process gas. Pre-sputtering was done for 10 min to clean the target surface prior to each sputtering experiment. Thickness of the films was varied by changing the sputtering time keeping other parameters constant. The average thickness of the films was determined to be 135 nm, 260 nm, 595 nm, and 1020 nm using stylus profilometer and these films are denoted as NMG1, NMG2, NMG3, and NMG4, respectively. As-deposited films were then annealed at 873 K for 30 min in the high vacuum furnace. The room temperature crystal structure was studied using Philips PW1320 diffractometer with Cu-Kα radiation. The microstructure of the films was observed using transmission electron microscope (TEM, Tecnai G^2 30ST (FEI)). The bright field images and dark field images from (2 2 0) diffraction plane were taken to show nanocrystalline structure of films. The film composition was determined by energy dispersive X-ray analysis (EDAX) attached in TEM. The magnetic properties of the films were studied by vibrating sample magnetometer (VSM, ADE EV9 Model) and Quantum design SQUID-VSM.

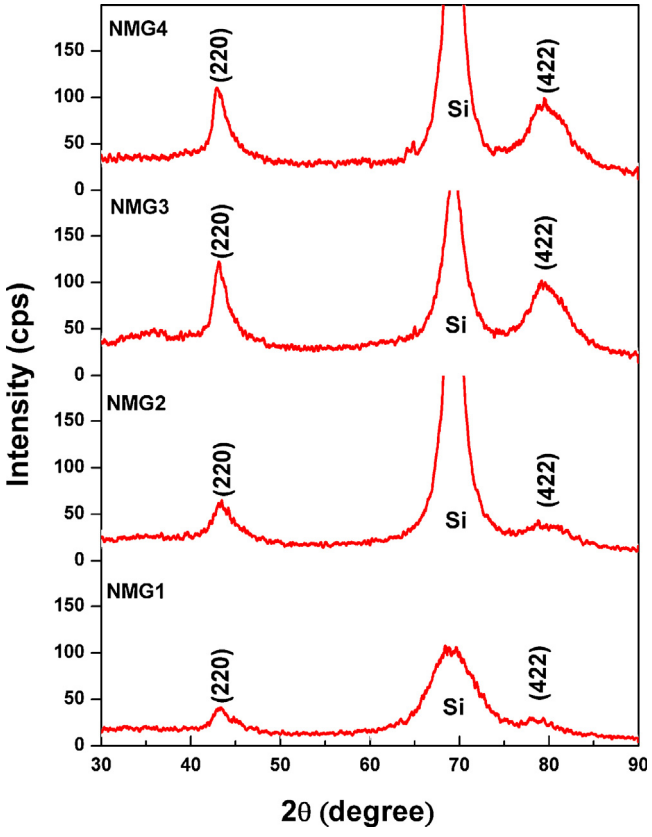

Fig. 1. XRD patterns of as-deposited Ni–Mn–Ga thin films recorded at room temperature.

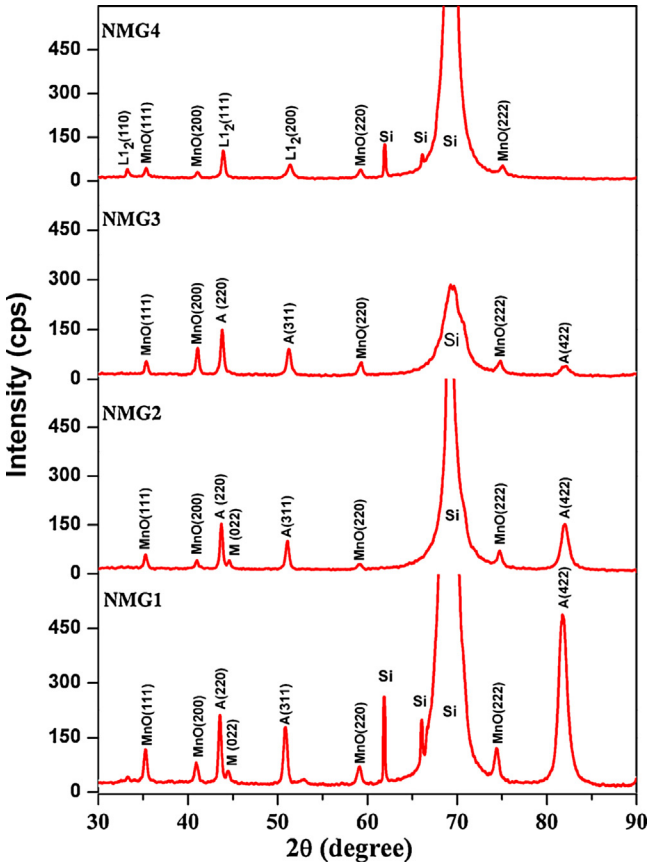

Fig. 2. XRD patterns of annealed NMG1, NMG2, NMG3, and NMG4 thin films recorded at room temperature.

3. Results and discussion

3.1. Compositional analysis

The composition of the annealed films was determined from the transverse section of the films using EDAX in TEM and is listed in Table 1.The composition of the films mainly depends on the sputtering parameters such as sputtering power, gas pressure, and time. Table 1 also lists the sputtering time and the corresponding thickness of the films. From Table 1 it can be seen that at lower thickness, the composition of NMG1, NMG2, and NMG3 films is very close to the target composition of $Ni_{49.6}Mn_{30.6}Ga_{19.8}$ (at%); however, at higher film thickness (NMG4) the composition of the film shifts