Journal of Magnetism and Magnetic Materials 323 (2011) 2797–2801

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Stress analysis, structure and magnetic properties of sputter deposited Ni–Mn–Ga ferromagnetic shape memory thin films

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ARTICLE INFO

Article history:
Received 12 February 2011
Received in revised form
7 June 2011
Available online 16 June 2011

Keywords:
Ni–Mn–Ga thin film
Ferromagnetic shape memory material
Residual stress
Magnetic property

ABSTRACT

The residual stress instituted in Ni–Mn–Ga thin films during deposition is a key parameter influencing their shape memory applications by affecting its structural and magnetic properties. A series of Ni–Mn–Ga thin films were prepared by dc magnetron sputtering on Si(1 0 0) and glass substrates at four different sputtering powers of 25, 45, 75 and 100 W for systematic investigation of the residual stress and its effect on structure and magnetic properties. The residual stresses in thin films were characterized by a laser scanning technique. The as-deposited films were annealed at 600 °C for 1 h in vacuum for structural and magnetic ordering. The compressive stresses observed in as-deposited films transformed into tensile stresses upon annealing. The annealed films were found to be crystalline and possess mixed phases of both austenite and martensite, exhibiting good soft magnetic properties. It was found that the increase of sputtering power induced coarsening in thin films. Typical saturation magnetization and coercivity values were found to be 330 emu/cm^3 and 215 Oe, respectively. The films deposited at 75 and 100 W display both structural and magnetic transitions above room temperature.

1. Introduction

Ni–Mn–Ga is a class of advanced multifunctional magnetic materials exhibiting technologically craving and exciting properties, viz. superelasticity, magnetic shape memory, magnetocaloric effect, negative magneto-resistivity etc., which attracted researchers to make use of its full potential in integrating with emerging technologies, which other shape memory materials cannot fulfill [1–3]. Among those exciting properties magnetic shape memory occupies a major research place for the reason that large reversible magnetostrains up to 10% can be produced for a field activation frequency of the order of about 1.5 kHz [4–6]. Such large strain output and high frequency response of Ni–Mn–Ga are associated with the selection of martensitic variants originating from the diffusionless displacive solid state structural phase transformation.

Motivated by the fascinating practical applications of bulk Ni–Mn–Ga alloys, a large interest has grown around the world for the preparation and study of Ni–Mn–Ga thin films to exploit their unique properties in micro- and nano system applications like micro-electro-mechanical systems (MEMS) [7–10]. Recently much effort has been put on sputtering techniques to produce such thin films [11,12]. Despite the unique and multifunctional properties of Ni–Mn–Ga its high brittleness, low mechanical strength and poor processability are of large constraints of this intermetallic compound, posing limit to its potential applications to a large extent [13–15]. Thin films of Ni–Mn–Ga are found to possess superior ductility compared to its bulk alloy [16,17], enabling them to be employed in micro and nano actuators without fracture failure under deformed conditions. Based on these developments, Ni–Mn–Ga thin films have already been successfully implemented in prototypes of microvalves and microscanners [12,18].

Ni–Mn–Ga ferromagnetic martensitic thin films possess large potential in the form of free standing films and films attached to substrates. The magneto-mechanical properties of polycrystalline Ni–Mn–Ga thin films still remain largely unexplored and they open up totally new possibilities for potential applications for which extensive basic research is still needed [11,19,20]. The presence of martensitic transformation and variant mobility in thin films is a prerequisite for applications in MEMS. Studies show that such a transformation is governed by microstructure and other film–substrate constraints, which depend on the residual stress present in the thin films mainly originating from structural defects and various misfits (lattice and thermal), influencing the structural and magnetic ordering [7,11,21,22]. To fulfill the requirements of small integrated devices like MEMS, small sized actuators (micro and nano) need to be developed with required properties, which needs

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doi:10.1016/j.jmmm.2011.06.017

thin film technology for its realization. Particularly, physical properties of magnetic shape memory thin films are largely influenced by the residual stresses present in it as the couplings among thermal, magnetic and mechanical properties are highly complex and interdependent. Thin films deposited on substrates often have residual stress, which may affect a variety of phenomena, viz. physical properties, adhesion, generation of crystalline defects, martensitic variant formation and formation of surface growth such as hillocks and whiskers, etc. Stresses in thin films are of two types: first— growth induced such as stresses arising from deposition and second— thermally induced such as stresses arising from a mismatch in thermal expansion coefficients. Relaxation processes such as plastic flow, creep and micro-cracking can act to reduce the stress. The workability and reliability of the active materials also depend on the residual stresses present in thin films. Therefore, the determination and control of stress is an important scientific issue for the functional thin films from the viewpoint of performance and integrity [23–26]. Hence the present work aims at the examination of residual stress present in Ni–Mn–Ga thin films and to study their effect on the structure and magnetic properties.

2. Experimental procedures

Polycrystalline Ni–Mn–Ga thin films were dc magnetron sputter deposited onto (2″ × 1″) Si(1 0 0) and glass substrates at argon pressure of 0.01 mbar and four different sputtering powers of 25, 45, 75 and 100 W for half an hour duration using alloy sputtering targets [$Ni_{50}Mn_{30}Ga_{20}$ (at%)] prepared in our laboratory. The films were also deposited onto 3″ diameter Si(1 0 0) wafer for residual stress analysis. The films were post-deposition annealed in vacuum at 600 °C for 1 h. The compositional analysis of the films was carried out using energy dispersive X-ray analysis. Crystal structure of the constituting phases was studied using PHILIPS3121 X-ray diffractometer (Cu-K_{α} radiation). Residual stress analysis of the thin films was carried out using a laser scanner [KLA Tencor model-Toho Technologies FLX-2320] by curvature measurement. Microstructure of the thin films was studied using a LEO440i scanning electron microscope. Magnetic properties of the thin films were measured using an ADE EV9 Model vibrating sample magnetometer to record magnetic hysteresis and thermo-magnetic curves. The thickness of the films was measured using a Veeco made atomic force microscope (AFM) and was found to vary from 1200 to 1500 Å.

3. Results and discussion

3.1. Structure

X-ray diffraction patterns of annealed Ni–Mn–Ga thin films deposited on glass substrates at different sputtering powers of 25, 45, 75 and 100 W are shown in Fig. 1. The annealed films show good crystallinity. The X-ray pattern reveals that films deposited at low sputtering power of 25 W reflect the cubic parent austenite phase characterized by (2 2 0) reflection and all other films show mixed phases of both austenite and martensite. The degree of martensitic formation was found to increase with increasing sputtering power and the film deposited at 100 W shows relatively high degree of martensitic phase. Some minor reflections at about 35° C are also observed and represented by a triangle symbol, which could not be indexed. The films deposited at higher powers also show the presence of super-lattice peaks (1 1 1) and (3 1 1). The origin of super-lattice and modulated martensitic peaks may be attributed to chemical ordering and presence of

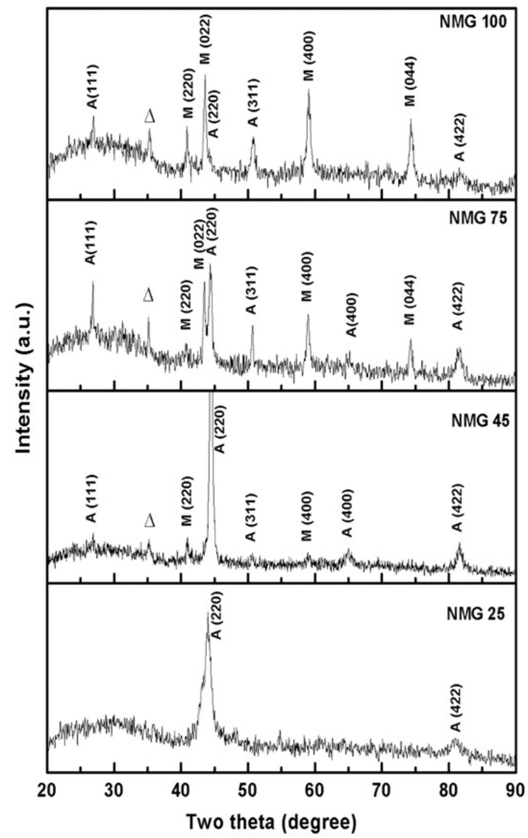

Fig. 1. X-ray diffraction patterns of annealed Ni–Mn–Ga thin films deposited on glass substrate at different sputtering powers keeping a constant pressure.

residual stresses in the thin films. The increase in degree of martensitic formation deposited at higher powers might be due to the high residual stresses associated with films deposited at high sputtering powers. These observations indicate that the presence of residual stresses in Ni–Mn–Ga thin films influences the microstructure and in turn formation of martensitic variants in the films.

Fig. 2 shows the backscattered electron (BSE) images of the annealed Ni–Mn–Ga thin films deposited on glass substrate at different sputtering powers. The microstructures of the films reveal that their morphology varies with sputtering power. The films deposited at low power of 25 W were found to be discontinuous with open structures whereas the films deposited at other powers of 45, 75 and 100 W are found to be continuous with grain sizes increasing with sputtering power due to atomic consolidation starting from fine grain to coarse grain when moving from low to high sputtering power levels. This shows that the increase of sputtering power induces coarsening in the thin films owing to densification of the thin films deposited at higher sputtering powers. The higher thickness of the thin films deposited at higher sputtering powers keeping the sputtering time constant for all depositions may also contribute to the formation of continuous films deposited at higher powers due to more atomic flux penetration into the thin film during its growth.

3.2. Stress analysis

Mechanical stress generation in Ni–Mn–Ga thin films is a key parameter for the suitability of shape memory applications [27]. There are several techniques to characterize residual stress, in which some are destructive while others are non-destructive. Techniques based on curvature measurements are frequently