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Thickness dependent exchange bias in co-sputter deposited Ni–Mn–Al Heusler alloy hard nanostructured thin films

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ABSTRACT

In the present work thin films of off-stoichiometric Ni–Mn–Al thin films have been successfully deposited on Si substrates. The films have been deposited by DC/RF magnetron sputtering by co-sputtering of the targets of Ni, Mn and Al. The films have been studied for their structural and magnetic properties. Nanoindentation has also been done for film hardness and resistant to crack properties. It has been observed that Martensitic transformation occurs in the film exhibiting large thickness (1.5 μm). All the films exhibit exchange bias at low temperature with the exchange bias field depending strongly on the thickness of the film. ac susceptibility result shows the existence of spin glass state at low temperature. The exchange bias appearing in the sample may be associated with the interface containing spin glass SG/FM phase. The appearance of exchange bias in all the samples shows that in Ni–Mn–Al system, exchange bias is independent of the occurrence of martensitic transition in the system. The existence of mixed phase ($L2_1$ and B2) is an intrinsic property of Ni–Mn–Al system and the formation of $L2_1$ phase can be controlled by using different deposition and annealing parameters. In this respect, exchange bias properties of Ni–Mn–Al may be tuned by controlling the formation of ferromagnetic $L2_1$ phase. Nanoindentation results reveal that the film exhibits high hardness (H) ~21 GPa and is resistant to scratch.

1. Introduction

In recent years, Heusler alloys have emerged as one of the promising materials exhibiting exchange bias due to their multifunctional properties such as shape memory effect, magnetocaloric effect, giant magnetoresistance and superelasticity [1–8]. Exchange bias has been studied in bulk Heusler alloys such as NiMnSn [9], NiMnSb [10] and NiMnIn [11] and Co substituted NiMnSb alloys [12]. Large EB has been observed in Ni–Mn–In bulk alloys after ZFC from an unmagnetized state [13]. For several decades, thin films have been an area of intense research due to the potential application of thin films in data storage devices based on spin polarized and exchange biased materials [14,15]. Various approaches have been undertaken in an attempt to fabricate Heusler alloy films with desirable characteristics. Thin films of Ni–Mn–Sn [16], Ni–Co–Mn–In [17] and Ni–Mn–In [18] have been successfully deposited from pre-synthesized targets. Thin films Ni–Mn–In and Ni–Co–Mn–In have been shown to exhibit martensitic phase transition while work on Ni–Mn–Sn thin film shows the evidence for exchange bias. The underlying mechanism for the observation of exchange bias in bulk and thin films of Heusler alloy is the interplay between ferromagnetic and antiferromagnetic regions present in the martensite phase only.

The practical application of thin films depends on their mechanical properties which is reflected in their hardness and resistant to corrosion properties. Among Heusler alloys, Ni–Mn–Al alloys are superior to the Ni–Mn–X alloys in terms of mechanical properties and are potential candidate for a high-temperature shape memory effect [19]. The magnetic properties of off-stoichiometric Ni–Mn–Al alloys are structurally dependent. The antiferromagnetism of Ni–Mn–Al is associated with the quenched B2 structure, whereas $L2_1$ structure promotes ferromagnetic ordering of the magnetic moments [20,21]. The stabilization of $L2_1$ phase is difficult and involves long time annealing [21]. The studied alloys are always found in a state that incorporates both ferromagnetic and antiferromagnetic ordering associated with $L2_1$ and B2 structures, respectively. The Neel temperature of antiferromagnetic phase T_N ~ 300 K and the Curie temperature of the ferromagnetic phase T_C ~ 375 K [22]. At low temperatures, the magnetic susceptibility of stoichiometric and off-stoichiometric alloys exhibits splitting of zero-field cooling and field cooling curves indicating a spin-glasslike behaviour. The structural and magnetic properties of Ni–Mn–Al system have been investigated in detail in bulk form, however, thin films of Ni–

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Mn–Al have received so far much less attention. Literature on Ni–Mn–Al thin films shows that the stoichiometric Ni_2MnAl films deposited at lower substrate temperatures (180 °C) favour non-ferromagnetic ordering exhibiting a B2 like crystal structure; while higher growth temperature (400 °C) favours ferromagnetic films exhibiting a $L2_1$ like structure [23]. For the stoichiometric Ni_2MnAl films, martensitic transformation is not observed. The high-temperature cubic structure is stable down to liquid helium temperature [24]. Large negative magnetoresistance [25] and martensite to austenite transition [26] has been observed for off-stoichiometric Ni–Mn–Al thin films. It has been well known that the properties of thin films crucially depend on the deposition technique and processing parameters involved. The studied Ni–Mn–Al thin films have been deposited by MBE, PLD or sputtering from pre-synthesized targets. However, there are no reports on the structural and magnetic properties of Ni–Mn–Al thin films deposited by co-sputtering using different elemental targets. Further the mechanical properties of Ni–Mn–Al thin film have not been explored so far.

In the present work thin films of off-stoichiometric Ni–Mn–Al thin films with various thicknesses have been successfully deposited on Si substrates. The films have been deposited by DC/RF magnetron sputtering by co-sputtering of the targets of Ni, Mn and Al. The films have been studied for their structural and magnetic properties. Nanoindentation has also been done for film hardness and resistant to crack properties. It has been observed that Martensitic transformation occurs in the film exhibiting large thickness (1.5 μm). All the films exhibit exchange bias at low temperature with the exchange bias field depending strongly on the thickness of the film. Nanoindentation results suggest that the film exhibit high hardness and resistant to scratch.

2. Experimental details

Ni–Mn–Al thin films with various thicknesses were deposited using DC/RF magnetron sputtering from three different targets of Ni, Mn and Al. Sputtering targets of Ni, Mn and Al with purity values of 99.98%, 99.95% and 99.34%, respectively, have been used for deposition. Sputtering was carried out at constant Ar (20 sccm) flow at 400 °C substrate temperature for different deposition times t_d ($5 \leq t_d \leq 20$ min). The DC power densities for Ni and Al targets were 75 W/cm^2 and 85 W/cm^2, respectively. For Mn target, 115 W RF power has been used. All depositions were carried out at a fixed substrate to target distance of 6 cm. The base pressure before deposition was lower than 4.0×10^{-6} Torr and the argon pressure was kept at 10 mTorr during sputtering. Prior to the deposition, the targets were pre-sputtered for 10 min. The post annealing of the films deposited at $T_s = 400$ °C have been carried out in vacuum for 2.5 h. The characterization of the films have been carried out using grazing angle X-ray diffraction (GAXRD) (Bruker, D8 advance), field emission scanning electron microscopy (FE-SEM) (FEI, QUANTA 200F) and high resolution transmission electron microscopy (HRTEM) (200 kV, FEI, TECNAI G2) for their structural, morphological and cross-sectional studies. The chemical composition of the thin films was examined by X-ray spectroscopy (EDX) in a TEM and in a scanning electron microscope. The magnetic properties were measured by superconducting quantum interference device (SQUID) magnetometer (MPMS, Quantum Design) in a temperature range of 5–300 K and maximum applied field of 50 kOe. For the measurements, the sample was initially cooled down to 5 K and then 100 Oe field was applied and measurements were recorded with increasing temperature. This is referred to as zero-field cooled (ZFC) curve. Again, the sample was cooled down to 5 K in the presence of field and measurements were recorded with increasing temperature. This is referred to as field-cooled heating (FCH) curve. Further, measurements were taken during cooling referred to as field-cooled cooling (FCC) curve. The hardness (H) and effective elastic modulus (E_r) of NiMnAl film deposited with thickness 1.15 μm was measured by a nano-indentation (NT-MDT, Nanoslerometry) using a Berkovich diamond indenter with normal angle of 65.3° between tip axis and faces of triangular pyramid. The H and E_r of NiMnAl film have been measured at 3000 μN force to assure that the penetration depth should not increase the 10% of total thickness of coating to minimize the substrate effect.

3. Result and discussion

The elemental composition analysis of Ni–Mn–Al thin films was carried out using an energy dispersive X-ray analysis (OXFORD, X-Max) with variation of ±0.3 at.% for heavy elements and ±2 at.% for light elements. The composition varies slightly with increasing deposition time with the average composition $Ni_{54}Mn_{27}Al_{19}$. Cross-sectional FE-SEM of the films shows that the thickness of the film varies monotonically with increasing deposition time. The thicknesses of the films deposited for 5 min, 10 min and 15 min are around 0.5, 1.15 and 1.5 μm, respectively. Fig. 1 shows the XRD patterns of the films having various thicknesses. For the film with thickness of ~0.5 μm, peaks corresponding to Si 100 substrate can also be seen. The peak at $2\theta = 54.30^0$ corresponds to 400 orientation of Si substrate, the other peak at $2\theta = 55.16^0$ may be attributed to the formation of oxides on the surface of the substrate. A close analysis of the XRD patterns shows that the structure consists of mixed $L2_1$ and B2 phases. With increasing film thickness from ~0.5 μm to ~1.5 μm, peak corresponding to $L2_1$ phase at $2\theta = 50.8°$ (311) and $2\theta = 71.7°$ (331) starts appearing. The reflections corresponding to $L2_1$ phase develop with increase in film thickness. To further confirm the phase present in the films, the crystal structure of the films has been examined by transmission electron microscopy. As an example, selected area electron diffraction (SAED) pattern for the film with thickness of ~1.5 μm is shown in Fig. 2. The SAED pattern taken from the part of the specimen corresponds to cubic B2 structure which shows that the structure mainly consists of cubic B2 phase.

The magnetic and structural transition temperatures of Ni–Mn–Al films have been determined from the magnetization measurement at H = 100 Oe. Fig. 3 shows the dc susceptibility for the films in the temperature range of 5 K ≤ T ≤ 300 K in zero-field-cooled heating (ZFCH), field-cooled heating (FCH) and field-cooled cooling (FCC) sequences. Any hysteresis in the FCH and FCC sequences is expected to be associated with a structural transition. For the film with thickness of ~0.5 μm, no evidence of structural transition is seen; for the film with thickness of ~1.15 μm, just a slight signature of the phase transformation was observed and for the film with thickness of ~1.5 μm, there exists a clear thermal hysteresis ΔT of about 6 K (inset of Fig. 3) between FCH and FCC which is attributed to a first order structural transition. The absence of thermal hysteresis for the film with thickness of ~0.5 μm may be due to the hindrance of transformation by a large number of grain boundaries. With increasing film thickness, the grain size increases

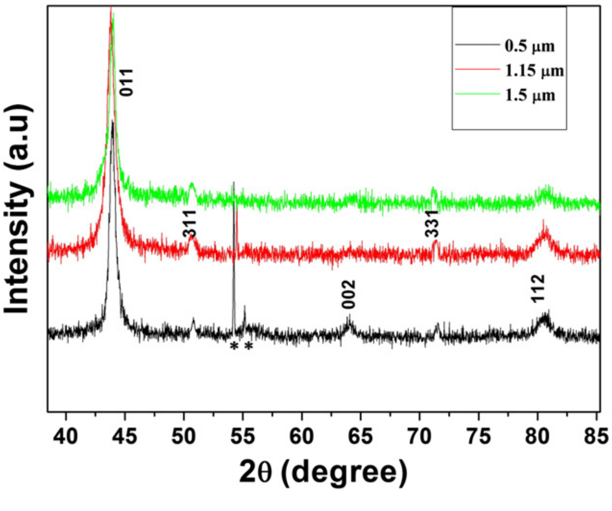

Fig. 1. X-ray diffraction patters of the thin films.