Structure and magnetic properties of $Ni_{53.5}Mn_{24.5}Ga_{22}$ films with optimized annealing temperature and thickness

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The off-stoichiometric $Ni_{53.5}Mn_{24.5}Ga_{22}$ thin films have been prepared by magnetron-sputtering technology, The composition, morphology, and magnetic properties of the films were analyzed by energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), X-ray diffraction patterns (XRD) and vibrating sample magnetometer (VSM). The results of structure measurements indicate that the as deposited films are amorphous, and show typical T-type martensitic structure after annealed due to increase of the degree of crystallization, especially at 1073 K. The films show a paramagnetism-ferromagnetism transition and the Curie temperature of film with 1.2 μm is highest. And the film is magnetic anisotropy at room temperature after annealed at 1073 K.

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1. Introduction

Ni-Mn-Ga alloy films, showing both heat-induced strain and magnetic shape memory (MSM) effect, have attracted considerable interest as promising drive and sensing materials. Since the discovery of magnetic shape memory (MSMS) alloys, the maximum strain obtained in this material class has increased to 10% [1, 2]. However, the potential application of Ni-Mn-Ga alloy is restricted due to its brittleness, low strength, and poor formability, either single crystal or polycrystalline form. Therefore, the preparation of Ni-Mn-Ga thin films emerged as a new research direction, including the methods of magnetron sputtering [3, 4], pulsed laser deposition [5] and molecular beam epitaxial [6]. The effects of thicknesses on phase transformation and magnetic properties also reported [7-9] .The research about the composition and magnetic property of Ni-Mn-Ga thin films has become hotter [3, 10,11] recently.

In this paper, the off-stoichiometric $Ni_{53.5}Mn_{24.5}Ga_{22}$ films have been prepared by magnetron-sputtering technology, and the structure and magnetic properties of the films with different heat treatment temperature and different thickness films have been studied. We also find the influence between heat treatment temperature and magnetic properties of the films.

2. Experimental

$Ni_{53.5}Mn_{22.5}Ga_{24}$ films were deposited on P-type Si (100) substrate by FJL560 Ⅱ ultra-high vacuum magnetron sputtering and ion beam joint device. To adjust instrument parameters, coating film under the base vacuum in the sputtering chamber was below 2.0×10^{-4}Pa. Test process parameters as follows: The Ar pressure was 0.8Pa; the distance between substrate and target was 70mm and the sputtering power was 200W; the substrate negative bias was 7V and chip substrate temperature was room temperature. Films with the thickness of 0.4, 0.8, 1.2 and 2.3 μm were prepared by changing sputtering time (1.8Ks, 3.6Ks, 5.4ks and 7.2Ks. After depositing, put the films into the high vacuum heat treatment furnace, heat treatment temperatures were 773K, 873K, 973K and 1073K, the base pressure was lower than 2×10^{-4}Pa, heat treatment time was 3.6Ks, then cooled with the furnace.

The compositions of the films were analyzed by the spectrometer comes with Hitachi S-4800 (FE-SEM) field emission scanning electron microscope. Agilent-5420 atomic force microscopy (AFM) was used to observe the surface morphology of the films. The structure was measured by Panalytical X'Pert PRO X-ray diffraction (XRD) (Cu-K_α radiation), and the test range is from 30° to 60°. The Magnetization V.S temperature curve and the hysteresis loop of the film were measured by Quantum Design's multi-use vibrating sample magnetometer (VSM) VersaLab system.

3. Results and discussion

Table 1 shows the composition and valence electrons concentration of Ni-Mn-Ga thin films with 1.2 μm thick after annealed at different temperatures. We can find that

there are no obvious changes of the element contents in the film after annealed at different temperature, indicating that annealing does not affect the composition of the films. The valence electron concentration of Ni-Mn-Ga films are at about 7.7, indicating that the martensitic phase transition temperatures are near their Curie temperature [12]. So, the films can be used as shape memory materials due to those properties.

Table 1. Compositions and valence electron density (e/at) *of four Ni-Mn-Ga thin films after the different annealing temperatures.*

Heat-treatment temperature	Content of Ni $(at.\%)$	content of Mn $(at.\%)$	content of Ga $(at.\%)$	Valence electron concentration(e/a)
773K	53.13	24.73	22.14	7.7250
873K	53.33	24.46	22.21	7.7083
973K	53.67	24.24	22.09	7.7115
1073K	53.55	24.25	22.20	7.7265

Fig. 2 shows three-dimensional morphology of Ni-Mn-Ga thin films at the test range of $2 \times 2\ \mu m^2$ after annealed at 773K, 873K, 973K and 1073K for 3.6 ks respectively. It can be seen from the figure that surface particle size Ni-Mn-Ga film increases with the annealing temperature increases. When the heat treatment reaches to 1073K, the film become more flat and smooth, indicating that the film is not crystallization or completely crystallization if the temperature is low and the film can be completely crystallized when the temperature rises to 1073K.

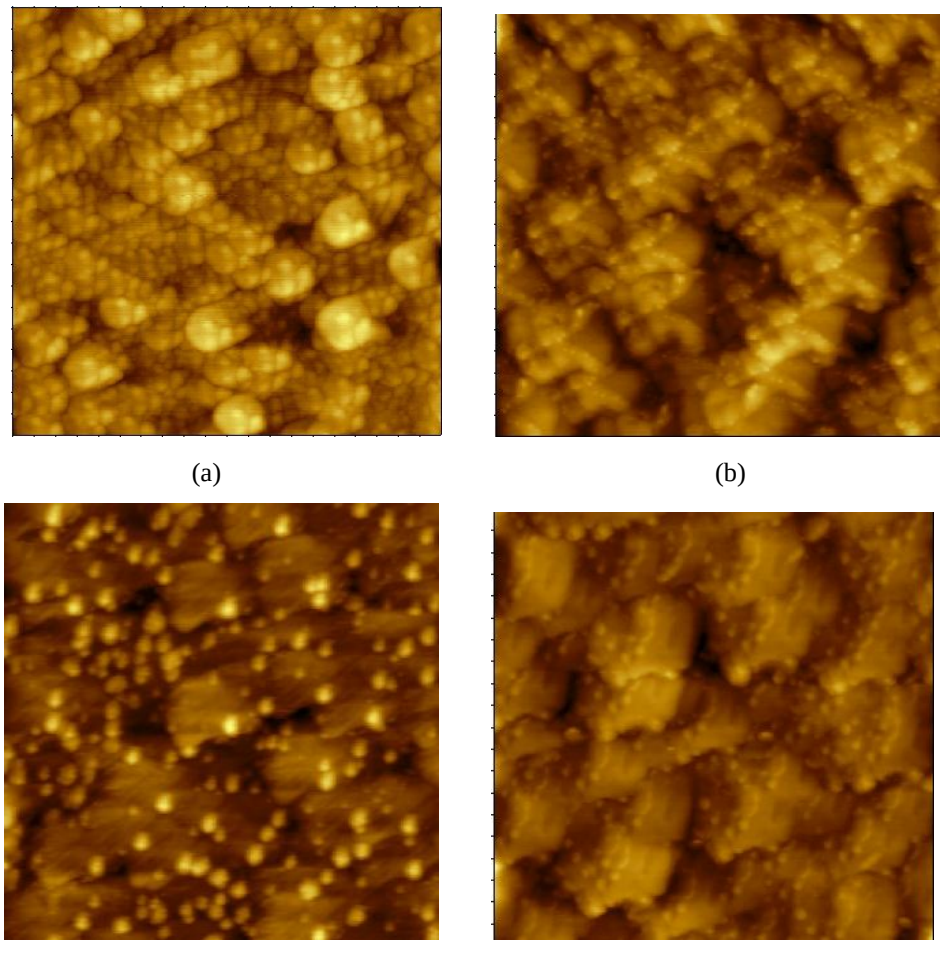

Fig. 2. The surface morphology of Ni-Mn-Ga thin films after annealed at different temperatures (a) 773 (b) 873K (c) 973K (d) 1073K.

Fig. 3 shows the X-ray diffraction patterns (XRD) of Ni-Mn-Ga thin films at room temperature in the range from 30° to 60°. No obvious sharp peak can be detected when the annealing temperature is 773K, indicating that the sample is amorphous. When the heat treatment temperature rises to 873K and 973K, there are two peaks corresponded to about 43 ° and 47 °. According to the literature [13], the two diffraction peaks corresponding to the diffraction plane, respectively (222) and (400), indicating the film is in the T-type martensitic structure. Since the diffraction peaks are not sharp, we can come to the conclusion that the sample was not fully crystallized yet. The most intense diffraction peaks appeared at 1073K, indicating the sample has been completely crystallized. It can be seen that the level of heat treatment temperature affect the crystallization of the sample, except the structure.

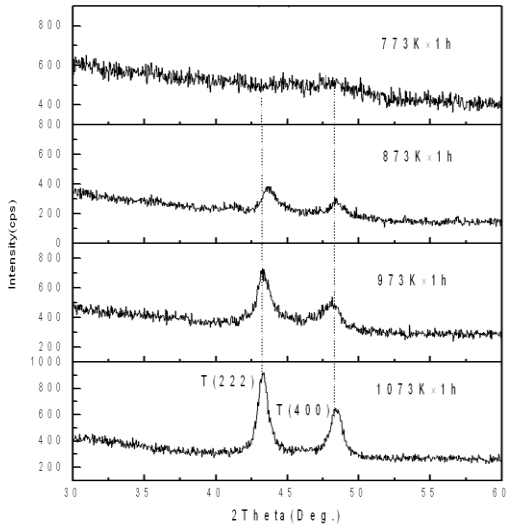

Fig. 3. XRD analysis of Ni-Mn-Ga thin films after annealed at different temperatures.

Fig. 4 shows the magnetization-temperature cures of the Ni-Mn-Ga thin films with different thicknesses. The test temperature ranged from 50K to 400K, and the external magnetic field under 100 Oe (8kA/m) parallels to the membrane surface in the performance testing process. We can find that all the samples show a transition with the decreasing of the temperature. There is no obvious phase changes in below room temperature, which indicates the films are the same type of martensitic structure. The results show that the Curie temperature does not increase with increasing of the film thickness and it achieves the maximum value (355 K) when the film thickness is 1.2 μm. As we know, The Curie temperature can be expressed as:

$$T_c = \frac{2ZA}{3k_B} S(S+1) \quad (1)$$

Where Z is the number of electrons, A is the exchange integral, S is the electron spin quantum number, and k_B is the Boltzmann constant. The formula indicates that the Curie temperature of ferromagnetic material is proportional to the exchange integral, and it is the macroeconomic performance of the electrostatic exchange interaction in the ferromagnetic materials: the stronger the exchange interaction, the ability of spin-parallel orientation tend to be larger, and more heat would be needed to destroy this effect, and the same as the higher Curie temperature. Curie temperature of the film reflects the level of internal spin exchange interaction between the strength of electronics. From the analysis above, Ni-Mn-Ga film Curie temperature relate to the thickness, 1.2 μm film has the highest Curie temperature compared to the other three films, which means 1.2 μm film has the strongest interaction of internal spin exchange between electrons.

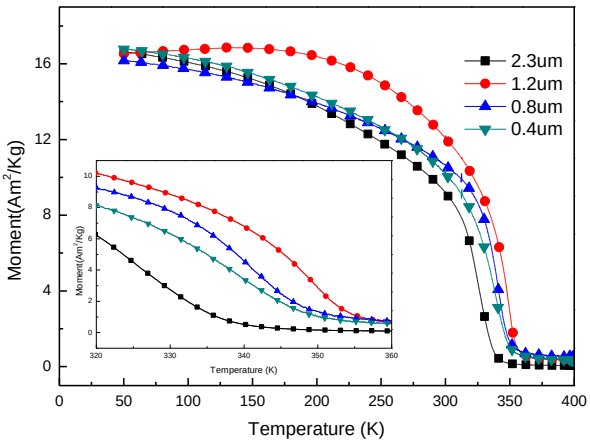

Fig. 4. Magnetization-temperature cures of the Ni-Mn-Ga thin films with different thicknesses.

Fig. 5 shows the Ni-Mn-Ga thin films hysteresis loops at different test temperature. The magnetic field is 800kA/m and the direction is parallel to the membrane surface. It can be found that the hysteresis loops are narrow at a variety of test temperatures and magnetic saturation intensity, remanence and coercivity are reduced with the increases of the test temperature. When the test temperature was 350K, the hysteresis loop was almost a straight line through the origin, indicating that the sample is paramagnetic changed from the low temperature ferromagnetic.

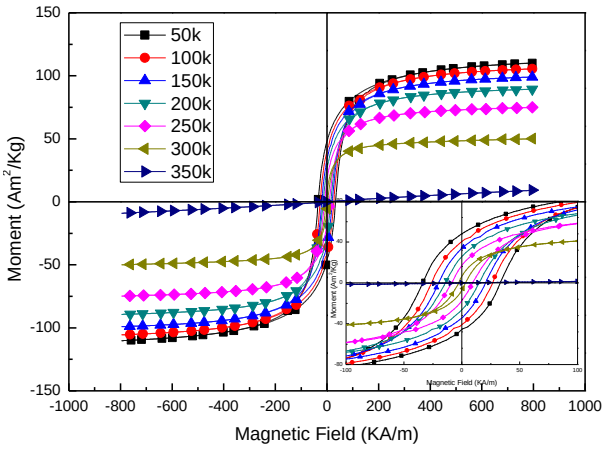

Fig. 5. Effect of testing temperature on magnetization hysteresis loops of the annealed thin film of 1.2 μm at 1073K for 3.6Ks.

Fig. 6 shows magnetic hysteresis loops of Ni-Mn-Ga films of 1.2 μm annealed at 1073K which was measured with the applied field parallel and perpendicular to the film surface (abbreviated as parallel and perpendicular direction below, respectively) at room temperature. According to the figure, the film is ferromagnetic and the coercivity are 50 Oe (4kA/m),in the parallel direction, and 25 Oe(2kA/m), in the perpendicular direction, respectively, indicating that the film is magnetic anisotropy.

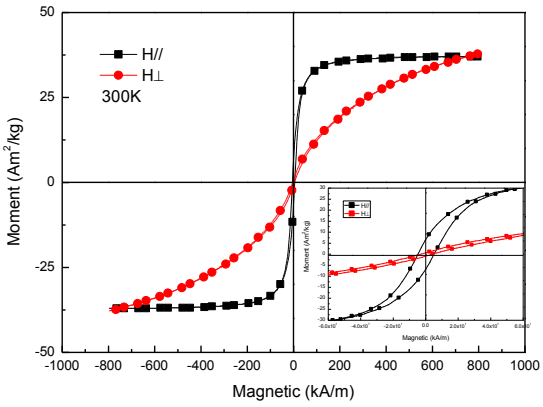

Fig. 6. Magnetization curves along in-plane and out-plane of Ni-Mn-Ga of 1.2 um thin films annealed at 1073K for 3.6Ks at 300K.

4. Conclusion

In conclusion, Ni53.5Mn24.5Ga22 films with different thickness were prepared by RF sputtering, and then annealed at different temperatures. The results indicate that the as deposited films are amorphous, and annealing can improve the degree of crystallization, resulting in T-type martensitic structure. Curie temperature does not increase with the increases of the thickness, and the film with 1.2 μm thickness has the highest Curie temperature due to strongest interaction of internal spin exchange between electrons compare to the 0.4 0.8 2.3 μm thickness films. From magnetic hysteresis loops, it is clear that the films after annealed at 1073 K is magnetic anisotropy with the easy magnetization axis of this system perpendicular to the film surface.

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