Fabrication of $D_{022}\cdot Mn_3Ge$ Thin Films by Alternate Sputtering Method

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The crystal structure and magnetic properties of $D_{022}\cdot Mn_3Ge$ thin films with a high perpendicular magnetic anisotropy constant ($K_u$) and a low magnetization ($M_s$) were investigated. $D_{022}\cdot Mn_3Ge$ thin films were grown on the single crystal of MgO (100) substrates with Cr buffer layer using alternate sputtering method. The Mn$_3$Ge thin films were prepared as $[Mn_x/Ge_y]$ multilayers ($2.8 \leq x \leq 3.7$) with $1 \leq n \leq 30$. We tried to fabricate $D_{022}\cdot Mn_3Ge$ that shows a high $K_u$ value of over $1.0 \times 10^7$ erg/cm$^3$ and a low $M_s$ value of approximately 100 emu/cm$^3$ by the modulation of composition between Mn layer and Ge layer. As a result, $D_{022}\cdot Mn_3Ge$ thin film with a high perpendicular magnetic anisotropy constant ($K_u \sim 1.0 \times 10^7$ erg/cm$^3$), a low saturation magnetization ($M_s = 119$ emu/cm$^3$) and good squareness from $[Mn_{3.5}/Ge]$ ($T_c = 450^\circ$C, $T_m = 500^\circ$C) multilayered film was obtained. Almost same magnetic properties were observed for the films of at $n = 20, 25$ without post annealing compared with the film annealed at $T_c = 500^\circ$C. It is confirmed that increase of the repetition number $n$ by the alternate sputtering method has a same effect of post annealing at $500^\circ$C.

Keywords: $D_{022}\cdot Mn_3Ge$, perpendicular magnetic anisotropy, coercivity, saturation magnetization, alternate sputtering method

1. Introduction

The magnetic thin films with a high perpendicular magnetic anisotropy (PMA) have been intensively studied in late years. These materials have been expected for the application of next generation hard disc drive (HDD) or spin transfer torque magnetic random access memory (STT-MRAM). Particularly, for the application of the STT-MRAM has much attention from the viewpoint of reduction of energy consumption in electronic devices. STT-MRAM is a non-volatile memory device including magnetic tunnel junctions (MTJs). The MTJ for STT-MRAM has required that a high thermal stability ($\Delta$, a tunnel magnetoresistance (TMR) ratio, and a low critical switching current ($I_C$) from the perspective of the ultra-large memory capacity with low power consumption. In order to realize a gigabit class STT-MRAM, the diameter of memory cells must be less than 20 nm, the uniaxial magnetic anisotropy constant ($K_u$) must be larger than 5.0 $\times 10^6$ erg/cm$^3$ which fulfill the relation of $J = K_u V / k_B T > 60^{2-4}$. A high spin polarization is also very important issue to achieve a high TMR ratio, nearly full spin-polarized magnetic layers of the MTJs have been required[5]. Furthermore, in order to realize the STT-MRAM with lower switching current, it has been required that magnetic materials having a small Gilbert damping constant ($\alpha$) and a low saturation magnetization ($M_s$)[5-4]. However, conventional magnetic materials have not fulfilled these properties, such as perpendicularly magnetized CoFeB thin films[5-10], [Co/Pt]$_n$ and [Co/Pd]$_n$ multilayers[7-10], CoCrPt thin films[11-12], [Co/Ni]$_n$ multilayers[13] and FePt thin films[14].

In recent years, Mn-based intermetallic compounds have been attracted much attention such as $D_{022}\cdot Mn_3Ga$, $D_{022}\cdot Mn_2Ga$, $L_{10}\cdot Mn_2Ga$, $L_{10}\cdot MnAl$ which show the tetragonal crystal structures[15-25], because they demonstrate a high $K_u$, a lower $M_s$, a small $\alpha$. The Mn-Ga binary alloys have tetragonal crystal structures of $L_{10}$ and $D_{022}$, through 1:1-3:1 content ratio of manganese and gallium. The $L_{10}\cdot MnGa$[15] shows ferromagnetism with a low $M_s \sim 600$ emu/cm$^3$[14]. On the other hand, $D_{022}\cdot Mn_3Ga$ and $D_{022}\cdot Mn_2Ga$ are ferrimagnetism with a low $M_s \sim 250-360$ emu/cm$^3$[13-15]. Both of $L_{10}$ and $D_{022}$ crystal structures in Mn-Ga binary alloys show a high $K_u \sim 1.2-2.35 \times 10^7$ erg/cm$^3$[14-15] and a small $\alpha \sim 0.008-0.015$[15] and a relatively high spin polarization ($P \sim 58\%$)[16]. The $L_{10}\cdot MnAl$ has a high $K_u \sim 1.5 \times 10^7$ erg/cm$^3$[17-18], a low $M_s \sim 550$ emu/cm$^3$[19-20], a small $\alpha \sim 0.006$[19-20]. These Mn-based intermetallic compounds have been well known as material of high potential for the STT-MRAM.

In remarkable Mn-based alloys, Mn-Ge binary alloys have been particularly attracted attention compared with other Mn-based compounds alloys. The Mn-Ge binary alloys have tetragonal crystal structure of $D_{022}$, in the case of content ratio of manganese and germanium is approximately 3:1 ($D_{022}\cdot Mn_3Ge$). According to the recent many studies, $D_{022}\cdot Mn_3Ge$ has been predicted that it possess a high $K_u \sim 2.3 \times 10^7$ erg/cm$^3$[17], a low $M_s \sim 180$ emu/cm$^3$, a very small $\alpha \sim 0.0009$[1], a very high $P \sim 100\%$[17], a very large $\Delta$[21]. In other experimental reports, the $D_{022}\cdot Mn_3Ge$ film prepared on Cr buffered MgO (100) single crystal substrate has a high $K_u \sim 1.2 \times 10^7$ erg/cm$^3$[22-24], a low $M_s \sim 120$ emu/cm$^3$[22-24] has been reported. Therefore, it is thought that $D_{022}\cdot Mn_3Ge$ is a very promising magnetic material for STT-MRAM[25].

http://www.jst.go.jp/kentei/2018/07/01/001.html
Fig. 1 XRD patterns and film structures for [Mn/Ge]_{15} multilayered films.
(a) MgO sub. / Cr / [Mn/Ge]_{15} (T_s = 450°C) / Cr
(b) MgO sub. / Cr / [Ge/Mn]_{15} (T_s = 450°C) / Cr
(c) MgO sub. / [Mn/Ge]_{15} (T_s = 450°C) / Cr

In this study, we focused on the preparation technique of alternate sputtering method, which enables superior the control of interface and the content compared with co-sputtering method. In order to achieve a high K_u > 1.0 × 10^6 erg/cm^3 and a low M_r < 120 emu/cm^3, effect of repetition number (n), dependence of Mn content (x) and post annealing in [Mn/Ge]_x multilayered films were investigated.

2. Experimental procedure

All of the [Mn/Ge]_x multilayered films were fabricated on MgO (100) single crystal substrates by alternate sputtering method using an ultra high vacuum magnetron sputtering system. The x was estimated from thickness ratio between Mn layers and Ge layers by using the density of manganese (\\(\rho_{Mn}\)) 7.88 × 10^28 atoms/m^3 and germanium 4.42 × 10^28 atoms/m^3, respectively. The base pressure was below 8.0 × 10^-6 Pa, and the Ar gas pressure was kept at 0.50 Pa during the deposition. The film structure was MgO (100) sub. / Cr buffer layer (5 nm) / [Mn/Ge]_x multilayer (100 nm) / Cr protection layer (10 nm). After cleaning MgO (100) single crystal substrates by thermal processing in the sputtering chamber, the Cr buffer layer was deposited at room temperature on MgO (100) single crystal substrates. Subsequently, to obtain an atomically flat surface, the Cr buffer layer was annealed at 700°C. The [Mn/Ge]_x multilayer was fabricated by alternate sputtering method using a Mn (3N) and a Ge (5N) target with total film thickness of 100 nm. The substrate temperature (T_s) was kept at 450°C during the deposition of [Mn/Ge]_x multilayer. Finally, the Cr protection layer was deposited at room temperature. The analysis of crystal structure for [Mn/Ge]_x films were performed by the X-ray diffraction (XRD). The magnetic properties of [Mn/Ge]_x films were characterized by the super-conductivity quantum interference device (SQUID) in the field up to ±70 kOe at room temperature.

3. Results and discussion

First, to investigate crystal growth of the [Mn/Ge]_{15} multilayered films, three samples which have film structures of (a) MgO (100) sub. / Cr (5 nm) / [Mn/Ge]_{15} (100 nm) / Cr (10 nm), (b) MgO (100) sub. / Cr (5 nm) / [Ge/Mn]_{15} (100 nm) / Cr (10 nm), and (c) MgO (100) sub. / [Mn/Ge]_{15} (100 nm) / Cr (10 nm) were prepared. Fig. 1 shows XRD patterns and film structures of the each multilayered films. In the sample (a) of the [Mn/Ge]_x on the Cr buffered MgO (100) substrate, (002) super-lattice and (004) fundamental diffraction peaks from D_{022}-Mn_{3}Ge were clearly observed. On the other hand, (004) fundamental and (220) diffraction peaks were observed, but (002) super-lattice diffraction peak was not observed in the samples (b) and (c). These results suggest that both Cr buffer and depositing Mn layer first are effective for the formation of ordered D_{022}-Mn_{3}Ge phase. Thus, turn of deposition which Mn layer deposited firstly was adopted afterward.

Fig. 2 shows XRD patterns of the [Mn/Ge]_{15} (T_s = 450°C) multilayered films at various x. In the all [Mn/Ge]_{15} samples with varied x, D_{022}-Mn_{3}Ge (002) super-lattice and (004) fundamental diffraction peaks were clearly observed. It is confirmed that in the condition of x ~ 3.2, intensity of D_{022}-Mn_{3}Ge (002) and (004) diffraction peaks were maximum. In the case of Mn poor at D_{022}-Mn_{3}Ge diagram phase, it is suggesting that D_{022}-Mn_{3}Ge phase was formed because of the occupation of Ge atoms in Mn sites for D_{022}-Mn_{3}Ge crystal structure. Therefore, intensity ratio of D_{022}-Mn_{3}Ge (002) and (004) diffraction peaks was decreased. On the other hand, in the condition of Mn rich, D_{022}-Mn_{3}Ge phase was formed by Mn atom invaded Ge site. In the sample of x = 3.1 ([Mn_{3.1}/Ge]_{15}), most well oriented D_{022}-Mn_{3}Ge single phase structure was obtained. M-H curves of the [Mn/Ge]_x multilayer films were shown in Fig. 3. With increasing x, M_s was decreased. On the other hand, high coercivity H_c = 23.6 kOe was obtained at x = 2.8, however, difference between the M_a and remanent magnetization M_r was very large. These curves indicate the mixture of relatively soft phase and hard phase. From the magnetization curves, the ([Mn_{3.1}/Ge]_{15} multilayered film exhibited highest M_s = 140 emu/cm^3 in this study.

Fig. 4 shows relations among x, c/a and M_s for the [Mn/Ge]_x films. From x = 2.8 to x = 3.1, c/a indicated approximately 1.910. At x = 3.1, the c-axis and the a-axis is estimated to be 7.23 Å and 3.79 Å respectively, and, the M_s showed a value (140 emu/cm^3) that was maximum in this study. And the degree of order S was estimated approximately 0.7 using a following relation.
In the condition of Mn rich content, c/a tended to decrease because the number of Mn atoms with anti-ferromagnetic coupling became large.

Fig. 5 shows XRD patterns of post annealing effect for the [Mn3.5/Ge]15 multilayered films. The peaks intensities were increased. Mixing between Mn and Ge becomes easy. As the results, the in-plane magnetization curve was improved by the post annealing. Peaks of the M-H curve in Fig. 6 (a) nearby zero field were improved by post annealing at 500°C (Fig. 6 (b)). The value of $K_u$ of the [Mn3.5/Ge]15 multilayered films was estimated from perpendicular and in-plane magnetization curves of Fig. 6, which was estimated using the following equation.

$$K_u = \frac{H_{0\text{eff}}M_s}{2} + 2\pi M_s^2$$

(2)

Where $H_{0\text{eff}}$ is anisotropic field estimated by extrapolating the in-plane magnetization curve. In sample of (b), $K_u$ was estimated to approximately $1 \times 10^7$ erg/cm$^3$.

Finally, the efficacy of the repetition number $n$ was investigated for $x = 3.5$. Fig. 7 shows XRD patterns of the [Mn3.3/Ge]$_n$ multilayered films with variation of $n$. The chemical content ratio of Mn was fixed as 3.5. On the conditions that $n$ is more than 5, $D0_{22}$-Mn$_3$Ge (002) super-lattice and (004) fundamental diffraction peaks were observed clearly. Further, it is confirmed that highly ordered $D0_{22}$-Mn$_3$Ge phase was prepared in the [Mn3.3/Ge]$_n$ multilayered films at $n = 15-30$. In this experiment, $n$ was varied within constant total thickness of the film. In other words, deposition thickness at once became thinner with increasing $n$. As a sputtered film thickness becomes thinner at once, it is thought that $D0_{22}$-Mn$_3$Ge become easy to crystallize because internal mixing between Mn and Ge becomes easy. As the results, with increasing $n$, $D0_{22}$-Mn$_3$Ge (002) and (004) direction peaks intensities were increased. $M$-H curves of [Mn3.3/Ge]$_n$ multilayered films were shown in Fig. 8. From magnetic properties, with increasing $n$, $M_s$ was increased, however $H_{c}$ was decreased. And $M_s = 112$
emission was observed on conditions that $n$ is 20 and 25. It is confirmed that almost same thin film can be obtained without annealing by the increase of repetition number $n$. On the other hand, in the case of $n$ is 1: Ge layer was deposited $\sim$ 34 nm after Mn layer was deposited $\sim$ 66 nm on the Cr buffer layer, a high $H_c$ = 38.4 kOe was observed. In the XRD patterns of Fig. 7, $D0_{22}$-Mn$_3$Ge (002) super-lattice diffraction peak intensity was extremely low, however, (004) and (220) diffraction peaks were clearly observed at $n = 1$. It is considered that disordered $D0_{22}$-Mn$_3$Ge structure exist mainly at $n = 1$. Therefore, $M_i$ showed a low value (63 emu/cm$^3$). At $n = 1$, each Mn and Ge sputtered film thickness were too thick to be crystallized for ordered $D0_{22}$-Mn$_3$Ge.

Fig. 9 shows relations among $n$, $c/a$ and $M_i$ for the
Fig. 9 $c/a$ and $M_s$ as function of repetition number $(n)$ for [Mn$_{3.5}$/Ge]$_n$ multilayered films. From $n = 5$ to $n = 25$, $c/a$ indicated approximately 1.9. From the XRD profiles ($n = 5$–25), it is thought that $c/a$ showed same value of bulk because a (002) super-lattice diffraction peak and a (004) fundamental peak appeared and ordered $D0_{22}$ Mn$_3$Ge phase exist mainly. On the other hand, with increase $n$, $M_s$ tended to increase. At $n = 25$, $c$-axis and $a$-axis indicated 7.22 Å and 3.80 Å respectively and because a $c/a$ value showed a value (1.903) at the same level as the bulk value, the $M_s$ showed the value (112 emu/cm$^3$) that was near to the bulk value. At $n = 30$, the $c$-axis indicated 7.23 Å and the $a$-axis indicated 3.81 Å. The $M_s$ was 101 emu/cm$^3$ that was slightly lower than the $M_s$ of $n = 25$ (112 emu/cm$^3$). Because the $M$-$H$ curves in Fig. 6 (b) and Fig. 8 (e), (h) are almost same, and the XRD patterns, the $c/a$ is also almost same to after post annealing at $n = 15, 20$, it is confirmed that increase of $n$ by alternate sputtering method has a same effect of post-annealing at 500°C.

4. Summary

A Cr buffer layer played an important role in epitaxial growth on MgO (100) crystal substrates from fabrication of a [Mn$_{3.5}$/Ge]$_n$ multilayer. Highly oriented $D0_{22}$ Mn$_3$Ge phase was grown on a Cr buffered MgO (100) single substrate by deposition of a Mn layer onto the Cr buffer layer before deposition of a Ge layer. The squareness of magnetization curves for $D0_{22}$ Mn$_3$Ge was improved by post annealing process ($T_a = 500°C$). $D0_{22}$ Mn$_3$Ge that has a high $K_u$ ~ ca. 1.0×10$^7$ erg/cm$^3$, $M_s = 119$ emu/cm$^3$ and good squareness for [Mn$_{3.5}$/Ge]$_n$ ($T_a = 450°C$, $T_a = 500°C$) multilayer film was obtained by using alternate sputtering method, with post annealing. it is confirmed that increase of $n$ by alternate sputtering method has a same effect of post annealing at 500°C.

Acknowledgments

This study was partly supported by Collaborative Research Based on Industrial Demand program from Japan Science and Technology Agency and a Grant-in-Aid for Scientific Research (A).

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Received May 19, 2016; Revised Feb. 15, 2017; Accepted Mar. 27, 2018