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Magnetic and structural properties of antiferromagnetic Mn2VSi alloy films grown at elevated temperatures

Magnetic and structural properties of antiferromagnetic Mn_2VSi alloy films grown at elevated temperatures

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Abstract

80 nm thick polycrystalline Mn_2VSi films have been deposited on silicon substrates with an 18 nm silver seed layer and a 3 nm aluminium capping layer using a sputtering system. The best quality film is obtained for 723 K growth. The Mn_2VSi thin film is verified to be antiferromagnetic, where an exchange bias is found when a 3 nm ferromagnetic CoFe layer has been deposited on the top of the Mn_2VSi layer. The exchange bias is measured to be 34 Oe at 100 K. The blocking and thermal activation temperature (T_{ACT}) of Mn_2VSi is estimated to be below 100 K and within a range between 100 K and 448 K, respectively. These properties can be improved by substituting the constituent atoms with the other elements (*e.g.*, Co and Al), suggesting a potential of Mn_2VSi to be used as an antiferromagnet in a spintronic device.

In 1903, Fritz Heusler found that a Cu_2MnAl alloy exhibited ferromagnetic properties. What is remarkable about this alloy is that neither copper, manganese nor aluminum are in themselves, ferromagnetic [1, 2]. Later, such Heusler alloys were reported to show half-metallic ferromagnetic behavior [3]. There are more than 2500 alloys predicted theoretically. By counting the number of valence electrons of the Heusler alloys, it is possible to predict the magnetic properties of the alloys. Those with 18 (half-Heusler) or 24 (full-Heusler) valence electrons are expected to have zero spin magnetic moment, which may exhibit antiferromagnetic behavior [4]. The magnetic properties of these alloys are strongly dependent on the substrate and the growth conditions [5]. For example, a small degree of substitution of Co or Fe atom for Mn in Mn_2VSi keeps a high degree of spin polarization and the total spin moment in the unit cell of the alloy stays almost half-metallic [6]. The total spin moment decreases by the substitution and the alloy becomes almost an ideal half-metallic compensated ferrimagnet or antiferromagnet which has advantages for realistic spintronic applications. These two magnetic materials can be differentiated as the ferrimagnet shows an intrinsic magnetic moment except in the vicinity of the compensation temperature, while the antiferromagnet does not show an intrinsic moment at elevating temperature.

In this study, polycrystalline Mn_2VSi films were investigated to develop a new antiferromagnetic Heusler alloys. We used a stoichiometric composition and demonstrated an exchange bias induced against a ferromagnetic CoFe layer attached to Mn_2VSi. Our finding proves that the disordered *A*2-phase, which can be crystallised at relatively low temperature, can induce antiferromagnetic behavior, which can be useful for spintronic devices.

Polycrystalline Mn_2VSi samples were prepared on Si (001) and (111) substrates with 3 nm Cr and 15 nm Ag as a seed layer, and was capped by an Al layer [8]. These layers and the Mn_2VSi thin films (25-80 nm thick) with a $Co_{0.6}Fe_{0.4}$ layer (0 or 3 nm thick) were deposited using a PlasmaQuest high target utilization sputtering system (HiTUS). The plasma was generated by a radio frequency (RF) field of 13.56 MHz in an Ar atmosphere of 3×10^{-1} Pa [7]. The plasma was focused onto a sputtering target using bias voltages between 250 V and 990 V. The deposition rate of the Mn_2VSi films is typically 0.07 nm/s.

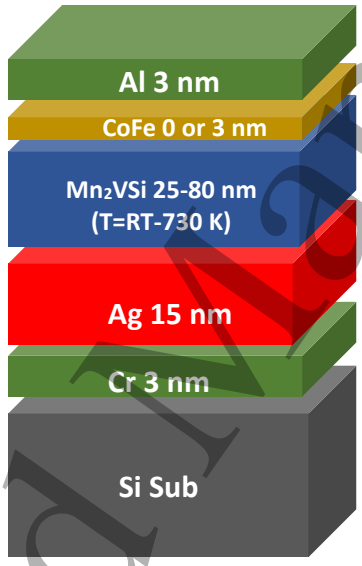

Fig. 1 Schematic diagram of Mn_2VSi films deposited.

During the Mn_2VSi deposition the substrates were heated to the temperatures between 523 K and 923 K. This was achieved by a heater lamp (Philips, Halogen 100 W) installed in the chamber directly above the back of the substrates with a separation of about 7 mm. The power supply (ALDA, Model 00160141) controls the temperature up to about 1000 K. A temperature sensor was placed on the heater housing which was connected to the thermometer. Ceramic rings were used to hold the substrate for thermal insulation to avoid the substrate holders from being melted. The overall performance of the heater was stable with a temperature fluctuation within ±12 K. A set of experiments were carried out to evaluate temperature effects during and after the alloy growth onto the crystallization using vibrating sample magnetometer (VSM, ADE, Model 10) and X-ray diffraction (XRD, Rigaku, SmartLab) with a Cu Kα as main X-ray source for structure analysis.

The θ-2θ XRD scan indicates the variation in the crystallization as shown in Fig. 2. Samples which were sputtered at the higher temperature (723 K) are found to form a significantly stronger $Mn_2VSi(220)$ peak at about 46.1° than those grown at lower temperature (<723 K) [see Fig. 2(a)]. This confirms the formation of the *A*2 phase. In particular, the films grown at 723 K provided the strongest $Mn_2VSi(220)$ Heusler peak, whose full width half maximum (FWHM) is measured to be 0.396° for 80 nm thick case. This is almost a half in FWHM as compared with the other samples, such as those grown at 523 K (FWHM= 1.27°). Several satellite peaks near Si(400) are also seen in the figures due to multi X-rays source (Kα, Kβ) with slightly different wavelengths.

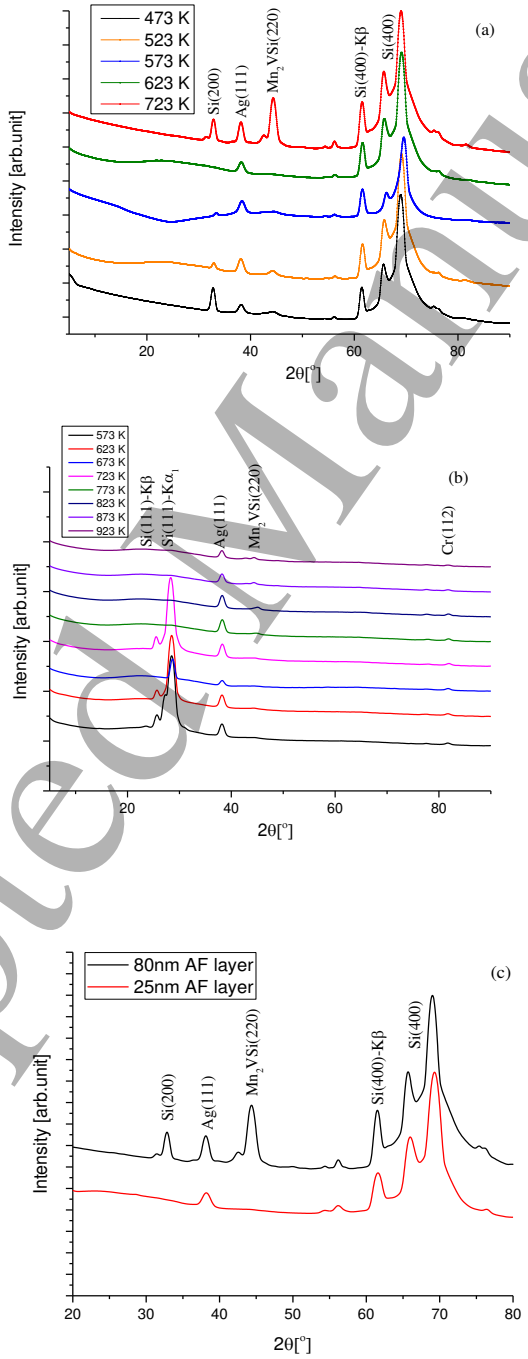

Figure. 2 XRD scans for (a) 80 nm Mn_2VSi samples grown at elevating temperatures, (b) 80 nm Mn_2VSi samples post-annealed at elevating temperatures and (c) different thickness of Mn_2VSi samples grown at 723 K.

Post-annealing was also used to compare with the heated growth method as described above. Here, the samples were grown at room temperature using HiTUS. The sputtered films were then placed into an annealing furnace (Carbolite, MTF 10/25/130, maximum temperature: 1273 K) for post-annealing at elevating temperatures between 573 and 923 K for 3 hours under 8×10^{-5} mbar. The XRD results for the post-annealed samples are shown in Fig. 2(b). The Mn_2VSi(220) peak at about 46.1° is much less significant (FWHM=0.52° for 873 K, for example, as listed in Table. 1) than those for the films grown at high temperature. In Fig. 2(c), a structural comparison is shown between 25 and 80 nm thick Mn_2VSi films. Here, 80 nm-thick Mn_2VSi films show the Mn_2VSi(220) peak, confirming the formation of the *A*2 phase.

Post anneal temperature	723 K	773K	823 K	873 K	923 K
FWHM of Mn_2VSi (220) peak	0.93°	1.80°	0.53°	0.52°	0.46°

Table 1, List of Mn_2VSi(220) peak with different post annealed temperature.

The corresponding X-ray reflectivity (XRR) results are shown in Fig. 3. For the post-annealing films, weak oscillations indicate that interface between layers are rough. This is because during the post-annealing process the whole sample is heated, causing the diffusion at the interface between each layer. The 25 nm thick Mn_2VSi film grown at 723 K shows the smoothest interfaces. By fitting the result, the estimated thicknesses are Cr (2.80 ± 1.80 nm)/Ag (17.23 ± 1.16 nm)/Mn_2VSi (24.00 ± 0.26 nm)/CoFe (3.7 ± 0.18 nm)/Al (2.28 ± 0.20 nm). On the other hand, the 80 nm thick Mn_2VSi film grown at 723 K shows rougher interface. These results indicate that the thinner films minimizes the interfacial diffusion during the deposition. The increased roughness in the 80 nm thick Mn_2VSi films show increase in the corresponding corecivity in the CoFe film to be 200 Oe as compared with 114 Oe for the 25 nm thick Mn_2VSi films. However, this did not affect the exchange bias as the degradation of the antiferromagnetic ordering in the Mn_2VSi film with increasing thickness dominates the magnetic properties. However the thinner samples show less crystallinity (no (220) peak shown at 46.1° for 25 nm) as compared with the thicker layer (FWHM= 0.396° for 80 nm), as shown in Fig. 2(c). This is because the thickness of Mn_2VSi is too thin for the XRD signal to be detected. Therefore, we used the heated growth for magnetic characterization and measured the thickness dependence of their magnetic properties.

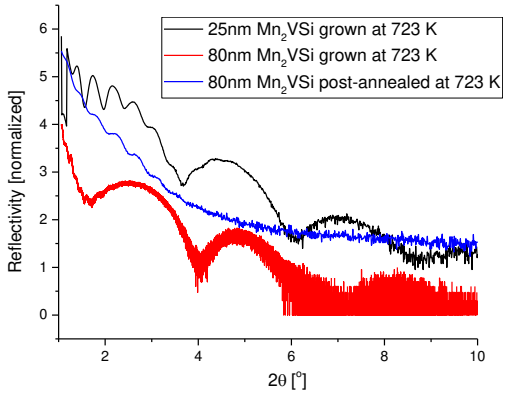

Figure. 3 XRR scans for Mn_2VSi/CoFe films grown at 723 K and post-annealed at 723 K.

In order to verify if the Mn_2VSi thin films are antiferromagnetic, a 3 nm ferromagnetic CoFe layer was deposited on the top of the Mn_2VSi layer. When materials with ferromagnetic (F) ordering and antiferromagnetic (AF) ordering are in close contact and are field-cooled below the Neel temperature (T_N) of the AF, an exchange bias is induced in the F layer. The exchange bias introduces a shift in the hysteresis loop along the field axis, which is in the opposite direction of the setting field. The loops also increase their coercivities H_C with the increase in the thickness of AF layer. It should also be noted that a significant decrease in remanence is observed as the AF layer thickness increases, indicating the thicker AF layer may form rough surface and induces the formation of magnetically dead layer at the Mn_2VSi/CoFe interface. If the measurement is performed at a temperature close to T_N of the AF, the changes in the hysteresis loop become smaller. In Mn_2VSi, we use the setting temperature of 498 K for 30 minutes to make the AF layer paramagnetic. Under an external field of 20 kOe, the spin moments in the CoFe layer are aligned along the direction of the field. The samples with different thicknesses of the Mn_2VSi layer are measured at 100 K. The samples with the 80 nm Mn_2VSi layer are found to induce the largest exchange bias of about 30 Oe, whereas the rest of the samples show their exchange biases of less than 10 Oe (see Fig.4). This indicates that the poor crystallinity of the Mn_2VSi cannot align their spin moments antiferromagnetically and hence cannot induce a large exchange bias. It should be noted that the Mn_2VSi films themselves do not show any magnetic hysteresis within the order of 2 emu/cm^3, confirming that these films are antiferromagnetic.

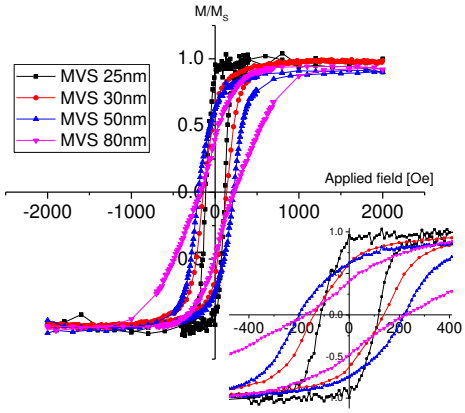

Figure. 4 Hysteresis loops of Mn_2VSi/ CoFe layers with different Mn_2VSi layer thicknesses grown at 723 K.

The activation temperature (T_{ACT}) is also measured to determine the blocking temperature (T_B), where the exchange bias becomes zero. Normally T_B is determined by increasing the activation temperature until the loop shift becomes zero. In polycrystalline systems, individual grains have their own T_B and hence the average T_B is measured using the York Protocol [9]. The samples are uniformly set by thermal activation to the same setting state as described above (498 K for 30 min.) before being cooled to T_{NA} (a temperature at which no thermal activation occurs), thereby removing any magnetic history. By using a saturating magnetic field (20 kOe) at a setting temperature (T_{SET}) that is above the T_N of the AF Mn_2VSi film (estimated to be below 498 K) but below the Curie temperature (T_C) of the F CoFe film (1273 K). A period of 30 min would reverse any activated grains to their original 'set' state. These times also negate any thermal activation that may occur during the temperature rise and fall [9]. The sample is then cooled down to T_{NA}, we have set T_{NA} to be 100 K because this is the lowest temperature VSM can achieve. The magnetization orientation of the F layer is reversed. The sample is then heated for 30 min to the activation temperature T_{ACT}, following by cooling back to T_{NA}. This procedure removes the first loop training effect and measuring at T_{NA} ensures that slow thermal training does not occur. The average exchange bias is measured to be 34 Oe at 100 K as shown in Fig.5. Here, the exchange bias did not go to zero as temperature changes. This result indicates that the blocking temperature is below 100 K. These characteristic temperatures can be engineered by substituting some constituent atoms in Mn_2VSi with the other atoms as similarly demonstrated in ferromagnetic Heusler alloy [10] which would increase the anisotropy of AF layer.

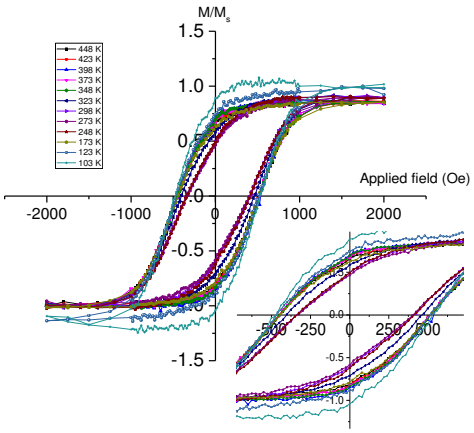

Figure. 5 Blocking temperature measurement for Mn_2VSi/ CoFe bilayers with the thickness of 80 nm.

Conclusion

Mn_2VSi is confirmed to be antiferromagnetic, where the corresponding exchange bias of 34 Oe at 100 K is measured when a 3 nm ferromagnetic CoFe layer is deposited on top of Mn_2VSi layer. The film with 80 nm thick AF layer is found to be optimized for the growth at 723 K. Post-annealed samples provided large surface roughness and causing the diffusion at the interface between each layers, resulting in no exchange bias induced at the Mn_2VSi/CoFe interfaces. The blocking temperature of Mn_2VSi grown at 723 K is estimated to be below 100 K. These magnetic properties can be improved by substituting the constituent atoms with the other elements, suggesting a potential of Mn_2VSi to be used as an antiferromagnet in a spintronic device.

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