High-quality $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterostructures for spin injection in silicon spintronic devices

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Abstract

For high-performance spin injectors in silicon (Si)-based spintronic applications, we have explored the growth technique of quaternary Co-based Heusler-compound $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ on Si(111) by using low-temperature molecular beam epitaxy (LTMBE). In our previous study, Al co-deposition induced an interfacial reaction between $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ and Si. Here, we dramatically improve the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterostructures by introducing a nonstoichiometric LTMBE technique. Atomically smooth $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterointerfaces and $L2_1$ -ordered $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films are simultaneously achieved. Even in as-grown conditions, the magnetic properties of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layers are nearly equivalent to those of the heat-treated ones on MgO reported. This study gives an important knowledge to realize the optimized highly spin-polarized ferromagnet/Si heterointerfaces for next-generation Si-based spintronic devices.

Keywords: Spintronics, Co-based Heusler compound, LTMBE, Nonstoichiometric deposition

1. Introduction

High-quality formation of ferromagnetic materials on a Si platform is desirable to combine spintronic technologies with existing Si ones. In particular, since it is essential for high-performance spintronic devices to fabricate highly spin-polarized materials, half-metallic Co-based Heusler compounds with high Curie temperature have been extensively

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studied as the most promising spintronic materials [1–9]. The crystal structure of ideal Co-based Heusler compounds with the chemical formula Co_2YZ ($L2_1$ -ordered structure, Y: transition metal, Z: main group element) is schematically illustrated in Fig. 1. In general, a highly $L2_1$ -ordered structure is strongly required to obtain half-metallic nature because atomic disorder can sensitively reduce spin polarization [10]. To date, we have also explored low-temperature molecular beam epitaxy (LTMBE) techniques for some Co-based Heusler alloys [11–14] and obtained highly ordered Co_2FeSi films on Si(111) [11, 14].

It is, however, well known that the Fermi level of ternary Co-based Heusler compounds is located near the edge of half-metallic energy gap, leading to the loss of the half-metallic property at finite temperatures [1, 4, 5, 15, 16]. In fact, although very large tunnel magnetoresistance (TMR) ratio was demonstrated for magnetic tunnel junctions using ternary Co-based Heusler compounds at low temperatures, strong temperature-dependent device performance was observed, giving rise to a significant reduction of the TMR ratio with increasing temperature [5]. To overcome this issue, doping a fourth element to the ternary Heusler compounds has been proposed [4, 15, 16]. For example, for $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ ($0 \leq x \leq 1$), the number of the valence electrons can be systematically increased with increasing x . This means that one can intentionally tune the position of the Fermi level toward the center of the half-metallic energy gap [15, 16]. Actually, in magnetic tunnel junctions with quaternary Co-based Heusler alloy $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ (Y = Fe, Z = $\text{Si}_{0.5}$ and $\text{Al}_{0.5}$) electrodes, a relatively small temperature dependence of the TMR ratio and a giant TMR ratio of 220 % at room temperature (RT) were demonstrated [6]. In this context, we should also explore formation of $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ on Si for spin injectors in Si-based spintronic devices.

In our previous work [14], to grow $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ thin films directly on Si(111), we co-deposited Co, Fe, Si, and Al with stoichiometric composition (Co : Fe : Si : Al = 2 : 1 : 0.5 : 0.5) using Knudsen cells, as shown in Fig. 2(a). Unexpectedly, a 4-nm-thick silicidation layer, which can significantly degrade spin injection efficiency, was formed at the heterointerface between $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ and Si(111) [14]. A similar phenomenon can also be confirmed for $\text{Co}_2\text{FeAl}/\text{Si}$ heterostructure [14]. We note that the chemical composition of the $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ layers ($0 < x \leq 1$) deviated from the stoichiometry

despite the stoichiometric LTMBE deposition. Si-rich and Al-poor nonstoichiometric chemical compositions were frequently obtained. From these results, the growth behavior of Co-based Heusler-compounds with Al atoms largely changes unlike that of Co_2FeSi [11]. On the basis of the previous examinations with stoichiometric depositions [14], we infer a possible mechanism of the silicidation reaction at the interface as follows [Fig. 2(a)]. First, the grown $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ alloys tend to form Al-poor layers by taking Si atoms from the substrate since Si atoms can easily occupy D site in the Heusler structure in our LTMBE conditions [14]. Namely, the diffusion of Si atoms from the substrate into the $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ layer is driven to compensate for the lack of Al atoms. As a result, an environment with excess Si atoms is induced in the vicinity of the $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x/\text{Si}$ heterointerface and then the silicidation reaction occurs because Co and Fe have high reactivity with excess Si atoms. It is considered that the silicidation reaction can be stopped at a certain point probably due to the very low growth temperature and the lack of Co and Fe atoms. At this time, the diffusion of the Si atoms from the substrate was blocked by the interfacial layer formed. Finally, the silicidation layer and Al-poor $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ (Co : Fe : Si : Al = 2.12 : 0.96 : 0.62 : 0.34) one are formed on Si. We have not clearly explained the reason why the deviation from the ideal stoichiometry for $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ can occur in our LTMBE conditions. However, we can interpret that deterioration of the quality of $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x/\text{Si}$ heterointerface is caused by the Al-poor nonstoichiometric chemical compositions. If the diffusion of the Si atoms from the substrate can be suppressed, an ideal $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterointerface may be obtained, as illustrated in Fig. 2(b).

In this paper, we utilize a nonstoichiometric deposition technique to form the stoichiometric $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films on Si(111) by means of LTMBE. Suppression of the formation of interfacial silicidation layers and $L2_1$ -ordered $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films on Si(111) are simultaneously achieved. Even in as-grown conditions, the magnetic properties of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layers are nearly equivalent to those of the heat-treated ones on MgO reported. This study shows a technological progress for Si-based spintronic devices with highly spin-polarized spin injectors.

2. Experiments

Prior to loading Si(111) substrates into a molecular beam epitaxy (MBE) chamber, their surfaces were chemically cleaned with an aqueous 1 % HF solution to remove native oxide and contamination [14]. The loaded substrate was heated at 450 °C for 20 min in the MBE chamber, followed by cooling down to the growth temperature (RT $\sim$ 30 °C). Before the growth of the $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ layers, the reflection high-energy electron diffraction (RHEED) pattern of the Si surface exhibited (1 $\times$ 1) structure. This condition is same as Ref. [14]. Subsequently, $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ thin films with a thickness of $\sim$ 25 nm were grown directly on Si(111), where we co-deposited Co, Fe, Si and Al using Knudsen cells. Chemical composition of the grown layers was measured by energy dispersive x-ray spectroscopy (EDS) with a Hitachi HF-2000 using an accelerating voltage of 200 kV and/or Auger electron spectroscopy (AES) with a JEOL JAMP-9500F using an accelerating voltage of 10 kV. To eliminate the Si signal coming from the Si substrate as possible, we performed EDS analyses under the condition that electron diffraction patterns of the $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ layers did not overlap with those of the Si substrate.

3. Results and Discussion

As a preliminary experiment, we examined the effect of a nonstoichiometric deposition technique on the quality of a ternary-compound, Co_2FeAl . In our previous study [14], since we have known the decrease in the atomic ratio of Al in the stoichiometric deposition conditions, we first tuned only a flux of Al by adjusting the cell temperature. With increasing the Al flux, we clearly observed an increase in the atomic ratio of Al and the atomic ratio of Al to Fe changed from Fe : Al = 1 : 0.4 toward Fe : Al = 1 : 1. We also confirmed that the diffusion of Si atoms from the substrate was markedly suppressed by a nonstoichiometric deposition technique. This indicates that the nonstoichiometric deposition technique acts effectively to achieve stoichiometric Co_2FeAl . However, even if we tuned the Al flux, the Co-rich chemical composition can be frequently formed in $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ systems. Thus, we further explored growth conditions by reducing a flux of Co. Figure 3 displays actual chemical composition ratios of Co-Fe-Al alloys as a function of atomic ratio of Al flux y to Fe (Co : Fe : Al = 1.8 : 1 : y). Even for $y = 1.5$, we

can still see the Al-poor and Co-rich nonstoichiometric chemical composition. However, with increasing y , the chemical composition ratio of Co and Al gradually changes toward the stoichiometry. On the other hand, the chemical composition ratio of Fe keeps almost ideal value fortunately. As a result, for $y = 2.5$, Co_2FeAl films with almost perfect stoichiometry are obtained by using nonstoichiometric deposition techniques. This result implies that the diffusion of the Si atoms from the substrate can be suppressed by supplying excess Al atoms. Accordingly, we applied this technique to the growth of quaternary Co-based Heusler-compound $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ on Si. For the growth of quaternary compounds, we changed only Al flux z with fixing a flux of the other elements, i.e, Co : Fe : Si : Al = 1.8 : 1 : 0.5 : z . By co-evaporating each element with $z = 1$, consequently, we obtained almost perfect stoichiometric $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films on Si. Since in-situ RHEED patterns of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layers clearly exhibited the symmetrical streaks during the growth, two-dimensional epitaxial growth of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layers on Si(111) can be demonstrated even for the nonstoichiometric deposition at RT.

To evaluate the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterointerface, we performed cross-sectional transmission electron microscopy (TEM) observations. The TEM observations were performed with a Hitachi H-9000NAR using an acceleration voltage of 300 kV. Figure 4 shows a TEM image near the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterointerface obtained by nonstoichiometric deposition techniques. Unlike our previous work [14], There is almost no interlayer between $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ and Si and an atomically flat heterointerface is evidently demonstrated. Namely, the interfacial silicidation reaction is markedly suppressed by supplying excess Al atoms from the Knudsen cell, implying the validity of our concept shown in Fig. 2(b). When we look at this TEM image in detail, some pyramidal structures are seen near the interface. This is probably because the diffusion of Si atoms from the substrate still somewhat remained at the initial stage of the growth. However, compared to our previous work [14], we emphasize that the crystallinity of $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterostructure is dramatically improved. The nanobeam electron diffraction (NED) pattern of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layer near the interface was also measured to characterize the ordering of the crystal structure (see the inset of Fig. 4) with a Hitachi HF-2000 using an acceleration voltage of 200 kV. Despite the nonstoichiometric RT growth, we clearly identify the superlattice reflections, $\langle 111 \rangle$ and $\langle 113 \rangle$, caused by

the presence of an $L2_1$ -ordered structure (solid circles), together with superlattice reflections corresponding to the ordered $B2+L2_1$ structures (dotted circles). We emphasize again that the $L2_1$ -ordered structure is crucial to get half-metallic nature in Heusler-compounds. That is, an atomic scale abrupt $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterointerface and $L2_1$ ordering of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layers that can achieve high spin injection efficiency are simultaneously obtained. From the obtained experimental results, we attribute the dramatic improvements of the crystallinity of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterostructure to the nonstoichiometric control of the chemical composition at the early stage of the growth of $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ on Si.

Furthermore, we investigated magnetic properties of the grown $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films by vibrating sample magnetometer (VSM) at 300 K using a physical property measurement system (Quantum Design, Model 6000). Figure 5 shows representative field-dependent magnetization ($M-H$) curve at 300 K for the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layer, where the applied field direction is parallel to the magnetic easy axis in the film plane. A clear ferromagnetic hysteretic curve is observed and the coercive force is a small value of ~ 9 Oe, which is consistent with the characteristics of the highly ordered films on MgO reported [17]. The estimated M_S value is $\sim 4.7 \mu_B/\text{f.u.}$, smaller than the theoretical value of $5.5 \mu_B/\text{f.u.}$ [15, 16]. Although the precise origin of this deviation of the M_S from the ideal value is still unclear, we can speculate that there are some magnetically disorders at the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ interfaces, giving rise to the reduction of M_S [18]. Therefore, as one of the possible methods to enhance the M_S up to the ideal one, it may be an effective way to perform post-growth annealing, leading to the increase in the degree of the structural ordering [7, 13, 17]. It should be noted that, despite the RT grown thin film, the obtained M_S is at least the highest value in as-grown $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ thin-film samples reported so far [17]. This fact means that our LTMBE techniques have large potential to realize half-metallic Co-based Heusler-compound spin injectors in Si-based spintronic devices.

4. Conclusion

We have demonstrated epitaxial growth of quaternary Co-based Heusler-compound $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ films on Si(111) with an atomic scale abrupt interface by using the non-

stoichiometric deposition techniques at room temperature. Even for such a low temperature growth, $L2_1$ -ordered structures and relatively high magnetic moment of the grown $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layer were simultaneously obtained. These results will accelerate the development of Si-based spintronic devices compatible with existing Si technologies.

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Figure Captions

Fig. 1: (Color online) A schematic diagram of the crystal structures for $L2_1$ -ordered Co-based Heusler compounds.

Fig. 2: (Color online) (a) Schematic diagrams of a growth mechanism of $\text{Co}_2\text{FeSi}_{1-x}\text{Al}_x$ films on Si(111) in our conventional deposition method [14]. (b) A concept for the improvement of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterostructure in this study.

Fig. 3: (Color online) Actual chemical composition ratios of Co-Fe-Al alloys, evaluated by AES and/or EDS, as a function of atomic ratio of Al flux y to Fe (Co : Fe : Al = 1.8 : 1 : y).

Fig. 4: (Color online) Cross-sectional TEM image of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ heterostructure fabricated by a nonstoichiometric deposition technique with LTMBE. The inset shows NED pattern for $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}$ layer near the interface. The zone axis is parallel to $[1\bar{1}0]$ directions.

Fig. 5: (Color online) Representative $M - H$ curve of the $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}(111)$ epilayer measured at 300K.

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