Finely Controlled Approaches to Formation of Heusler-Alloy/Semiconductor Heterostructures for Spintronics

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We present recent progress of the low-temperature growth of Heusler-alloy/silicon(Si) or Heusler-alloy/germanium(Ge) heterostructures and of their applications for spintronics. First, a concept of the realization of the low-temperature heteroepitaxy for high-quality Heusler alloy/Si or Heusler alloy/Ge heterostructures is shown. Despite very low-growth temperatures, B2 or L21 ordered full-Heusler alloys are achieved. Next, by applying this concept to the growth of Ge on a Heusler alloy or a Heusler alloy on another Heusler alloy, we can also achieve unusual heterostructures for the possibility of novel spintronics applications. Finally, we demonstrate the pure spin current transport in Cu and Ge using these Heusler-alloy spin injectors and detectors. Our approaches will open new avenues for developing high-performance spintronic applications with Heusler alloys. [doi:10.2320/matertrans.ME201503]

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1. Introduction

In the field of spintronics, ferromagnetic full-Heusler alloys with the chemical formula of X2YZ, where X and Y are transition metals and Z is a main group element such as Si and Ge, are promising materials as half-metallic ferromagnets with a fully spin-polarized (100% spin polarization) density of state at the Fermi level.1–4 In particular, lots of high-performance full-Heusler alloys have already been reported as ferromagnetic electrodes in magnetic tunnel junctions (MTJs),5–7 current-perpendicular-to-plane giant magnetoresistive (CPP-GMR) structures,8–11 and lateral spin valves (LSVs)12–15 for the metal-based spintronics. Recently, highly efficient spin injection and detection in semiconductor layers were explored even for the semiconductor-based spintronics.16–20 That is, it will be essential for future high-performance spintronic applications to integrate these Heusler alloys into device structures.

One of the most important parameters for Heusler alloys is a chemical ordering. To obtain high-performance spintronic devices, one should realize B2 or L21 ordered structures in the full-Heusler alloys.1–4,21,22 In general, the high-temperature annealing was conducted for obtaining B2 or L21 ordered full-Heusler alloys,1–4 and the high tunneling magnetoresistance and CPP-GMR effects were observed for the devices formed above 400°C.6–11 Unfortunately, since the high-temperature annealing is not compatible with the formation of heterostructures consisting of the full-Heusler alloys and semiconductors, the low-temperature formation techniques are required. Although recent theoretical studies suggested that very large CPP-GMR effects can be seen in all-Heusler stacking structures with the electronic band matching,23–26 the influence of some magnetic dead layers and the atomic interdiffusion between Heusler alloys was found in actual Heusler bilayers formed by the sputtering method and the post-growth annealing even at 200°C.27 Here we introduce our recent progress of the developments for the fine control of the formation of heterostructures con-sisting of B2 or L21 ordered Heusler-alloys and Si or Ge. First, a concept of the realization of the low-temperature heteroepitaxy for Heusler alloy/Si or Heusler alloy/Ge heterostructures is shown. Next, by applying this concept to the growth of Ge on a Heusler alloy or a Heusler alloy on another Heusler alloy, we show the achievement of unusual heterostructures for the possibility of novel spintronics applications. Finally, we demonstrate the pure spin current transport in Cu and Ge using these Heusler spin injectors and detectors.

2. Low-Temperature MBE of Heusler-Alloys

A concept of the formation of the finely controlled structures consisting of Heusler alloys and Si or Ge is explained as follows. First of all, we note that the crystal structure of typical full-Heusler alloys is different from that of Si or Ge, as shown in Fig. 1(a). The lattice mismatch between ideally ordered full-Heusler alloys and Si or Ge is less than 4%. Here we find that there is a good atomic-arrangement matching at the (111) plane.28 For example, an L21-ordered X2YZ has a

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Fig. 1 Schematics of (a) crystal structures and (b) atomic-layer stacks of L21-ordered X2YZ and Si or Ge along [111]. The solid lines mean a (111) plane for each Heusler alloy and for Si or Ge.
periodic stacking structure consisting of two X, one Y, and one Z layers along [111], as shown in Fig. 1(b).

In this special condition, we have explored the low-temperature epitaxial growth of some of Heusler alloys, Fe₃Si, Fe₃MnSi, Fe₃,₅Mn₃Si, Co₂FeSi, Co₂FeAl, Co₂Fe₁₋ₓMnₓSi, Co₂MnSi, Co₂FeAl, Co₂FeAl₁₋ₓSiₓ, on Si or Ge. Interestingly, for Fe₃MnSi, the substrate-element dependence of crystallinity is evidently observed at a growth temperature of 200°C. The grown Fe₃MnSi film on Si(111) was almost amorphous although a highly ordered phase was obtained on Ge(111). These results mean that it is important to understand the correlation between the crystallization energy of the Heusler alloys on the Si or Ge(111) surface and the reaction energy of the silicide or germanide compounds.

As an example, Fig. 3 shows a cross-sectional transmission electron microscopy (TEM) image and the nanobeam electron diffraction (NED) pattern of the Co₂FeAl layer grown at room temperature on Si(111). The formation of an atomically smooth Co₂FeAl/Si heterointerface and a B2 ordered structure was simultaneously achieved. For Co₂FeAl, the RHEED pattern showed three-dimensional epitaxial growth, derived from the segregation of Al atoms on the surface of the grown Co₂FeAl films. The Al segregation was due to the nonstoichiometric LT-MBE technique. The magnetic moment of the Co₂FeAl layer was about 4.0 μₜ (Bohr magneton) per unit formula, which was the 90% value of those of the atomic compositions for the Heusler-alloy films were precisely adjusted. For Co₂FeAl and Co₂FeAl₁₋ₓSiₓ, nonstoichiometric LT-MBE techniques were used.

Figure 2 shows some examples of the in-situ reflection high-energy electron diffraction (RHEED) patterns for the each surface of the LT-MBE-grown binary and ternary Heusler-alloy films at growth temperatures below 200°C. After the observation of an atomically smooth surface of Si(111) or Ge(111), we codeposited each element with controlled atomic compositions for the Heusler-alloy films. During the growth, we confirmed different features depending on the combination of materials [see Fig. 2]. For Fe₂Si and Co₂FeSi on Si or Ge, the two-dimensional epitaxial growth was guaranteed, on the other hand, we could not obtain the two-dimensional epitaxial growth for Co₂MnSi and Co₂FeAl on Si or Ge. Interestingly, for Fe₂MnSi, the substrate-element dependence of crystallinity is evidently observed at a growth temperature of 200°C. The grown Fe₂MnSi film on Si(111) was almost amorphous although a highly ordered phase was obtained on Ge(111). These results mean that it is important to understand the correlation between the crystallization energy of the Heusler alloys on the Si or Ge(111) surface and the reaction energy of the silicide or germanide compounds.

The observation of the cross-sectional TEM image revealed that there were mixed phases, amorphous and B2 or L₂₁ ordered ones, in the Co₂MnSi films. Thus, Co₂MnSi has no compatibility for LT-MBE on Si or Ge. Even if we consider the growth of such Heusler alloys on a Heusler alloy, it can be expected that the LT-MBE techniques enable us to achieve highly epitaxial growth because of the satisfaction of the special growth conditions as shown in Fig. 1. Figure 4 displays the tendency of the epitaxial growth of Co₂FeSi or Co₂MnSi on Fe₃Si. The in-situ RHEED patterns also indicate the material dependence as well as the growth on Si or Ge, as shown in Fig. 2. It should be noted that Co₂MnSi has also no compatibility for the LT-MBE on Fe₃Si. In our opinion, Fe in the grown Heusler alloys seems to be a key element for promoting the heteroepitaxy in the special growth conditions. When the low-temperature growth was achieved, the atomic interdiffusion at the interface between one Heusler and another Heusler alloys might be sufficiently suppressed.

Figure 5(a) shows a cross-sectional TEM image of the room-temperature-grown Co₂FeSi/Fe₃Si on Si, together with NED patterns and chemical compositions measured by
nanobeam energy dispersive x-ray spectroscopy (EDX). The TEM image and NBD patterns indicate that the grown bilayer is single crystalline. Also, the chemical composition along [111] is abruptly changed at around 15 nm from the Si substrate: The almost perfectly tuned chemical composition of Fe$_3$Si (Fe : Si = 75 : 25) below ~15 nm and of Co$_2$FeSi (Co : Fe : Si = 50 : 25 : 25) above ~15 nm can be observed. This feature indicates that the LT-MBE enables the controlled chemical composition of each of the layers within a few nanometer thick. Because the chemical compositions were precisely controlled, we can see <111> and <113> superlattice reflections resulting from the presence of DO$_3$-Fe$_3$Si and L2$_1$-Co$_2$FeSi (yellow broken circles), caused by the suppression of the atomic interdiffusion at the interface.

Recently, this technique was expanded to the formation of all epitaxial trilayer structures. A cross-sectional TEM image and other structural characterizations are also shown in Fig. 5(b). By using the FeSi intermediate layer, we demonstrated all epitaxial Fe$_3$Si/FeSi/Co$_2$FeSi. Even for such trilayer structures, the chemical composition was precisely controlled for each of layers. If the Fe-Si composition was precisely controlled, a B2-ordered FeSi layer can be obtained and the Curie temperature of the FeSi intermediate layer can be adjusted to around 30 K. As a result, the magnetization reversal process of these trilayers was controlled with changing temperatures because of the presence of the ferromagnetic-paramagnetic transition in the FeSi layer. This is also evidence for the finely controlled heterostructures consisting of all epitaxial trilayers with Heusler alloys.

3. Growth of Ge on Heusler Alloys

Since the lattice mismatch between one of the Heusler alloys, Fe$_3$Si (~0.565 nm), and Ge (~0.565 nm) is almost zero, the special growth conditions shown in Fig. 1 can also be considered even for the growth of Ge on Fe$_3$Si. Figure 6 shows a concept of the low-temperature growth of the Ge layer on Fe$_3$Si. Using the surface of the Fe$_3$Si/Ge(111) structure, we have explored the epitaxial growth of Ge layers. Although the DO$_3$-ordered structure should have an Fe or a Si atomic layer on the top of the Fe$_3$Si(111) surface, the actual top layer of the grown Fe$_3$Si consists of the mixed layer with Fe and Si atoms because of some structural disorders. However, an atomically smooth surface is guaranteed even for the mixed layer as shown in the middle left in Fig. 6 (disordered surface).

We tried to grow Ge layers (deposition rate: 0.3 nm/min) on the top of the disordered Fe$_3$Si with increasing the growth temperature from 200 to 400°C. As shown in the left picture of Fig. 6, the RHEED pattern during the growth is weakly spotty (see arrows), indicating that the actual top layer of the grown Fe$_3$Si, consisting of the mixed layer with Fe and Si, cannot defend the three-dimensional epitaxial growth of Ge films.

Considering the above data, we suggested an artificially controlled arrangement of the surface atoms on Fe$_3$Si. Since there is a Si atomic layer in the ideal Fe$_3$Si at the (111) plane, we can artificially form a Si(111) atomic layer on the
disordered surface of the grown Fe₃Si(111) by precisely controlling the evaporation of Si atoms. Even if the surface of the Fe₃Si layers is terminated with a few Si atomic layers, the RHEED pattern can still show streaks, as displayed in Fig. 6. Note that there is almost no difference in the RHEED patterns between before and after the Si-termination. We define the atomically smooth surface as the Si-terminated surface. Using the Si-terminated surface, we grew Ge layers on Fe₃Si. Very interestingly, we demonstrated the two-dimensional epitaxial growth of the Ge layer (see the upper center in Fig. 6) even with the same conditions shown in the above experiment. To confirm the effect of the Si-termination, we also investigated the growth for the Fe-terminated surface, where the surface of the Fe₃Si layers was terminated with a few Fe atomic layers. Although the Fe-terminated surface was also atomically flat, we could not demonstrate the two-dimensional epitaxial growth of the Ge layer (see the right RHEED patterns in the upper right panel in Fig. 6). Therefore, we conclude that the Si-termination of the disordered Fe₃Si layers is very important to obtain the high-quality Ge layers on Fe₃Si(111). Because Fe₃Si can be grown on Si(111), the growth of Ge layers on Si(111) with an ultrathin Fe₃Si layer can be achieved.

Using a conventional LT-MBE, we can also grow D₀₂₋₁Fe₃Si layers on the epitaxial Ge layer grown on D₀₂₋₁Fe₃Si by LT-MBE. Figures 7(a) and 7(b) shows cross-sectional TEM images of D₀₂₋₁Fe₃Si/Ge/D₀₂₋₁Fe₃Si grown on Ge(111) and Si(111), respectively. As can bee seen, uniform heterostructures were obtained, and the NED patterns of the epitaxial Ge layer were almost equivalent to that of the Ge substrate (not shown). These are amazing structures from the viewpoints of the crystal growth of Heusler alloys and semiconductors.

We also present magnetic properties of the grown D₀₂₋₁Fe₃Si/Ge/D₀₂₋₁Fe₃Si. Magnetization curves with two-step behavior were reproducibly observed for many samples, and the top Fe₃Si layers showed unexpected large coercivity of ~1.0 mT. Since we have observed unexpected in-plane anisotropy of D₀₂₋₁Fe₃Si layers on Ge, we now speculate that there is an interfacial magnetic anisotropy between the top Fe₃Si layer and the grown Ge epilayer. We will explore the detection of the spin-dependent transport in the vertical Ge-based spin devices.

Recently, we have also demonstrated the growth of the epitaxial Ge layers on C₀₂Fe₃Si which is a highly spin-polarized material. These experimental developments will open a new way for developing vertical spin transistors with Heusler-alloy source and drain.

4. Lateral Spin Valves with Heusler Alloys

Since the high-quality epitaxial Heusler-alloy films were
obtained on Si, Ge, and other Heusler alloys, we can examine electrical spin injection from these Heusler-alloys into non-magnetic materials. Figure 8(a) displays a representative scanning electron microscopy image of an LSV with Co2FeSi spin injector and detector and a Cu wire-shaped channel. The low-damage fabrication processes were developed for the epitaxial Heusler-alloy films in elsewhere.12,13,39,45,52) By using conventional electron-beam lithography and Ar + milling techniques with precisely tuning the etching depth, we patterned wire-shaped Co2FeSi electrodes.12,13) Then, as a typical nonmagnet, the 100-nm-thick Cu strip was fabricated by a conventional lift-off technique, where just the surfaces of the Co2FeSi electrodes were well cleaned by using Ar + milling with a very low accelerating voltage. As a result, we obtained highly transparent Co2FeSi/Cu interfaces (< 0.1 fΩm²).13,39,45) If this cleaning process was omitted, we could not see spin signals in these LSVs. Since the edge regions of the Heusler-alloy electrodes were oxidized in the fabrication processes, we could not also obtain the spin signals via the Heusler-alloy edge regions.

Figure 8(b) shows a room-temperature nonlocal spin-valve signal of a Co2FeSi -Cu- Co2FeSi LSV. The data was obtained from the LSV with a junction size of (~130 × 180 nm²) and a center-to-center distance of ~300 nm. By sweeping external magnetic fields (H), the relative magnetization orientation of the used two wire-shaped Co2FeSi electrodes was controlled because of the different switching fields. Clear hysteretic behavior with different magnetization switching fields is seen. It should be noted that a giant spin signal (ΔRₛ = ΔV/I) of ~18.3 mΩ is obtained, which is the present largest value in our LSVs with Co2FeSi electrodes. Using a simple one-dimensional spin diffusion equation,53,54 we can roughly estimate the spin polarization of the Co2FeSi electrodes. Assuming that the spin diffusion length of Co2FeSi is 3.0 nm and using other experimental values,12,13,39,45,52) we can obtain the spin polarization of 0.66 at room temperature. The room-temperature resistivity of the Co2FeSi electrodes is ~48.6 μΩcm. The correlation between the spin polarization and the resistivity is quantitatively consistent with our previous works.13,52)

Recently, these Heusler alloys also begin to open a new possibility of spin caloritronics,55–59) combining thermoelectric effects with spintronics for the energy harvesting technology. Using Cu-based LSV devices, we have demonstrated a conversion between a heat current and a spin current at Cu/Co2FeSi interfaces.60) The thermally induced spin injection from Co2FeSi into Cu due to the spin-dependent Seebeck effect,57,58) and a heat current generation due to the spin-dependent Peltier effect59) can be detected even in the LSV structures.60) A conversion efficiency between a heat current and a spin current at Cu/Co2FeSi interfaces was relatively large compared to that at Py/Cu interfaces.57) Further exploration of Heusler materials should be needed for the highly efficient heat/spin conversion.

We finally show the electrical spin injection into one of the high-mobility semiconductors, Ge, using the obtained Heusler-alloy/Ge heterostructures.19,61–63) For electrical spin injection and detection in n-Ge, it is very important to understand the Schottky-tunnel contacts consisting of Heusler-alloy/n-Ge interfaces. In general, electrical properties of such interfaces are dominated by the Fermi-level pinning phenomena64–66) and doping conditions.67,68) By carefully tuning these conditions, the LSVs were fabricated, as shown in Fig. 9(a), where an Sb δ-doped layer (~1.0 × 10¹⁴ cm⁻²) was...
inserted between Co$_2$FeSi and n-Ge ($\sim 7.0 \times 10^{17}$ cm$^{-3}$). Nonlocal magnetoresistance curves with hysteretic nature were observed at 200 K by applying in-plane magnetic fields (not shown here). Figure 9(b) shows nonlocal Hanle-effect curves obtained by applying out-of-plane magnetic fields (H$_2$) under parallel and anti-parallel magnetic configurations for the Co$_2$FeSi electrodes. Clear Hanle-type spin precession curves, which are evidence for the generation, manipulation, and detection of pure spin currents in the n-Ge channel, can be seen at 200 K. From a one-dimensional spin drift diffusion model, we can extract spin lifetime ($\sim 550$ ps) and diffusion constant ($\sim 2.2$ cm$^2$/sec) for the n-Ge channel used. The details for another device were described elsewhere. The high-quality Co$_2$FeSi spin generation efficiency of $\sim 0.3$ was achieved by using the Co$_2$FeSi electrodes. Clear Hanle-type spin precession curves obtained by applying out-of-plane magnetic fields (not shown here). Figure 9(b) shows nonlocal Hanle-effect curves with hysteretic nature.

5. Summary

We have shown our recent progress of the formation of Heusler-alloy/Si or Heusler-alloy/Ge heterostructures and of their applications for spintronics. Despite very low-growth temperatures, B$_2$ or L$_2$, ordered full-Heusler alloys were achieved. Even if the growth of Ge on a Heusler alloy or a Heusler alloy on another Heusler alloy is considered, we can achieve unusual heterostructures for the possibility of novel spintronics applications. We have also demonstrated the pure spin current transport in Cu and Ge using these Heusler spin injectors and detectors. Our novel experimental approaches will open new avenues for developing high-performance spintronic applications with Heusler alloys.

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