Axial orientation of molecular-beam-epitaxy-grown Fe₃Si/Ge hybrid structures and its degradation

Yoshihito Maeda and Takafulmi Jonishi
Department of Energy Science and Technology, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Kazumasa Narumi
Advanced Science Research Center, Japan Atomic Energy Agency, Takasaki 370-1292, Japan

Yu-ichiro Ando, Koji Ueda, Mamoru Kumano, Taizoh Sadoh, and Masanobu Miyao
Department of Electronics, Kyushu University, Motooka, Fukuoka 819-0395, Japan

(Received 21 August 2007; accepted 3 October 2007; published online 26 October 2007)

The axial orientation of molecular-beam-epitaxy (MBE)-grown Fe₃Si(111)/Ge(111) hybrid structures was investigated by Rutherford backscattering spectroscopy. We confirmed that during MBE above 300 °C, the interdiffusion of Fe and Ge atoms results in a composition change and the epitaxial growth of FeGe in Fe₃Si. Low-temperature (≤200 °C) MBE can realize fully ordered DO₃–Fe₃Si with highly axial orientation [minimum yield (χₘᵟᵢₙ)=2.2%]. Postannealing above 400 °C results in a composition change and the degradation of axial orientation in the off-stoichiometric Fe₃Si. The significance of stoichiometry with regard to thermal stability and the interfacial quality of Fe₃Si(111)/Ge(111) hybrid structures was also discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2801705]

Ordered DO₃–Fe₃Si has been attracting much attention as a highly spin-polarized ferromagnetic material that can be adapted to a few spin-injection devices. Fe₃Si can be classified as a Heusler alloy and can be expected to have half-metallic properties and a high Curie temperature of 840 K, both of which are advantageous in enhancing spin-injection efficiency. The molecular beam epitaxy (MBE) growth of Fe₃Si on GaAs can be successfully conducted since the lattice constants of GaAs [a=0.5654 nm (Ref. 7)] and Fe₃Si [a=0.565 nm (Refs. 8 and 9)] are almost identical. Moreover, the epitaxial growth of Fe₃Si on Si [a=0.5431 nm], Ge [a=0.5658 nm (Ref. 7)], or SiGe substrates could further enhance its applicability to IV-group-based spin-electronic devices. The epitaxial growth on Si or Ge substrates has been investigated and certain interesting results indicating the strong dependence of this growth on the type of crystal plane were obtained. In the case of both substrates, we have successfully accomplished high-quality MBE growth only on the (111) planes. The dominant factor influencing the epitaxial growth of Fe₃Si on Ge and Si has not yet been investigated in detail; however, we can infer that the differences in the nucleation and two-dimensional growth processes of each crystal plane may affect the quality of epitaxy.

In this study, we report the characterization of epitaxial single-crystal Fe₃Si/Ge(111) hybrid structures synthesized by MBE and discuss the crucial factors for the realization of high-quality epitaxial growth on Ge(111) substrates. Ferromagnetic Fe₃Si layers with off-stoichiometric (Fe₆₀Si₂₀) and stoichiometric (Fe₇₅Si₂₅) compositions, denoted by (4:1)- and (3:1)-Fe₃Si, respectively, were grown on 20-nm-thick Ge buffer layers grown epitaxially on Ge(111) substrates by employing a solid-source MBE process using Fe and Si coevaporation (deposition rates: 0.12–0.16 nm/s for Fe and 0.04 nm/s for Si). The growth temperature (T_G) was controlled at 60–400 °C. Rutherford backscattering spectroscopy (RBS) using 2 MeV-⁴He⁺; random spectra for determining the depth profiles of the concentration and aligned spectra for evaluating the quality of the axial orientation of Fe₃Si along Ge(111) were measured. The depth profiles of Fe and Ge atoms were deduced from the random spectra by using the layer model presented in the SIMNRA code.

Figure 1 shows the Fe-channel random and aligned spectra along the Ge(111) axis for each composition film, which were prepared at the T_G=200 and 300 °C, respectively. In this T_G range, we observed spectrum changes for both films. Figures 2(a) and 2(b) show the changes in the Fe and Ge concentrations near the interface and χₘᵟᵢₙ as a function of

---

4Also at Advanced Science Research Center, Japan Atomic Energy Agency; electronic mail: ymaeda@zenon.energy.kyoto-u.ac.jp
respectively. These indicate that high-quality epitaxial growth can be realized when $\chi_{\text{min}}$ is smaller than 4% at 130 °C and below 200 °C for (4:1)- and (3:1)-Fe$_3$Si, respectively. In the case of stoichiometric (3:1)-Fe$_3$Si grown below 130 °C, we succeeded in realizing highly axial oriented crystal growth for the smallest $\chi_{\text{min}}$ value (2.2%). However, with the increase in $\chi_{\text{min}}$ the Fe concentration decreased and the Ge concentration increased above 200 or 300 °C. We found that this change in concentration due to the interdiffusion between Ge and Fe atoms at the interface strongly induces pronounced degradation in the epitaxial growth with the axial orientation of Fe$_3$Si.

These results reveal the following crucial factors for achieving high-quality epitaxial growth of Fe$_3$Si on Ge: First, the stoichiometry of Fe$_3$Si is a very important factor influencing layer growth. Second, the growth temperature should be lower than 130 °C. For the epitaxial growth of Fe$_3$Si(100)/GaAs(001) hybrid structures, the optimal $T_E$ range providing excellent crystalline and interfacial characteristics was reported to be 150 °C < $T_E$ < 250 °C. For higher $T_E$, the reactions of Fe and/or Si with Ga and/or As were similar to those observed during the epitaxial growth of Fe on GaAs. Spin injection from Fe$_3$Si into GaAs at room temperature was carried out using a 35-nm-thick Fe$_3$Si layer grown on a n-GaAs layer at $T_E$ = 200 °C. At a lower $T_E$ (130 °C), higher quality epitaxial growth of Fe$_3$Si(111) on Ge(111) can be realized, as compared to that on GaAs. The improvement in the quality of epitaxy with the decrease in the $T_E$ can be attributed to the activity of Fe atomic diffusion during MBE growth.

Let us discuss the dependence of epitaxial growth on the stoichiometry of Fe$_3$Si. With regard to typical semiconductor epitaxy, the lattice mismatch between the grown films and substrates should be discussed first. The lattice constant of (4:1)-Fe$_3$Si at 300 K ($a$ = 0.5673 nm) (Ref. 11) is slightly larger than that of (3:1)-Fe$_3$Si ($a$ = 0.5655 nm) 8,12

We can calculate the lattice mismatch ratio $\Delta(T)$ at a given temperature using $a$ = 0.5658 nm at 300 K for Ge (Ref. 7) and their thermal expansion coefficients ($\alpha$). For this calculation, we use the thermal expansion coefficient of $\alpha$ = 12.2 × 10^{-6} °C for bcc iron due to its uncertainty with regard to Fe$_3$Si. The $\Delta(T)$ values for (4:1)-Fe$_3$Si and (3:1)-Fe$_3$Si are +0.27% and −0.5% at 60 °C, +0.28% and −0.03% at 200 °C, and +0.30% and −0.02% at 300 °C, respectively. We observed a very small difference between the $\Delta(T)$ values of off-stoichiometric and stoichiometric Fe$_3$Si. It is unreasonable to hypothesize that such a small difference can lead to the pronounced degradation observed in the case of (4:1)-Fe$_3$Si grown above $T_E$ = 200 °C.

Next, we focus our attention on the composition change due to atomic diffusion and on the formation of Fe–Ge compounds. Binary compounds, such as Fe$_3$Ge, FeGe, and FeGe$_2$ may be formed by the diffusion of Ge atoms from the substrate during the MBE growth.

The growth layers formed at 60 and at 400 °C were investigated by transmission electron microscopy (TEM) and selected area electron diffraction (SAD). Figure 3 shows the high resolution TEM images and SAD patterns. We confirmed that the atomically flat interface was formed at 60 °C; it suggests that no interdiffusion of Fe and Ge atoms through the interface occurred. On the other hand, in the case of growth at 400 °C, a very rough interface due to atomic interdiffusion was observed. The SAD pattern (zone axis [110]) in Fig. 3(a) shows fundamental diffraction (220) and (004) spots for fcc lattice, (002) and (222) spots for ordered B2 structure, and superlattice reflection (111) and (113) spots for the ordered DO$_3$ structure of Fe$_3$Si. The analysis of the SAD pattern (b) of the two structures revealed that the superlattice spots (111) and (113) of the ordered DO$_3$ structure were lost, and that B2-Fe$_3$Si and cubic FeGe (c-FeGe) were assigned. From the concentration deduced from RBS, we can obtain the phase ratio of (B2-Fe$_3$Si):(c-FeGe) = 1:3.

The growth at 400 °C results in the increase in the Ge concentration of the Fe$_3$Si layer, thereby allowing c-FeGe to precipitate in the Fe$_3$Si layer. X-ray diffraction (XRD) also indicated the presence of c-FeGe with highly oriented crystallinity. The SAD pattern shown in Fig. 3(b) reveals the crystallographic relationships between Fe$_3$Si(202) and c-FeGe precipitates: c-FeGe(003)||Fe$_3$Si(222) and c-FeGe[110]||Fe$_3$Si[110]. The large lattice mismatch of $\Delta$ = −4.5% for this epitaxy may be allowed partially. TEM observations (not shown) also revealed a clear phase separation between c-FeGe and B2-Fe$_3$Si. This results in lattice strain, which could be responsible for the degradation of the axial orientation of Fe$_3$Si. This hypothesis was also supported by the fact that $\chi_{\text{min}}$ was 22% in Fig. 2(a).

In order to ensure the applicability of the Fe$_3$Si/Ge hybrid structure to certain spin-injection devices, we need
double or multiheterostructures such as SiGe/Fe₃Si/Ge or [Fe₃Si/Ge,Si,SiGe]ₙ. We need to examine the thermal stability of Fe₃Si epitaxial layers already grown on Ge(111) and the interfacial structures before conducting MBE using Ge, Si, or SiGe on Fe₃Si layers. After postannealing high-quality samples with ε<sub>min</sub>=2.2% –4.0% below the postannealing temperature T<sub>a</sub>=300 °C, very few significant changes were observed in the interdiffusion and ε<sub>min</sub> of the Fe₃Si layers.

Figure 4 shows the random and aligned spectra of RBS after annealing above T<sub>a</sub>=300 °C. Only in the (4:1)-Fe₃Si layer annealed at T<sub>a</sub>=400 °C for 2 h, a pronounced increase in the aligned yield, corresponding to the increase in ε<sub>min</sub>, and an increase in the width of the random RBS spectrum were observed.

Figures 5(a) and 5(b) show the concentration of the Fe₃Si layer and ε<sub>min</sub> as a function of T<sub>a</sub>, respectively. Moreover, in this case, we found that there exists a very clear correlation between the concentration change due to interdiffusion near the interface and the increase in ε<sub>min</sub> (degradation of axial orientation), and that the thermal stability behaviors of the Fe₃Si layers of both the compositions differ significantly. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one. The stoichiometric Fe₃Si layers are more thermally stable than the off-stoichiometric one.

We can conclude that the T<sub>a</sub> should be lower than 130 °C under the present deposition rates. It should be emphasized that the stoichiometry of Fe₃Si layers is very important to realize highly axial orientation and improved thermal stability of the ordered structure. The thermal stability observed in this study might be related to the diffusion activity of Fe atoms in Fe₃Si. It has been reported that in Fe-rich DO₃–Fe₃Si bulk crystals, the excess Fe atoms can diffuse into the Si lattice site. If this scheme is applied to the Fe₃Si layers in MBE growth, the Fe atoms at the Si site might be sufficiently unstable to diffuse actively into the Ge substrate. Hertford et al. investigated electrical conduction of Fe₃Si₋ₓSiₓ and reported the distinct minimum resistivity due to structural ordering around stoichiometric Fe₃Si and the significant increase due to disordering in the off-stoichiometric compositions. This result is important in considering the relationship between stoichiometry and structural ordering, which might be affected by the Fe atom diffusion. However, in order to discuss this further, we need to conduct a detailed investigation on the activity of Fe or Ge atomic diffusion near the growing interface during MBE.

This study was supported by a Grant-in-Aid for Scientific Research on Priority Area No. 18063018 and the Grant No. 17360011 from the MEXT in Japan.

FIG. 5. Concentrations of the Fe and Ge atoms of the silicide layers at the interfaces and ε<sub>min</sub> as a function of postannealing temperature. The annealing time was 2 h.