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Epitaxial growth of Heusler alloy Co_2MnSi/MgO heterostructures on Ge(001) substrates

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We prepared Heusler alloy Co_2MnSi/MgO heterostructures on single-crystal Ge(001) substrates through magnetron sputtering for Co_2MnSi and electron beam evaporation for MgO as a promising candidate for future generation spin-based functional devices. Structural investigations showed that the Co_2MnSi/MgO heterostructure was grown epitaxially on a Ge(001) substrate with extremely smooth and abrupt interfaces and showed the $L2_1$ structure for the Co_2MnSi film. Furthermore, a sufficiently high saturation magnetization (μ_s) value of 5.1 μ_B/f.u. at 10 K, which is close to the theoretically predicted μ_s of 5.0 μ_B/f.u. for half-metallic Co_2MnSi, was obtained for prepared Co_2MnSi films. © *2011 American Institute of Physics*. [doi:10.1063/1.3605675]

There has been growing interest in spintronic devices in which both the charge and spin of the electron are utilized to provide functionalities such as nonvolatility and reconfigurability.[1] In particular, injection of spin-polarized electrons into semiconductor channels and manipulation of the injected spins have been intensively studied recently.[2–4] A Heusler alloy/MgO heterostructure is one of the promising candidates as the spin source in spintronic devices, including magnetic tunnel junctions (MTJs) and spin-based semiconductor devices. This is because of (1) the half-metallic nature predicted theoretically for many Heusler alloys[5–7] and (2) enhanced tunneling spin polarization by coherent tunneling through a single-crystalline MgO(001) tunnel barrier.[8,9] Indeed, high tunnel magnetoresistance ratios of 236% at room temperature (RT) and 1135% at 4.2 K of fully epitaxial Co_2MnSi (CMS)/MgO/Co_2MnSi MTJs have been demonstrated owing to these two characteristics, where the Co_2MnSi thin film was used not only as a lower electrode but also as an upper electrode.[10,11] In addition, a heterostructure consisting of Heusler alloy upper electrode/MgO barrier/semiconductor channel is advantageous for spin injection into the semiconductor channel because of the effectiveness of MgO tunnel barrier insertion to solve the conductivity-mismatch problem between a ferromagnetic electrode and a semiconductor channel.[12] As a next-generation semiconductor channel material for metal-oxide-semiconductor devices, germanium (Ge) has attracted much interest because of the high mobility of electrons and holes in Ge.[13,14] However, previous studies have been restricted to epitaxial growth of Heusler alloy thin films (Fe_2MnSi (Ref. 15) or Co_2MnSi (Ref. 16)) directly on Ge single-crystal substrates and that of ferromagnetic layers on Ge single-crystal substrates via a MgO interlayer only for Fe (Ref. 17) and CoFe.[18] Thus, our purpose in the present study has been to prepare epitaxial Heusler alloy Co_2MnSi films on Ge(001) substrates, via an ultrathin MgO(001) interlayer. Note also that the MgO insertion between a Heusler alloy thin film and a semiconductor provides a barrier against possible interdiffusion between a Heusler alloy thin film and a semiconductor during annealing at about 500 °C.

First, we describe the preparation of the Co_2MnSi/MgO heterostructure. The fabricated layer structure was as follows: (from the upper side) Ru cap (5 nm)/CMS (20 nm)/MgO interlayer (3 nm), grown on a Ge(001) single crystal substrate. Before the Ge(001) substrate was installed in an ultrahigh-vacuum (UHV) chamber, it was oxidized at 500 °C for 1 h and then cleaned with hydrofluoric acid solution. The Ge substrate was then annealed at 650 °C for 1 h in the UHV chamber. All the layers in the heterostructure were successively deposited in the UHV chamber (base pressure of $\sim 6 \times 10^{-8}$ Pa) through the combined use of magnetron sputtering for CMS and electron beam evaporation for MgO. The MgO interlayer was deposited at 125 °C. CMS films were prepared with a Mn-rich composition according to our previous finding that the spin polarization of sputter-deposited CMS films with a Mn-rich composition of $\alpha > 1$ in the $Co_2Mn_\alpha Si$ expression is higher than that of sputter-deposited CMS films with a stoichiometric composition ($\alpha = 1.0$) because of the suppressed Co_{Mn} antisites.[11] The CMS layer was deposited by co-sputtering with a nearly stoichiometric CMS target and a Mn target at RT and successively annealed *in situ* at various temperatures, T_a, ranging from 400 °C to 525 °C. The CMS film composition was determined to be $Co_2Mn_{1.32}Si_{0.88}$, i.e., Mn rich with respect to Co, through inductively coupled plasma optical emission analysis with accuracy of 2%–3% for Co and Mn and 5% for Si.

We investigated the structural properties of the fabricated CMS/MgO/Ge(001) heterostructures through cross-sectional high resolution transmission electron microscope (HRTEM) observations, micro-beam electron diffraction, and *in-situ* reflection high-energy electron diffraction (RHEED) observations. Magnetic properties were investigated using a superconducting quantum interference device magnetometer at 10 K and 300 K. The magnetization (M) versus magnetic field (H) curves measured at both 10 K and 300 K for the n-type Ge(001) substrate showed diamagnetic behavior. Furthermore, we confirmed that the almost linear decrease in M with H in

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the H range over about 3 kOe for CMS/MgO/Ge(001) samples could be ascribed to the diamagnetic contribution from the Ge substrates. Thus, the contribution from the Ge substrate was subtracted by extrapolating the M-H curve in the H range over 3 kOe to $H=0$ to estimate the saturation magnetization for CMS films.

To obtain the saturation magnetization per formula unit (f.u.), μ_s, from that per volume, we had to precisely measure the thickness of CMS films deposited by co-sputtering with a designed thickness of 20 nm. To do this, we performed low-angle x-ray reflectivity measurements. Then the CMS film thickness was determined through the fitting of the experimental low-angle x-ray reflectivity data. The lattice constants in the plane, a, and perpendicular to the plane, c, also had to be determined for the CMS films on MgO/Ge(001) substrates to obtain the μ_s values. However, the x-ray diffraction peaks for CMS and Ge in the prepared CMS/MgO/Ge(001) were not separated because (1) the lattice constant of bulk CMS is equal to that of Ge within about 0.1%, (2) a cube-on-cube crystallographic relationship existed between the CMS layer and the Ge(001) substrate in the prepared CMS/MgO/Ge(001) as described below, and (3) the forbidden Ge diffraction peaks (for example, the Ge(002) and Ge(042) peaks) appeared, probably due to multiple diffraction.[19] On the other hand, if we compare a and c values obtained from the unseparated (002) and (042) diffraction peaks for CMS/MgO/Ge(001) and those obtained for a CMS film on MgO-buffered MgO(001) substrate, the difference is negligible. Thus, we approximated a and c from the values obtained for a CMS film on a MgO-buffered MgO(001) substrate; these films had nominally the same film composition as that of the CMS films used in this study.

Figure 1(a) shows an HRTEM lattice image of a heterostructure consisting of CMS (5 nm)/MgO interlayer (3 nm)/Ge(001) substrate with a co-sputtered $Co_2Mn_{1.32}Si_{0.88}$ film, where the MgO interlayer was deposited at 125 °C and the CMS layer was deposited at RT and successively annealed *in situ* at 500 °C. The electron injection was along the [1-10] direction of the Ge substrate (corresponding to the $[1\text{-}10]_{CMS}$ direction). This image clearly shows that both the MgO interlayer and the CMS layer were grown epitaxially and

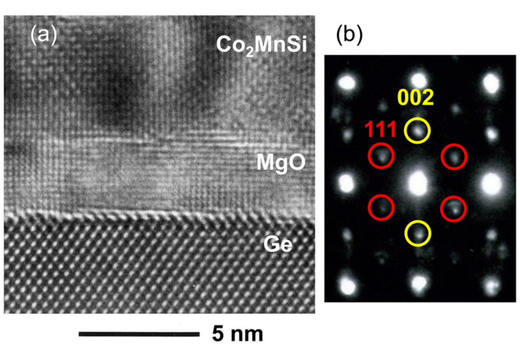

FIG. 1. (Color online) (a) Cross-sectional HRTEM lattice image of a heterostructure consisting of CMS (5 nm)/MgO interlayer (3 nm)/Ge(001) substrate with a co-sputtered $Co_2Mn_{1.32}Si_{0.88}$ film along the [1-10] direction of the Ge substrate (corresponding to the $[1\text{-}10]_{CMS}$ direction), where the CMS film was annealed *in situ* at 500 °C after it was deposited at RT. (b) Electron diffraction pattern for the CMS film (5 nm). The electron beam diameter was 2.5 nm.

were single-crystalline. It also confirmed that extremely smooth and abrupt interfaces were formed. Figure 1(b) shows micro-beam electron diffraction patterns of the CMS film for a beam diameter of 2.5 nm; in these patterns, 111 spots were observed, indicating the $L2_1$ structure for the CMS thin film prepared by co-sputtering. Note that unidentified spots were superimposed onto the Heusler $L2_1$ spots in some regions of the CMS thin film, indicating the coexistence of unidentified materials or structures in addition to the Heusler $L2_1$ structure. This was in agreement with the micro-beam electron diffraction patterns for CMS films grown on MgO-buffered MgO(001) substrates by co-sputtering with a Mn-rich film composition of $Co_2Mn_{1.29}Si_{1.06}$.[11]

We observed streak patterns dependent on the electron injection direction, parallel to $[100]_{Ge}$ or $[110]_{Ge}$, for each successive layer in the CMS/MgO/Ge(001) heterostructure during fabrication through *in-situ* RHEED observations. Furthermore, the spacing of the observed streak patterns of the MgO interlayer agreed well with that of the Ge(001) substrate for both electron injection directions, parallel to $[100]_{Ge}$ and $[110]_{Ge}$, indicating that the MgO interlayer was grown epitaxially on a Ge(001) substrate with a crystallographic relationship of MgO(001)[110]||Ge(001)[100]. The epitaxial relationship of MgO(001)[110]||Ge(001)[100] is as expected from the relatively small lattice mismatch (5.2%) between MgO(001) and Ge(001) on a 45° in-plane rotation. This relationship is consistent with previous work on MgO/Ge(001) heterostructures[17,18] and in contrast to the cube-on-cube epitaxial growth of MgO on GaAs(001)[20,21] and MgO on Si(001)[22] with a 4:3 coincident site lattice.

Similarly, the spacing of the observed streak patterns of the CMS layer agreed well with that of the MgO(001) interlayer for both electron injection directions, parallel to $[100]_{Ge}$ and $[110]_{Ge}$, indicating that the CMS film was also grown epitaxially on a MgO(001) interlayer (3 nm)/Ge(001) substrate with a crystallographic relationship of CMS(001)[100] ||MgO(001)[110]. This crystallographic relationship agreed with that obtained for CMS films epitaxially grown on MgO-buffered MgO(001) substrates.[23] Summarizing the obtained relationship from the *in situ* RHEED observations, we concluded that the crystallographic relationship for the prepared CMS/MgO/Ge(001) heterostructure was CMS(001)[100]||MgO (001)[110]||Ge(001)[100].

Next, we describe the magnetic properties of 20-nm-thick CMS films on MgO(001) interlayer (3 nm)/Ge(001) substrates. Magnetic hysteresis curves for a CMS film with $T_a=500$ °C at 300 K, where H was applied in the plane of the film along the CMS [1-10], [100], and [110] directions, showed that the curves for $[1\text{-}10]_{CMS}$ and $[110]_{CMS}$ were equivalent. However, the coercive force $H_c=5$ Oe for $[100]_{CMS}$ was lower than the $H_c=20$ Oe for $[1\text{-}10]_{CMS}$ and $[110]_{CMS}$. These characteristics of the hysteresis curves show the in-plane cubic magnetic anisotropy with easy axes of $\langle 110\rangle_{CMS}$ and hard axes of $\langle 100\rangle_{CMS}$ for the epitaxial CMS film grown on a Ge(001) substrate via a 3-nm-thick MgO(001) interlayer induced by the cubic crystal symmetry of the single crystalline CMS. Figure 2(a) shows magnetic hysteresis curves for CMS films with various T_a values in the range from 400 to 525 °C up to ±10 kOe at 10 K, where H was applied in the plane of the film along the $[1\text{-}10]_{CMS}$ easy

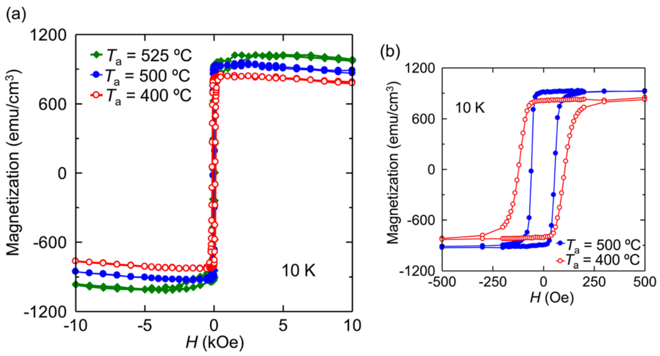

FIG. 2. (Color online) Typical magnetic hysteresis curves for CMS films (20 nm) on MgO interlayer (3 nm)/Ge(001) substrates at 10 K, where H was applied in the plane of the film along the $[1\text{-}10]_{CMS}$ easy axis. (a) Magnetic hysteresis curves for CMS films with various T_a values in the range from 400 to 525 °C up to ±10 kOe. (b) Magnetic hysteresis curves for CMS films with $T_a = 400$ or 500 °C at 10 K up to smaller magnetic fields of ±500 Oe.

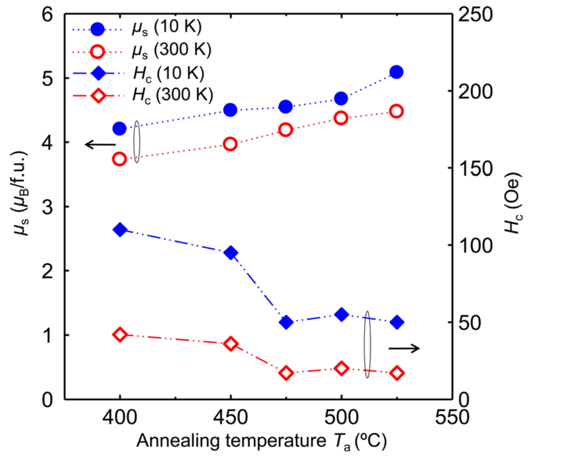

FIG. 3. (Color online) Saturation magnetization per formula unit (μ_s) and coercive force (H_c) for CMS films (20 nm) on MgO(001) interlayer (3 nm)/Ge(001) substrates as a function of T_a at 10 K and 300 K, where H was applied in the plane along the $[1\text{-}10]_{CMS}$ easy axis. The film composition was intentionally Mn-rich $Co_2Mn_{1.32}Si_{0.88}$.

axis. Magnetic hysteresis curves for CMS films with $T_a = 400$ or 500 °C up to smaller magnetic fields of ±500 Oe at 10 K are also shown in Fig. 2(b). With increasing T_a from 400 to 525 °C, the saturation magnetization increased and H_c decreased. Along with the decrease in H_c with increasing T_a, the hysteresis curve became more square-like, as shown in Fig. 2(b).

Figure 3 shows μ_s and H_c for CMS films at 10 K and 300 K as a function of T_a. The μ_s values at 10 K increased with increasing T_a from $\mu_s = 4.2$ μ_B/f.u. for $T_a = 400$ °C up to $\mu_s = 5.1$ μ_B/f.u. for $T_a = 525$ °C (the corresponding values at 300 K increased from $\mu_s = 3.7$ μ_B/f.u. for $T_a = 400$ °C to $\mu_s = 4.5$ μ_B/f.u. for $T_a = 525$ °C). The $\mu_s = 5.1$ μ_B/f.u. at 10 K obtained for 525 °C-annealed CMS films was close to the theoretically predicted μ_s of 5.0 μ_B/f.u. for half-metallic CMS, and in good agreement with the 5.1 μ_B/f.u. for CMS films grown on MgO-buffered MgO(001) substrates with nominally the same film composition. These comparisons indicate that the CMS films prepared on Ge(001) substrates via an ultrathin MgO interlayer possessed sufficiently high μ_s values. The H_c values at 300 K decreased with increasing T_a from $H_c = 42$ Oe for $T_a = 400$ °C to $H_c = 17$ Oe for $T_a = 525$ °C (the corresponding values at 10 K decreased from $H_c = 110$ Oe for $T_a = 400$ °C to 50 Oe for $T_a = 525$ °C). The decrease in H_c with increasing T_a was probably induced by a decrease in the pinning center density for the magnetic domain motion[24] with increasing T_a up to 525 °C.

In summary, we prepared epitaxially grown Heusler alloy Co_2MnSi (CMS) films on Ge(001) substrates via a MgO interlayer. A cross-sectional HRTEM lattice image of the CMS (5 nm)/MgO interlayer (3 nm)/Ge(001) heterostructure showed that both MgO and CMS layers were grown epitaxially and were single-crystalline. It also confirmed that extremely smooth and abrupt interfaces were formed. 111 diffraction spots observed for CMS by micro-beam electron diffraction indicated the $L2_1$ structure for CMS films. Furthermore, sufficiently high saturation magnetization (μ_s) values at 10 K close to the theoretically predicted μ_s for half-metallic CMS were obtained for prepared CMS films. These results confirm that fully epitaxial CMS/MgO/Ge(001) heterostructures offer great potential as a key device structure for efficient spin injection into a semiconductor channel of Ge featuring high mobility.

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[1] S. A. Wolf *et al.*, Science **294**, 1488 (2001).
[2] X. Lou *et al.*, Nat. Phys. **3**, 197 (2007).
[3] O. M. J. van't Erve *et al.*, Appl. Phys. Lett. **91**, 212109 (2007).
[4] S. P. Dash *et al.*, Nature **462**, 491 (2009).
[5] S. Ishida *et al.*, J. Phys. Soc. Jpn. **64**, 2152 (1995).
[6] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **66**, 094421 (2002).
[7] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).
[8] W. H. Butler *et al.*, Phys. Rev. B **63**, 054416 (2001).
[9] J. Mathon and A. Umerski, Phys. Rev. B **63**, 220403(R) (2001).
[10] T. Ishikawa *et al.*, Appl. Phys. Lett. **95**, 232512 (2009).
[11] M. Yamamoto *et al.*, J. Phys.: Condens. Matter **22**, 164212 (2010).
[12] E. I. Rashba, Phys. Rev. B **62**, R16 267 (2000).
[13] M. L. Lee *et al.*, Appl. Phys. Lett. **79**, 3344 (2001).
[14] C. O. Chui *et al.*, IEEE Electron Device Lett. **23**, 473 (2002).
[15] K. Ueda *et al.*, Appl. Phys. Lett. **93**, 112108 (2008).
[16] M. A. I. Nahid *et al.*, Appl. Phys. Lett. **96**, 142501 (2010).
[17] W. Han *et al.*, J. Cryst. Growth **312**, 44 (2009).
[18] K.-R. Jeon, C.-Y. Park, and S.-C. Shin, Cryst. Growth Des. **10**, 1346 (2010).
[19] H. Cole, F. W. Chambers, and H. M. Dunn, Acta Cryst. **15**, 138 (1962).
[20] L. D. Chang *et al.*, Appl. Phys. Lett. **60**, 1753 (1992).
[21] S. Kawagishi *et al.*, J. Appl. Phys. **103**, 07A703 (2008).
[22] G. X. Miao *et al.*, Appl. Phys. Lett. **93**, 142511 (2008).
[23] H. Kijima *et al.*, IEEE Trans. Magn. **42**, 2688 (2006).
[24] E. C. Stoner and E. P. Wohlfarth, Phil. Trans. R. Soc. London, Ser. A **240**, 599 (1948).