

RAPID COMMUNICATIONS

Synthesis of metastable B2-type Fe–Sn alloy epitaxial films and study of their magnetic properties

To cite this article: Yuki Goto et al 2018 Jpn. J. Appl. Phys. 57 120302

View the article online for updates and enhancements.

You may also like

- Electric-field effect on magnetic anisotropy in Pt/Co/Pd/MgO structures deposited on GaAs and Si substrates Yohei Hayashi, Yuki Hibino, Fumihiro Matsukura et al.
- The effect of Al content on the structural, mechanical, and thermal properties of B2-FeAl and D0₉-Fe₃Al from atomistic study Rongcheng Wang, Yongxin Zhao, Zhuxin Li et al.
- <u>A critical comparative review of</u> <u>generalized gradient approximation: the</u> <u>ground state of FeaAl as a test case</u> Monika Všianská, Martin Friák and Mojmír Šob

Synthesis of metastable B2-type Fe–Sn alloy epitaxial films and study of their magnetic properties



Yuki Goto¹, Masato Araki¹, Nozomi Takahashi¹, Takashi Yanase², Toshihiro Shimada², Masahito Tsujikawa^{3,4}, Masafumi Shirai^{3,4,5}, Akira Kamimaki^{6,7}, Satoshi Iihama⁶, Shigemi Mizukami^{4,5,6}, and Taro Nagahama^{2*}

¹Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

⁴Center for Spintronics Research Network (CSRN), Tohoku University, Sendai 980-8577, Japan

⁵Center for Science and Innovation in Spintronics (Core Research Cluster), Tohoku University, Sendai 980-8577, Japan

⁶WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

⁷Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

*E-mail: nagahama@eng.hokudai.ac.jp

Received June 27, 2018; accepted September 12, 2018; published online October 24, 2018

The metastable phases of $Fe_{1-x}Sn_x$ alloys were stabilized by their epitaxial growth on MgO(100). The $Fe_{1-x}Sn_x$ alloys with a body-centered-cubicbased structure were realized in the range of $0 \le x \le 0.4$. For x = 0.25, the B2 structure was observed by transmission electron microscopy and X-ray diffraction analysis, although the hexagonal D0₁₉ structure was a thermodynamically stable phase. With respect to magnetic properties, all the compositions show similar hysteresis curves except for x = 0.25. According to ab initio calculations, D0₃-Fe₃Sn and B2-Fe₃Sn have band structures similar to that of Fe, which results in a large tunnel magnetoresistance by coherent tunneling. © 2018 The Japan Society of Applied Physics

In spintronics, various alloys and intermetallic compound films play important roles in devices. For example, Heusler alloys are used in magnetic tunnel junctions (MTJs) as highly spin-polarized electrodes, with which a tunnel magnetoresistance (TMR) ratio of 1000% has been realized.¹⁻³⁾ L1₀-FePt is used in perpendicular MTJs owing to its large magnetic anisotropy.⁴⁻⁶⁾ Thus, alloys and intermetallic compounds find significant applications in spintronic devices, and the development of such materials is of great importance in this research field. Metastable materials have attracted much attention owing to their useful characteristics.^{7,8)} In particular, thin films have the potential to stabilize the metastable phase through epitaxial growth on single-crystal substrates. In this study, we explore Fe–Sn alloys with metastable crystal structures.

Among the material properties of these alloys, the lattice constant, which can be controlled by epitaxial growth, is the most fundamental parameter in the fabrication of epitaxial films or multilayers. It affects not only the crystal structure but also the physical properties of the films. In MTJs, the lattice constant is an important factor for realizing a large TMR effect, because scattering caused by defects at interfaces results in the degradation of TMR. A typical MTJ, Fe/MgO/Fe, has a lattice mismatch of 3.4% between Fe and MgO. If we resolve the lattice mismatch problem, significant improvements could be expected for TMR.^{9–12}

A simple solution to the aforementioned issue is to control the lattice constant of the tunnel barrier layer. Sukegawa et al. fabricated Fe/MgAl₂O₄/Fe MTJs with a lattice mismatch of -0.2% and improved the bias dependence of TMR ratio significantly.¹³ This study emphasizes the importance of the suppression of interface defects due to a lattice mismatch. Unfortunately, it is difficult to fabricate a MgAl₂O₄ tunnel barrier because it is a complex oxide.

Another approach is to enlarge the lattice constant of Fe electrodes, which could be easier than using the tunnel barrier method. Bonell and coworkers succeeded in expanding the lattice of Fe by alloying it with $V.^{16,17}$ They reported the increase in the TMR ratio of Fe–V/MgO/Fe compared with

that of Fe/MgO/Fe. With respect to intermetallic compounds, Yamada et al. grew Fe₃Si films epitaxially with a D0₃ or B2 structure that was based on the body-centered cubic (bcc) structure¹⁸⁾ as shown in Figs. 1(b) and 1(c). In the D0₃ structure, the Fe and Sn atoms at the body-centered site were perfectly ordered, while the body-centered sites in the B2 structure were occupied by Fe and Sn randomly. The D0₃/B2 crystal structure is critical to realizing coherent tunneling because the electrodes must possess a fourfold symmetry. Unfortunately, the lattice constant of Fe₃Si is smaller than that of MgO (lattice mismatch is 5.97%), and the band structure is not suitable for realizing a giant TMR effect (see Fig. 6).^{9,10)} Fujita et al. observed a TMR of 35% in Fe₃Si/Al₂O₃/FeCo junctions.¹⁹⁾

To expand the lattice constant of the electrodes, we considered that Sn could be a candidate for alloying with Fe because Sn is a group IV element and has a larger atomic radius than Si. Although the hexagonal $D0_{19}$ structure shown in Fig. 1(a) is stable for Fe₃Sn according to the phase diagram,^{14,20} there are few studies on $D0_3$ -type alloys.^{21,22} In this study, we investigated the growth, crystal structure, and magnetic characteristics of an Fe–Sn alloy on a MgO(100) substrate.

The films were grown on MgO(100) substrates by a molecular beam epitaxy method with a base pressure of 7×10^{-8} Pa. The film structures were MgO(100)/Fe_{1-x}Sn_x (30 nm)/ Al₂O₃. Before the deposition, the MgO(100) single-rystal substrates were prebaked at 800 °C for 30 min. Fe and Sn were deposited simultaneously at 100 °C. Their deposition rates were controlled independently. Subsequently, the films were annealed at 300 °C in a vacuum to improve crystallinity, and then an Al₂O₃ layer was deposited at room temperature (RT) to prevent surface oxidation. The epitaxial growth and surface morphology were confirmed by reflection highenergy electron diffraction (RHEED) analysis and atomic force microscopy (AFM), respectively. Crystal structures were investigated by X-ray diffraction (XRD) analysis and scanning transmission electron microscopy (STEM; EFI Titan G2). Magnetization curves were measured using a

²Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

³Research Institute of Electrical Communication (RIEC), Tohoku University, Sendai 980-8577, Japan



Fig. 1. (Color online) Schematics of crystal structures of Fe₃Sn alloys. (a) D0₁₉ structure, (b) D0₃ structure, and (c) B2 structure.^{14,15}



Fig. 2. (Color online) RHEED patterns and AFM images of $Fe_{1-x}Sn_x$. (a, d) x = 0, (b, e) x = 0.25, and (c, f) x = 0.5.

vibrating sample magnetometer (VSM) at RT. The all-optical time-resolved magneto-optical Kerr effect (AO-TRMOKE) with a maximum applied field of 2T and broadband ferromagnetic resonances (FMRs) of 5-15 GHz were measured to evaluate the magnetic Gilbert damping constant.^{23–25)} To estimate the spin polarization, density functional theory (DFT) calculations were performed by the projector augmentedwave method²⁶⁾ using the plane-wave basis set in the Vienna ab initio simulation package (VASP).^{27,28)} The exchangecorrelation potential was treated by the generalized gradient approximation proposed by Perdew et al.²⁹⁾ An energy cutoff of 500 eV was used for the plane-wave expansion. A $12 \times$ 12×12 Monkhorst-Pack k-point grid was used for the sampling of the Brillouin zone.³⁰⁾ To discuss the chemical disorder effect on the electronic structure, we also performed DFT calculation using the Korringa-Kohn-Rostoker (KKR) method³¹⁾ within the coherent potential approximation (CPA)³²⁾ developed by Akai.³³⁾

Figure 2 shows the RHEED patterns and AFM images of the Fe_{1-x}Sn_x (x = 0, 0.25, and 0.5) films. For x = 0, or a pure Fe film, an epitaxial film with a flat surface was obtained as shown in Figs. 2(a) and 2(d). In the case of x = 0.25, which corresponds to Fe₃Sn, a clear streak RHEED pattern with threefold periods was observed in Fig. 2(b), which indicates epitaxial growth and surface reconstruction. A similar threefold RHEED pattern was reported for Fe₃Si



Fig. 3. (a) Cross-sectional STEM image of $Fe_{0.75}Sn_{0.25}$ and (b) electron diffraction pattern.

films, although the surface structure has not been clarified.¹⁹⁾ From the AFM image in Fig. 2(e), the surface roughness was estimated to be 0.17 nm. For x = 0.5, as shown in Figs. 2(c) and 2(f), the RHEED pattern was no longer a streak, and the surface roughness was estimated to be very large (3.9 nm), which implies that the structure of x = 0.5 was polycrystalline.

To investigate the crystal structure, a cross-sectional STEM observation was conducted. In Figs. 3(a) and 3(b), a STEM image of $Fe_{1-x}Sn_x$ (x = 0.25)/MgO and the electron diffraction pattern of the $Fe_{1-x}Sn_x$ layer are shown, respectively. The epitaxial growth of the $Fe_{1-x}Sn_x$ layer on the MgO



Fig. 4. (Color online) (a) $\theta - 2\theta$ profiles for various compositions of $\text{Fe}_{1-x}\text{Sn}_x$ and (b) lattice constants obtained from $\theta - 2\theta$ profiles. The red dot indicates the lattice constant of Fe₃Si and the horizontal line at c = 2.98 is $a_{\text{MgO}}/\sqrt{2}$.



Fig. 5. (Color online) (a) Hysteresis curves for various compositions of $Fe_{1-x}Sn_x$ films. The inset shows M_r/M_s as a function of composition, and (b) hysteresis curves for $Fe_{0.75}Sn_{0.25}$ in the external magnetic field along [100] and [110].

substrate was confirmed. In the electron diffraction results, we observed (111) and (110) peaks, which are not observed in the case of Fe. These results implied that we succeeded in forming an alloy of Sn with Fe while maintaining the bcc structure. We observed no peculiar peaks for the $D0_3$ structure, i.e., (311). Hence, it was concluded that our Fe₃Sn alloy had a B2 structure.

To investigate the composition dependence of the crystal structure, we performed XRD measurements for various x values. In Fig. 4(a), θ -2 θ profiles are shown for various compositions. For x = 0, we observed only a (002) peak for the Fe layer. The lattice constant of Fe was estimated to be 0.284 nm. This is slightly smaller than the bulk value of 0.288 nm, which could be attributed to the epitaxial growth on the MgO substrate. The (002) peak positions shifted to a low 2θ by increasing the composition of Sn. There was clear evidence of the alloy formation of Sn with a larger atomic radius in the Fe. The lattice parameters estimated from the (002) peaks are plotted as a function of x in Fig. 4(b). The lattice parameters increased with increasing Sn composition in accordance with Vegard's law in the range of $0 \le x \le 0.3$. All the lattice constants were larger than those of Fe₃Si. The lattice constant of Fe_{0.75}Sn_{0.25} almost corresponded to $a_{MgO}/\sqrt{2}$. In addition,

for x = 0.25, 0.3, and 0.4, peaks assigned to $\text{Fe}_{1-x}\text{Sn}_x(001)$ were observed in Fig. 4(a), while no (001) peak was observed for x = 0 and 0.1 owing to the extinction rule. From these XRD measurements, we concluded that the $\text{Fe}_{1-x}\text{Sn}_x$ $(0 \le x \le 0.3)$ films fabricated on MgO(001) did not have a D0₁₉ hexagonal structure. The appearance of (001) peaks indicated that Sn atoms occupied the body-centered position selectively in the $\text{Fe}_{1-x}\text{Sn}_x$ lattice. For x = 0.5, the (001) peak was divided into two peaks, thus indicating that the B2 structure was not maintained, which is consistent with the RHEED patterns.

The magnetic characteristics of the alloy depend on its elemental composition and crystal structure. We investigated the magnetic hysteresis curves of $\text{Fe}_{1-x}\text{Sn}_x$ alloys using a VSM for various *x* values, as shown in Fig. 5. All the coercive fields were similar except that at *x* = 0.5, and it was confirmed that the alloy did not show a bcc-type structure. The magnetization decreased with increasing in *x* linearly for 0 < x < 0.3. With respect to the ratio of remnant magnetization (M_r) to saturate magnetization (M_s) , i.e., M_r/M_s , all the films exhibited good squareness, i.e., $M_r/M_s = 1$ except at *x* = 0.25, which corresponds to Fe₃Sn. This indicates that there is a possibility for an intermetallic compound, such as



Fig. 6. (Color online) Electronic states of D0₃-Fe₃Si and D0₃-Fe₃Sn. The top panels show spin-resolved DOS (a), (b) and the bottom panels show band dispersion in the Γ -H direction of (c) Fe₃Si and (d) Fe₃Sn. The red lines are Δ_1 bands.

Fe₃Si or Fe₃Al, to exist at this composition. Figure 5(b) shows the hysteresis loops of Fe_{0.75}Sn_{0.25} in the applied fields along the [100] and [110] directions. The hysteresis loops clearly altered their shapes between the magnetic fields in the [100] and [110] direction. For MgO(100)/Fe₃Si, cubic in-plane magnetic anisotropy was observed.³⁴⁾ We also performed AO-TRMOKE and FMR measurements to estimate the Gilbert damping factor α . The values of α were estimated to be 0.003–0.004. These values are much smaller than that of permalloy 80NiFe (approximately 0.008)³⁵⁾ and are similar to those of Fe₃Si (0.003–0.004).^{36,37)} Such a small α value could be an advantage for spin-transfer-torque magnetization switching.³⁸⁾

In the application of such materials in spintronic devices such as MTJs, spin polarization is the most important property to be considered. In the case of Fe_3Sn with a DO₃ (or B2) structure, a high spin polarization is expected because the crystal structure is similar to that of Heuslar alloys.¹⁸⁾ We conducted an ab initio calculation of D0₃-Fe₃Sn to explore the possibility of a large spin polarization. We use the ab initio calculation package VASP to calculate the electronic states in Fe₃Sn. Figures 6(a) and 6(b) show the density of states (DOS) in Fe₃Si and Fe₃Sn, respectively. Unfortunately, the spin polarization of Fe₃Sn is estimated to have a rather small value of -23%. The characteristic feature of Fig. 6(b) was that the DOS has a negative spin polarization, which enables us to control the sign of the tunnel magnetoresistance effect in diffusive tunneling with an amorphous Al₂O₃ tunnel barrier. Figures 6(c) and 6(d) show the band dispersions of Fe₃Si and Fe₃Sn in the Γ -H direction, which resembles the band dispersion of Fe. The red lines represent the Δ_1 band. Note that the Δ_1 band of Fe₃Sn crosses the Fermi level whereas the Δ_1 band of Fe₃Si is above E_F. Such band features of Fe₃Sn are appropriate for exhibiting coherent tunneling similar to that of $Fe/MgO/Fe;^{9-12}$ therefore, a large TMR ratio is expected for Fe₃Sn/MgO/Fe₃Sn MTJs. As the crystal structure of Fe₃Sn films was estimated as B2, we calculated the band structure, assuming a B2 structure based on the KKR-CPA method. The obtained results were almost the same as those obtained for the DO_3 structure except for the band broadening due to the random positions of the body-centered Fe and Sn atoms.

We fabricated epitaxial films of metastable Fe₃Sn on MgO(001) substrates. From XRD and STEM analyses, the crystal structure of the film was found to be B2, and the lattice constant was found to increase to 2.98 nm. From ab initio calculations, the spin polarization was estimated at -23%, and the Δ_1 band maintains the feature of the Δ_1 band dispersion in Fe. The lattice constant, which is close to $a_{MgO}/\sqrt{2}$, and the Fe-like band structure indicate the potential of Fe₃Sn a highly functional spintronic material. This alloy introduces a new class of Heusler alloys containing Sn.

Acknowledgements We would like to express our gratitude to Professor Uemura's group and Professor Tokeshi's group for their cooperation in the microfabrication, and Professor Masubuchi for the VSM measurements. We would especially like to thank Professor Sakaguchi for his advice and helpful suggestions regarding the STEM observations. This work was partly supported by JSPS KAKENHI Grant Numbers 15H05702, 23686006, and 26103004, the Collaborative Research Program of the Institute for Chemical Research, Kyoto University (Grant 2016-57), the Center for Spintronics Research Network, Tohoku University, and the Open Facility, Hokkaido University Souse Hall and Nanotechnology Collaborative Research in Hokkaido University.

- 1) H. Liu, Y. Honda, T. Taira, K. Matsuda, M. Arita, T. Uemura, and M. Yamamoto, Appl. Phys. Lett. **101**, 132418 (2012).
- S. Trudel, O. Gaier, J. Hamrle, and B. Hillebrands, J. Phys. D 43, 193001 (2010).
- T. Graf, C. Felser, and S. S. Parkin, Prog. Solid State Chem. 39, 1 (2011).
 M. Yoshikawa, E. Kitagawa, T. Nagase, T. Daibou, M. Nagamine, K.
- Nishiyama, T. Kishi, and H. Yoda, IEEE Trans. Magn. 44, 2573 (2008). 5) H. M. Lee, Y. C. Lee, H. H. Chen, L. Horng, J. C. Wu, C. M. Lee, T. H.
- Wu, and G. Chern, SPIN **2**, 1230002 (2012).
- S. Ikeda, H. Sato, M. Yamanouchi, H. Gan, K. Miura, K. Mizunuma, S. Kanai, S. Fukami, F. Matsukura, N. Kasai, and H. Ohno, SPIN 2, 1240003 (2012).
- M. J. Stolt, X. Sigelko, N. Mathur, and S. Jin, Chem. Mater. 30, 1146 (2018).
- 8) N. Saunders and A. P. Miodownik, J. Mater. Sci. 22, 629 (1987).
- 9) W. H. Butler, X. G. Zhang, T. C. Schulthess, and J. M. Maclaren, Phys.
- on the KKR-CPA method. The 10 J. Mathon and A. Umerski, Phys. Rev. B 63, 220403(R) (2001).

- S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and A. Ando, Nat. Mater. 3, 868 (2004).
- 12) S. S. P. Parkin, C. Kaiser, A. Panchula, P. M. Rice, B. Hughes, M. Samant, and S. Yang, Nat. Mater. 3, 862 (2004).
- 13) H. Sukegawa, H. Xiu, T. Ohkubo, T. Furubayashi, T. Niizeki, W. Wang, S. Kasai, S. Mitani, K. Inomata, and H. Hono, Appl. Phys. Lett. 96, 212505 (2010).
- 14) B. C. Sales, B. Saparov, M. A. McGuire, and D. J. Singh, Sci. Rep. 4, 7024 (2014).
- 15) J. Karel, J. Juraszek, J. Minar, C. Bordel, K. H. Stone, Y. N. Zhang, J. Hu, R. Q. Wu, H. Ebert, J. B. Kortright, and F. Hellman, Phys. Rev. B 91, 144402 (2015).
- 16) F. Bonell, S. Andrieu, C. Tiusan, F. Montaigne, E. Snoeck, B. Belhadji, L. Calmels, F. Bertran, P. Le Fevre, and A. Taleb-Ibrahimi, Phys. Rev. B 82, 092405 (2010).
- 17) F. Bonell, S. Andrieu, F. Bertran, P. Lefevre, A. T. Ibrahimi, E. Snoeck, C.-V. Tiusan, and F. Montaigne, IEEE Trans. Magn. 45, 3467 (2009).
- 18) S. Yamada, J. Sagar, S. Honda, L. Lari, G. Takemoto, H. Itoh, A. Hirohata, K. Mibu, H. Miyao, and K. Hamaya, Phys. Rev. B 86, 174406 (2012).
- 19) Y. Fujita, S. Yamada, G. Takemoto, S. Oki, Y. Maeda, M. Miyao, and K. Hamaya, Jpn. J. Appl. Phys. 52, 04CM02 (2013).
- 20) M. Hansen and K. Anderko, Constitution of Binary Alloys (McGraw-Hill, New York, 1958) p. 718.
- 21) C. Bansal, Z. Q. Gao, L. B. Hong, and B. Fultz, J. Appl. Phys. 76, 5961 (1994).
- 22) E. P. Yelsukov, E. V. Voronina, G. N. Konygin, V. A. Barinov, S. K. Godovikov, G. A. Dorofeev, and A. V. Zagainov, J. Magn. Magn. Mater. 166, 334 (1997).

- 23) S. Mizukami, F. Wu, A. Sakuma, J. Walowski, D. Watanabe, T. Kubota, X. Zhang, H. Naganuma, M. Oogane, Y. Ando, and T. Miyazaki, Phys. Rev. Lett. 106, 117201 (2011).
- 24) S. Mizukami, A. Sugihara, S. Iihama, Y. Sasaki, K. Z. Suzuki, and T. Miyazaki, Appl. Phys. Lett. 108, 012404 (2016).
- 25) S. Mizukami, D. Watanabe, M. Oogane, T. Ando, Y. Miura, M. Shirai, and T. Miyazaki, J. Appl. Phys. 105, 07D306 (2009).
- 26) P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
- 27) G. Kresse and J. Hafner, J. Phys.: Condens. Matter 6, 8245 (1994).
- 28) G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
- 29) J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- 30) H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- 31) W. Kohn and N. Rostoker, Phys. Rev. 94, 1111 (1954).
- 32) P. Soven, Phys. Rev. 156, 809 (1967).
 33) H. Akai, J. Phys.: Condens. Matter 1, 8045 (1989).
- 34) Kh. Zakeri, I. Barsukov, N. K. Utochkina, F. M. Römer, J. Lindner, R. Meckenstock, U. von Hörsten, H. Wende, W. Keune, and M. Farle, Phys. Rev. B 76, 214421 (2007).
- 35) S. Mizukami, H. Abe, D. Watanabe, M. Oogane, Y. Ando, and T. Miyazaki, Appl. Phys. Express 1, 121301 (2008).
- 36) Y. Ando, K. Ichiba, S. Yamada, E. Shikoh, T. Shinjo, K. Hamaya, and M. Shiraishi, Phys. Rev. B 88, 140406(R) (2013).
- 37) S. Oki, Y. Sasaki, Y. Kasatani, S. Yamada, S. Mizukami, Y. Nozaki, and K. Hamaya, to be published in J. Phys.: Condens. Matter.
- 38) E. Chen, D. Apalkov, Z. Diao, A. Driskill-Smith, D. Druist, D. Lottis, V. Nikitin, X. Tang, S. Watts, S. Wang, S. A. Wolf, A. W. Ghosh, J. W. Lu, S. J. Poon, M. Stan, W. H. Butler, S. Gupta, C. K. A. Mewes, T. Mewes, and P. B. Visscher, IEEE Trans. Magn. 46, 1873 (2010).