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ARTICLE

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# Giant converse magnetoelectric effect in a multiferroic heterostructure with polycrystalline $\text{Co}_2\text{FeSi}$

Shumpei Fujii<sup>1</sup>, Takamasa Usami<sup>2</sup>, Yu Shiratsuchi<sup>2,3</sup>, Adam M. Kerrigan<sup>4</sup>, Amran Mahfudh Yatmeidhy<sup>5</sup>, Shinya Yamada<sup>1,2</sup>, Takeshi Kanashima<sup>1</sup>, Ryoichi Nakatani<sup>2,3</sup>, Vlado K. Lazarov<sup>4</sup>, Tamio Oguchi<sup>2</sup>, Yoshihiro Gohda<sup>2,5</sup> and Kohei Hamaya<sup>1,2,6</sup>

## Abstract

To overcome a bottleneck in spintronic applications such as those of ultralow-power magnetoresistive random-access memory devices, the electric-field control of magnetization vectors in ferromagnetic electrodes has shown much promise. Here, we show the giant converse magnetoelectric (CME) effect in a multiferroic heterostructure consisting of the ferromagnetic Heusler alloy  $\text{Co}_2\text{FeSi}$  and ferroelectric-oxide  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) for electric-field control of magnetization vectors. Using an in-plane uniaxial magnetic anisotropy of polycrystalline  $\text{Co}_2\text{FeSi}$  film grown on PMN-PT(011), the nonvolatile and repeatable magnetization vector switchings in remanent states are demonstrated. The CME coupling coefficient of the polycrystalline  $\text{Co}_2\text{FeSi}$ /PMN-PT(011) is over  $1.0 \times 10^{-5}$  s/m at room temperature, comparable to those of single-crystalline  $\text{Fe}_{1-x}\text{Ga}_x$ /PMN-PT systems. The giant CME effect has been demonstrated by the strain-induced variation in the magnetic anisotropy energy of  $\text{Co}_2\text{FeSi}$  with an  $L2_1$ -ordered structure. This approach can lead to a new solution to the reduction in the write power in spintronic memory architectures at room temperature.

## Introduction

Switching the magnetization vectors via spin transfer torque using an electric current has been utilized as a method of writing information for next-generation spintronic nonvolatile memories such as magnetoresistive random-access memory (MRAM) devices<sup>1–4</sup>. In general, a high electric current density is required to switch the magnetization vectors of ferromagnetic electrodes in magnetic tunnel junctions (MTJs) during the information writing process, and it is a serious bottleneck in the application of spintronic devices. For this problem, several methods for manipulating magnetization vector via an electric field are

expected to markedly reduce the power consumption<sup>5</sup>. However, there are limitations on the usage environment of ferromagnetic semiconductors<sup>6,7</sup> and ultrathin ferromagnets<sup>8,9</sup> to control and/or change the magnetization vectors. In practical applications, it is very desirable to switch the magnetization vectors by an electric field without using an assist-magnetic field above room temperature.

The realization of these requirements has been the focus of numerous studies on multiferroic materials<sup>10–13</sup>. For robust operation above room temperature and a wide variety of material selections, artificial ferromagnetic (FM)/ferroelectric (FE) multiferroic heterostructures have been explored because of their potential advantages, such as high operation temperatures<sup>14–24</sup>. In particular, when  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$  (PMN-PT) was utilized as an FE material, relatively high magnetostriction through the piezostain and repeatable switching of the remanent magnetization states with a nonvolatile nature were

Correspondence: Kohei Hamaya ([hamaya.kohei.es@osaka-u.ac.jp](mailto:hamaya.kohei.es@osaka-u.ac.jp))

<sup>1</sup>Department of Systems Innovation, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

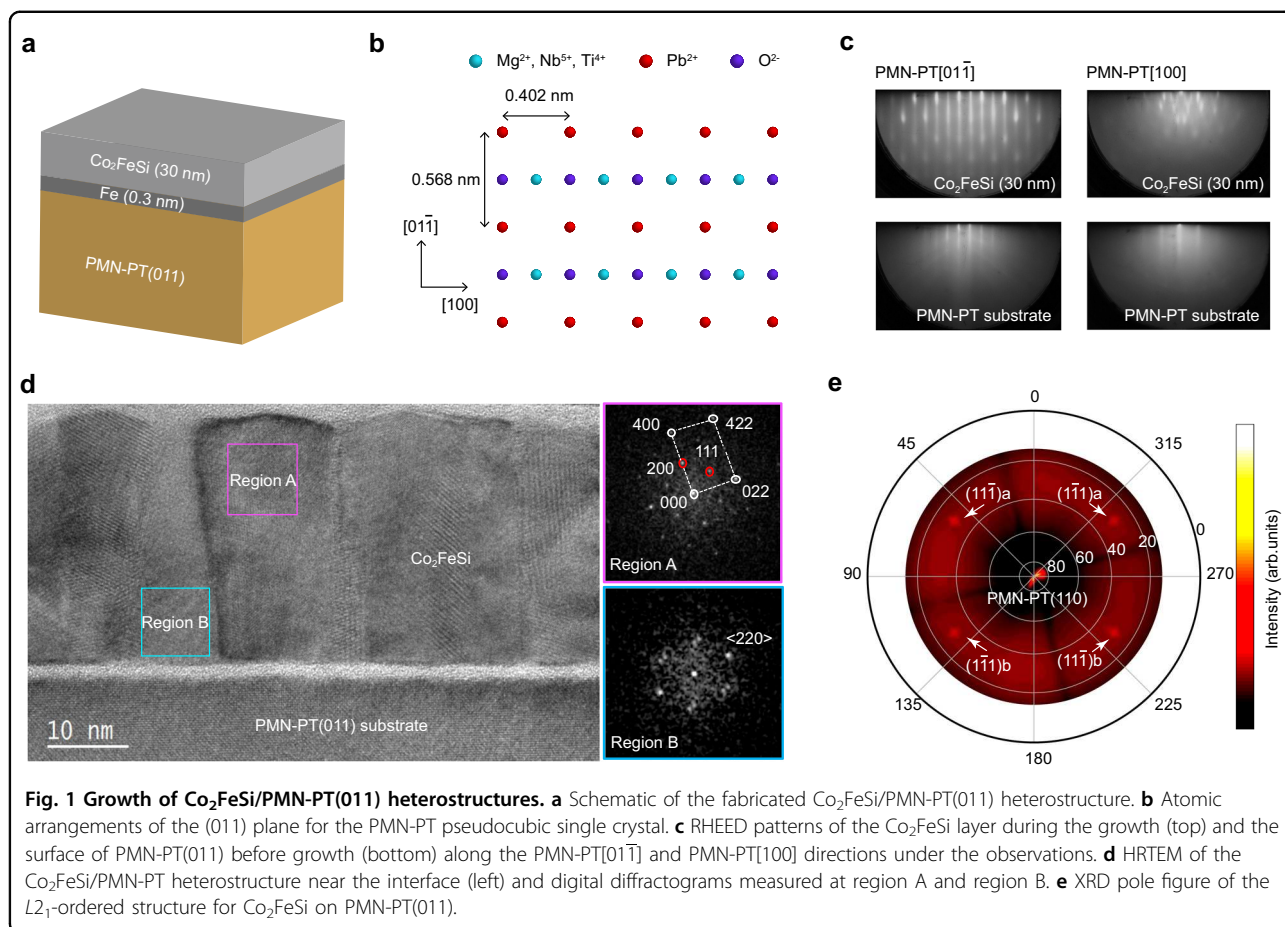
<sup>2</sup>Center for Spintronics Research Network, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

Full list of author information is available at the end of the article

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experimentally observed<sup>25–30</sup>. Recently, nonvolatile switching of the magnetization vector via an electric field was repeatedly demonstrated in MTJs with high magnetoresistance ratios at room temperature<sup>31,32</sup>. By sequentially applying uniaxial stress in FM/PMN-PT systems<sup>33</sup>, complete 180° magnetization reversal of FM on PMN-PT and large magnetoresistance (MR) changes can be performed without using an assist-magnetic field, even for MTJs<sup>32</sup>. The combination of the above technique and giant magnetoelectric (ME) coupling coefficients of more than  $1.0 \times 10^{-5}$  s/m are required for future spintronic logic and memory architectures to efficiently switch the magnetization vectors via an electric field<sup>23–25</sup>.

With respect to the giant ME coupling coefficients of more than  $1.0 \times 10^{-5}$  s/m, single-crystalline  $\text{Fe}_{1-x}\text{Ga}_x$  alloys grown on PMN-PT are promising materials<sup>34,35</sup>, as  $\text{Fe}_{1-x}\text{Ga}_x$  alloys are good magnetostrictive materials for strain sensors, actuators, and energy harvesters<sup>36,37</sup>. However, spin polarization at the Fermi level of  $\text{Fe}_{1-x}\text{Ga}_x$  alloys is less than that of spintronic materials<sup>36</sup>. Thus, high-performance spintronic materials, such as FM half-metals grown on PMN-PT, should be explored to realize magnetization switching with ultralow power consumption<sup>23–25</sup>. Here, we have chosen Co-based Heusler alloys,

since they are expected to be half-metallic materials with high Curie temperatures<sup>38–40</sup>. In this work, we focus particularly on  $\text{Co}_2\text{FeSi}$  as an FM material because the  $L2_1$ -ordered  $\text{Co}_2\text{FeSi}$  has already shown a half-metallic nature<sup>40–42</sup>. We demonstrate giant ME coupling coefficients of more than  $1.0 \times 10^{-5}$  s/m by utilizing high-performance polycrystalline  $\text{Co}_2\text{FeSi}$  films with the  $L2_1$ -ordered structure on PMN-PT(011). The findings in the present study have the potential to overcome the current bottleneck in spintronic devices.

## Results

### Polycrystalline $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$ heterostructures

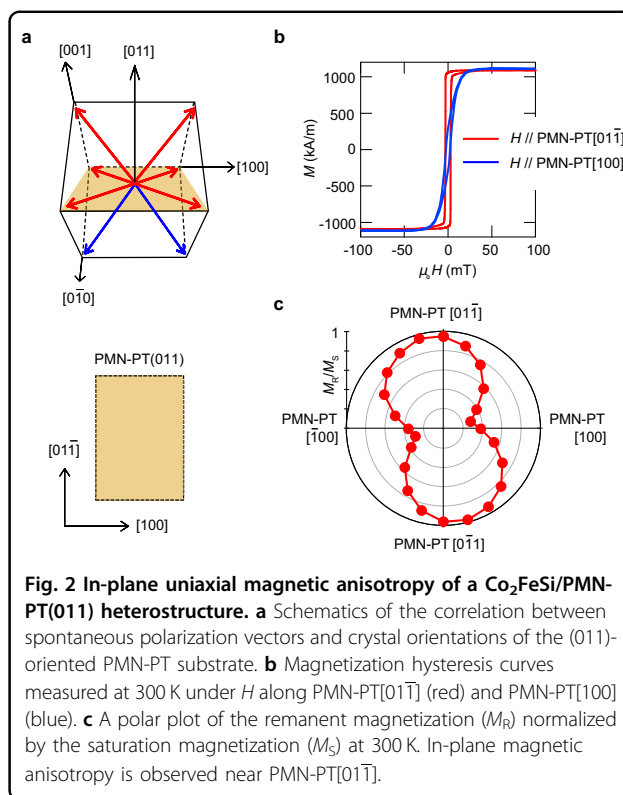
We use an FE rhombohedral PMN-PT pseudocubic substrate with a large piezoelectric constant<sup>43</sup>. Unlike in the previous report on PMN-PT(001)<sup>29</sup>, the PMN-PT(011) single crystal is chosen because there have been many studies on the electric-field control of the magnetization vector<sup>26–28</sup>. The detailed growth procedure of  $\text{Co}_2\text{FeSi}$  films on PMN-PT(011) is described in the Materials and methods.

A schematic of the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure is shown in Fig. 1a, where a 0.3-nm-thick Fe layer is inserted between  $\text{Co}_2\text{FeSi}$  (30 nm) and PMN-PT(011). This layer was added to improve the crystallinity of the

$\text{Co}_2\text{FeSi}$  films, since films with poor structural quality are unlikely to have a substantial converse ME (CME) effect<sup>29</sup>. In Fig. 1b, we present a schematic of the atomic arrangements of a (011) plane for the PMN-PT pseudocubic single crystal. An evident difference in the atomic arrangement between PMN-PT[01 $\bar{1}$ ] and PMN-PT[100] crystallographic directions is expected. Prior to the growth of  $\text{Co}_2\text{FeSi}$  films, we confirm that in situ reflection high-energy electron diffraction (RHEED) patterns indicate two different atomic arrangements of the PMN-PT[01 $\bar{1}$ ] and PMN-PT[100] directions, as shown at the bottom of Fig. 1c. During the growth of the  $\text{Co}_2\text{FeSi}$  layers, we can also find a distinct difference in the RHEED patterns of the  $\text{Co}_2\text{FeSi}$  surface between the PMN-PT[01 $\bar{1}$ ] and PMN-PT[100] azimuths in the top of Fig. 1c. The two different RHEED patterns indicate that the growth mode of the  $\text{Co}_2\text{FeSi}$  layer on the (011) surface of PMN-PT is anisotropic.

Figure 1d is a high-resolution transmission electron microscopy (HRTEM) image from a region at the interface that shows the PMN-PT substrate and the  $\text{Co}_2\text{FeSi}$  film. The HRTEM clearly shows that between the substrate and film, an amorphous layer forms during growth, since the in situ RHEED from the substrate shows a well-ordered crystalline PMN-PT(011) surface. The EDX spectra from the amorphous interface layers (not shown here) showed that the amorphous layer in Fig. 1d is an oxide with little Co, Fe or Si. The grown film is polycrystalline with a grain width of  $13 \pm 4$  nm.  $\text{Co}_2\text{FeSi}$  grains are highly textured; hence, the RHEED patterns indicate epitaxial like film growth. The digital diffractograms from the labeled regions of the grains (Fig. 1d) show the grain orientations and the  $L_{21}$  structure of the  $\text{Co}_2\text{FeSi}$  grains by observing the (111) ordering spots. We also performed nanodiffraction (see Figs. S1 and S2 of Supplementary information<sup>44</sup>) from individual grains that show the preferred grain growth along the [422] and [220] directions, and the results are further confirmed and discussed in the next paragraph.

The structural analysis from the X-ray diffraction (XRD)  $\omega$ - $2\theta$  scan (out-of-plane) for the  $\text{Co}_2\text{FeSi}$ /PMN-PT(011) heterostructure is shown in Fig. S3 of the Supplementary information<sup>44</sup>. Weak diffraction peaks from the (220) and (422) planes were observed in the out-of-plane XRD measurement (Fig. S3a), indicating that the grown  $\text{Co}_2\text{FeSi}$  layer was not a highly oriented structure on PMN-PT(011), consistent with the data shown in Fig. 1d. On the other hand, from the pole figure measurement ( $2\theta = 27.55$  degrees) shown in Fig. 1e, we clearly observed {111} diffraction peaks, indicating the presence of the  $L_{21}$ -ordered structure of  $\text{Co}_2\text{FeSi}$ . These results are consistent with the results observed in the HRTEM image and diffractogram shown in Fig. 1d and the results presented in Figs. S1 and S2 of the Supplementary information<sup>44</sup>. From these structural characterizations, we conclude that the grown  $\text{Co}_2\text{FeSi}$  layer is a textured polycrystalline film on PMN-PT(011), in which

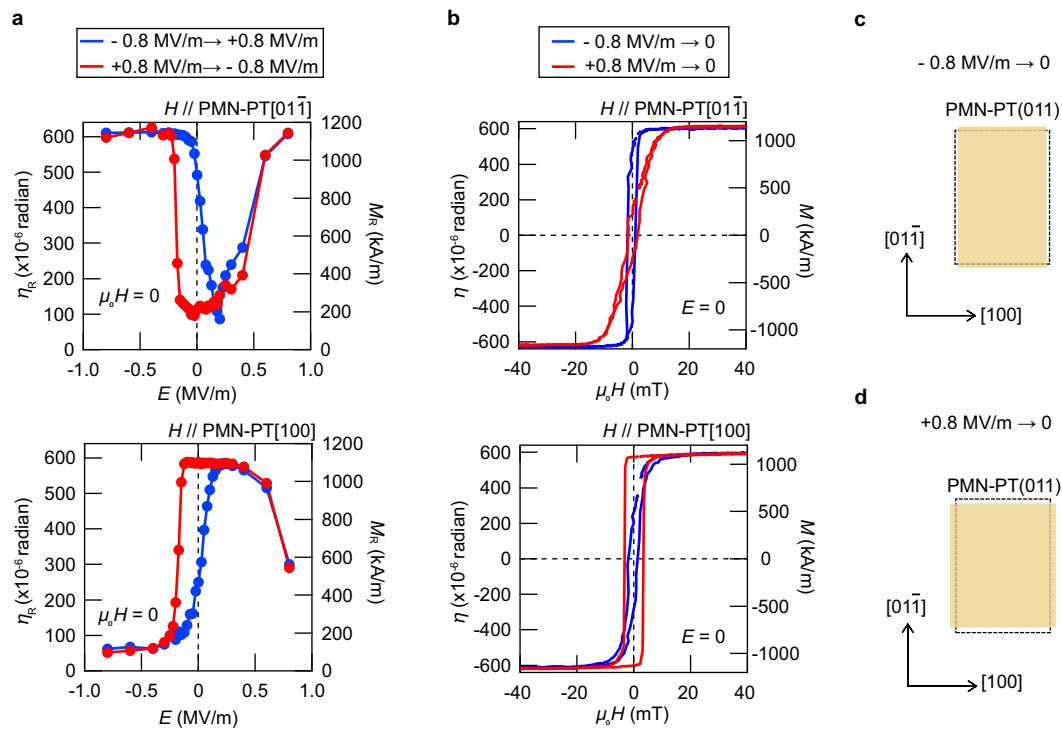


the polycrystalline  $\text{Co}_2\text{FeSi}$  film includes the high spin polarization  $L_{21}$ -ordered structure<sup>40–42</sup>.

### Initial in-plane uniaxial anisotropy

Prior to the investigation of magnetic properties of the  $\text{Co}_2\text{FeSi}$ /PMN-PT(011) heterostructure, we briefly present the well-known unpoled state of the PMN-PT(011) substrate<sup>21</sup>, as schematically shown in Fig. 2a. The spontaneous piezoelectric polarizations of (011) cut PMN-PT lie along the diagonals of the (011) plane and  $01\bar{1}$  plane, as shown in the top section of the figure<sup>21</sup>. In this situation, the (011) plane of the PMN-PT pseudocubic single crystal has a rectangular shape with a long axis along the  $01\bar{1}$  direction, as depicted at the bottom of the figure.

We first measure general magnetic properties of the  $\text{Co}_2\text{FeSi}$ /PMN-PT(011) heterostructure at room temperature. Magnetic-field ( $H$ )-dependent magnetization, measured along the PMN-PT[01 $\bar{1}$ ] and PMN-PT[100] crystallographic directions in the film plane, is presented in Fig. 2b. An anisotropic feature of the magnetization curves is present along the two different crystal axes, where the two different RHEED patterns are observed during the growth in Fig. 1c. Because the value of the saturation magnetization ( $M_s$ ) ( $1090 \pm 30$  kA/m) is nearly the same as that in our previous works on  $\text{Co}_2\text{FeSi}$  films<sup>29,42,45</sup>, we regard the relatively high  $M_s$  value as a consequence of the formation of the  $L_{21}$ -ordered structure. Figure 2c shows a polar plot of the squareness of the



**Fig. 3 Converse magnetoelectric effect.** **a**  $E$ -dependent remanent magnetization measured along PMN-PT[011] and PMN-PT[100] at room temperature. The blue and red plots are the up-sweep and down-sweep data, respectively, within an  $E$  of  $\pm 0.8$  MV/m. **b** Room-temperature magnetization curves measured along PMN-PT[011] and PMN-PT[100] for the two different states at  $E = 0$ . The blue and red curves were measured after  $E$  sweeping from  $-0.8$  MV/m to 0 or from  $+0.8$  MV/m to 0, respectively. **c, d** Lattice deformation of the (011) plane at  $E = 0$  when  $E$  is changed from  $-0.8$  MV/m to 0 and from  $+0.8$  MV/m to 0, respectively, in the presence of the anisotropic piezostain of the (011) plane.

magnetization curves, where the remanent magnetization ( $M_R$ ) is normalized by  $M_S$  in various  $H$  directions in the film plane. In the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure, an evident in-plane uniaxial magnetic anisotropy along the PMN-PT[011] with a small off-axis orientation is induced. These features are reproduced for multiple samples. Since the observed uniaxial anisotropy is almost parallel to the long axis of the rectangular shape of the (011) plane of PMN-PT (the bottom of Fig. 2a), the in-plane uniaxial magnetic anisotropy can be understood by the anisotropic lattice distortion induced from the (011) plane of the PMN-PT substrate. This evidence shows that by utilizing our growth method, as illustrated in Fig. 1, moderate in-plane uniaxial magnetic anisotropy can be induced even in polycrystalline  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures. Because the (011) surface of the pseudo-cubic PMN-PT unit cell is distorted with shear strain along the red polarization vectors<sup>46</sup>, we infer that the small deviation of the uniaxial easy axis from PMN-PT[011] is an intrinsic property of this system.

#### Strain-induced converse magnetoelectric effect

To characterize the electric field ( $E$ ) effect on magnetic properties for the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures,

we perform magneto-optic Kerr ellipticity ( $\eta$ ) measurements at room temperature by applying  $E$ , where  $H$  is applied to the crystallographic direction along PMN-PT[011] or [100] while  $E$  is applied to the PMN-PT[011] direction. Here, as a reference, the reported polarization switching process of a PMN-PT(011) single crystal is described in Fig. S4 of the Supplementary information<sup>44</sup>. Figure 3a shows the plots of the Kerr-ellipticity magnitude in the remanent state ( $\eta_R$ ) as a function of  $E$  at room temperature, in which each point is obtained by measuring  $H$ -dependent Kerr-ellipticity curves along the PMN-PT[011] and PMN-PT[100] direction, as shown in Fig. 3b. Because we can clearly observe the saturation behavior of the Kerr-ellipticity magnitude ( $\eta_S$ ) in Fig. 3b, we can assume that the value of  $\eta_S$   $\{(611 \pm 3) \times 10^{-6}$  radian $\}$  corresponds to the value of  $M_S$  ( $1090 \pm 30$  kA/m) measured in Fig. 2b. On the basis of the assumption, the  $M_R$  values in the right axes in Fig. 3a are determined as  $M_R = M_S (\eta_R/\eta_S)$ .

Both  $\eta_R - E$  curves shown in Fig. 3a indicate the presence of two magnetization states at  $E = 0$ . These features greatly differ from the conventional strain-induced magnetization vector switching processes that can be easily predicted from the polarization switching of PMN-PT(011), as shown in Fig. S4<sup>21</sup>. The appearance of the two magnetization states at



$E=0$  is reproduced in multiple  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures, as shown in Fig. S5a of the Supplementary information<sup>44</sup>. To consider the origin of the two magnetization states at  $E=0$ , we first refer to the general behavior of the lattice deformation of the (011) plane<sup>21</sup> after  $E$  is changed from 0 to  $\pm 0.8$  MV/m and from  $\pm 0.8$  MV/m to 0 in Fig. S4. When the large  $E$  of  $\pm 0.8$  MV/m is applied (Fig. S4b, e), the long axis of the (011) rectangle plane is elongated along  $\text{PMN-PT}[01\bar{1}]$ , and the short axis along  $\text{PMN-PT}[100]$  is simultaneously contracted. In contrast, when  $E$  is increased from  $-0.8$  MV/m to 0 (Fig. S4c), the long axis along  $\text{PMN-PT}[01\bar{1}]$  is contracted, and the short axis along  $\text{PMN-PT}[100]$  is elongated. In this situation ( $E=0$ ), it is generally expected that the strain-induced magnetic easy axis of the  $\text{Co}_2\text{FeSi}$  film is aligned toward the  $\text{PMN-PT}[100]$  direction. However, the data presented in blue in Fig. 3b indicate that the  $\text{PMN-PT}[100]$  and  $\text{PMN-PT}[01\bar{1}]$  axes are magnetic hard and easy axes, respectively, in contrast to the simple expectation described above based on the reported polarization switching of the  $\text{PMN-PT}(011)$  substrate<sup>21</sup>. Thus, we next consider the presence of the anisotropic piezostress at the  $\text{PMN-PT}(011)$  surface, as discussed in previous works on polycrystalline  $\text{Ni}/\text{PMN-PT}(011)$ <sup>16</sup> and amorphous  $\text{CoFeB}/\text{PMN-PT}(011)$ <sup>28</sup> systems.

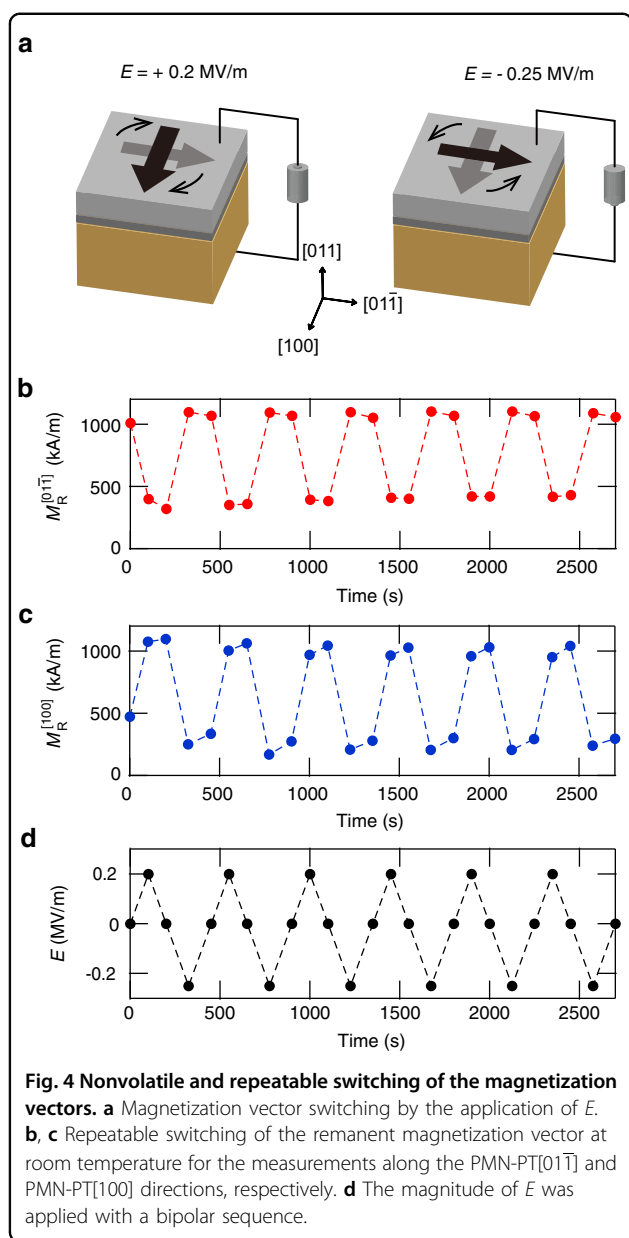
In-plane piezostress curves of the (011) surface of a representative  $\text{PMN-PT}(011)$  substrate are shown in Fig. S6 of the Supplementary information<sup>44</sup>. We clearly observed the anisotropic piezostress of the (011) plane of the  $\text{PMN-PT}$  substrate between the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions, as described in a previous report<sup>28</sup>. Because there were two different piezostress states in the (011) plane between the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions at  $E=0$  (Fig. S6c), we should consider the competition between the initial in-plane uniaxial magnetic anisotropy and the strain-induced magnetic anisotropy in the  $\text{Co}_2\text{FeSi}$  film at the two states. The two different states of the lattice deformation of the (011) plane at  $E=0$  are schematically shown in Fig. 3c, d. When  $E$  is increased from  $-0.8$  MV/m to 0, the tensile strain along  $\text{PMN-PT}[01\bar{1}]$  is maintained at  $E=0$  (Fig. 3c). In this situation, the strain-induced uniaxial magnetic anisotropy of the  $\text{Co}_2\text{FeSi}$  film along the  $\text{PMN-PT}[01\bar{1}]$  direction is added to the initial uniaxial magnetic anisotropy along  $\text{PMN-PT}[01\bar{1}]$  with a small off-axis orientation. As a result, the magnetization direction of the  $\text{Co}_2\text{FeSi}$  film is maintained along a magnetic easy axis in the  $\text{PMN-PT}[01\bar{1}]$  direction. On the other hand, when  $E$  is decreased from  $+0.8$  MV/m to 0, compressive strain along  $\text{PMN-PT}[01\bar{1}]$  is observed (Fig. 3d); this compressive strain decreases the magnitude of the uniaxial magnetic anisotropy of the  $\text{Co}_2\text{FeSi}$  film along the  $\text{PMN-PT}[01\bar{1}]$  direction. In this situation, the remanent magnetization direction of the  $\text{Co}_2\text{FeSi}$  film can switch from near the  $\text{PMN-PT}[01\bar{1}]$  to the  $\text{PMN-PT}[100]$  direction. Thus, we can qualitatively explain the origin of the two

magnetization states at  $E=0$ , shown in Fig. 3a, b, by considering the presence of the anisotropic piezostress of the (011) surface of the  $\text{PMN-PT}$  substrate along the  $\text{PMN-PT}[01\bar{1}]$  direction at  $E=0$ . However, if the initial in-plane uniaxial anisotropy of the  $\text{Co}_2\text{FeSi}$  film along the  $\text{PMN-PT}[01\bar{1}]$  direction was weaker or stronger than that in the present study, the two magnetization states at  $E=0$  could have been unstable. To quantitatively understand its origin, we should further investigate the correlation among the magnitude of the initial in-plane uniaxial magnetic anisotropy, local domain structures, and the magnitude of the global piezostress<sup>46,47</sup> for many  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures at  $E=0$ .

As shown in Fig. 3b, the magnetization directions at two different states at  $E=0$  are nearly switched from the uniaxial hard axis to the uniaxial easy axis or the uniaxial easy axis to the uniaxial hard axis during the  $E$  sweeping process. Therefore, nearly  $90^\circ$  magnetization vector switching can occur in the remanent state ( $H=0$ ) after the application of positive or negative  $E$  values, as schematically shown in Fig. 4a. Figure 4b, c display nonvolatile switching of the remanent magnetization vector for the measurements along the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions, respectively, and the sequence of the  $E$  application to  $\text{PMN-PT}[011]$  is also displayed in Fig. 4d. Evident variations in two different magnetic states with high/low  $M_R$  can be repeatedly demonstrated for both measurements along the  $\text{PMN-PT}[01\bar{1}]$  (b) and  $\text{PMN-PT}[100]$  (c) directions. Notably, the observed variation in  $M_R$  was more than  $\sim 700$  kA/m. The repeatable and nonvolatile magnetization vector switchings can be utilized as a part of the technology for voltage-induced magnetization switching in storage and/or memory devices having polycrystalline Co-based Heusler alloys.

### Giant CME coupling coefficient

We quantitatively evaluate the CME effect of the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures. To estimate the CME coupling coefficient ( $\alpha_E$ ), we define the value of  $\alpha_E$  as follows:  $\alpha_E = \mu_0 \frac{dM_R}{dE}$ , where  $\mu_0$  is the vacuum permeability. Figure 5a displays the value of  $\alpha_E$  as a function of  $E$ , estimated from the data in Fig. 3a, for the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure in both measurements by applying  $H$  along the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions. Very interestingly, the value of  $\alpha_E$  was over  $1.0 \times 10^{-5}$  s/m when  $E \sim -0.25$  MV/m at room temperature, as shown in Fig. 5a. In the relevant fields, an  $\alpha_E$  of more than  $1.0 \times 10^{-5}$  s/m has thus far been reported in multiferroic heterostructures consisting of  $\text{PMN-PT}$  substrates and single-crystalline magnetostrictive materials such as  $\text{FeRh}$ <sup>22</sup> and  $\text{FeGa}$  alloys<sup>34,35</sup>. On the other hand, we observe the giant  $\alpha_E$  of more than  $1.0 \times 10^{-5}$  s/m even in the polycrystalline  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure, where  $\text{Co}_2\text{FeSi}$  is one of the most



representative spintronic Co-based Heusler alloys<sup>38,39</sup>. This evidence indicates that magnetostrictive materials and single-crystalline structures are not strict conditions for obtaining a giant  $\alpha_E$  of more than  $1.0 \times 10^{-5} \text{ s/m}$ .

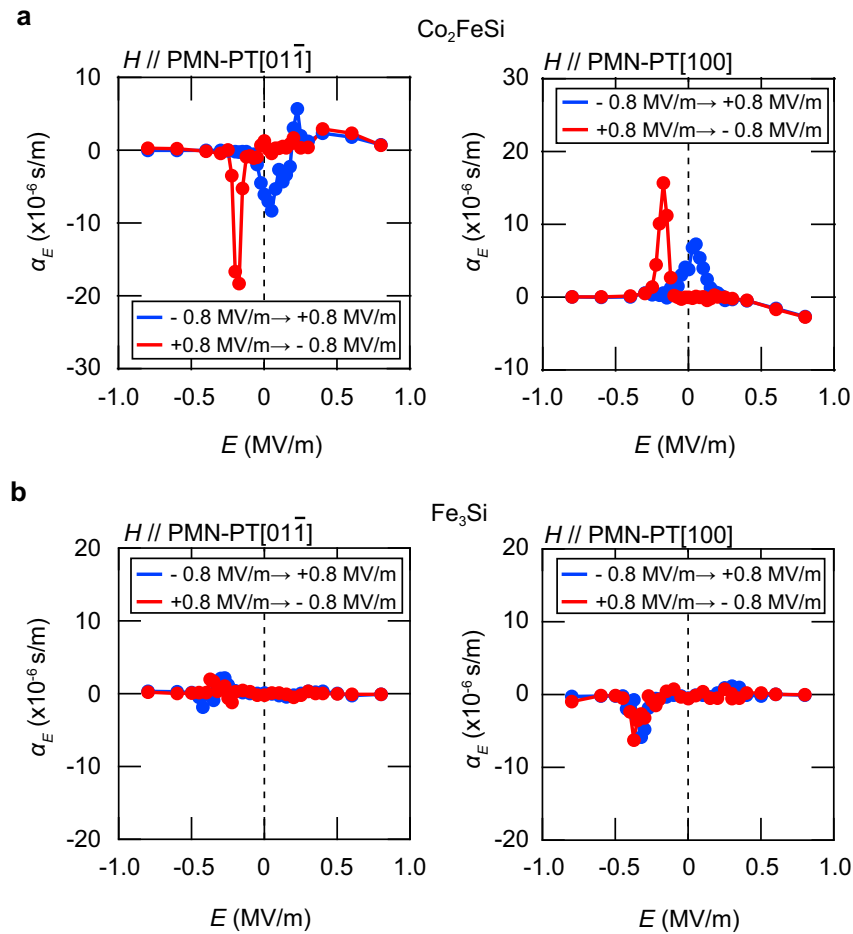
To verify the importance of  $\text{Co}_2\text{FeSi}$ , we also investigate the CME effect of the  $\text{Fe}_3\text{Si}/\text{PMN-PT}(011)$  heterostructure, where  $\text{Fe}_3\text{Si}$  is a binary Heusler alloy<sup>42</sup>, and the growth of the heterostructure, including its characterizations, is also shown in Fig. S7 of the Supplementary information<sup>44</sup>. Here, the  $\text{Fe}_3\text{Si}/\text{PMN-PT}(011)$  heterostructure is also polycrystalline and shows an in-plane uniaxial magnetic anisotropy between the PMN-PT[011] and PMN-PT[100] directions, similar to the case of the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures. Figure 5b shows the value of  $\alpha_E$  as a

function of  $E$  for the polycrystalline  $\text{Fe}_3\text{Si}/\text{PMN-PT}(011)$  heterostructure in both measurements along the PMN-PT[011] and PMN-PT[100] directions. Although similar peaks and dips are observed at  $|E| \sim 0.20 \text{ MV/m}$ ,  $\alpha_E$  is relatively small compared to  $1.0 \times 10^{-5} \text{ s/m}$  at room temperature. This feature is slightly different from that for the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures.

In Table 1, we summarize the reported values of the giant  $\alpha_E$  for various multiferroic heterostructures and compared them to those of this study. Apart from the  $\text{Fe}_{50}\text{Rh}_{50}/\text{BaTiO}_3(001)$  system<sup>22</sup>, a giant CME effect was observed in various FM/PMN-PT systems<sup>28,34,35</sup>. As previously described, because ferroelectric PMN-PT has a piezoelectric constant<sup>43</sup> that is relatively large compared to that of  $\text{BaTiO}_3$ , a large piezostress can be induced from PMN-PT to FM layers via multiferroic heterointerfaces<sup>26–29,34,35</sup>. For magnetostrictive materials such as  $\text{Fe}_{1-x}\text{Ga}_x$ , one has to achieve a metastable bcc (A2) phase with  $x \sim 30\%$  as a single crystalline film on PMN-PT to obtain a giant  $\alpha_E$  of more than  $1.0 \times 10^{-5} \text{ s/m}$ <sup>35</sup>. For spintronic materials such as  $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}$ <sup>28</sup> and  $\text{Co}_2\text{FeSi}$  in this study, amorphous and polycrystalline films grown on PMN-PT have also shown giant values of  $\alpha_E$ . Although these spintronic materials did not have a large magnetostrictive constant, an induced uniaxial magnetic anisotropy ( $6 \text{ kJ/m}^3$  for  $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}$  in ref. <sup>28</sup>,  $5.8 \text{ kJ/m}^3$  for  $\text{Co}_2\text{FeSi}$  in this work) can be largely and steeply modulated in the film plane by applying  $E$ . The above results show that electric-field control of the magnetization vector can be efficiently achieved by utilizing the strain-mediated magnetic anisotropy for high-performance spintronic materials with a giant  $\alpha_E$ .

## Discussion

For the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  multiferroic heterostructures, we should consider the strain-mediated variation in the magnetic anisotropy, which is an extrinsic mechanism. To discuss a substantial contributor to the CME effect in the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure, we focus on the correlation between the magnetocrystalline anisotropy energy for  $\text{Co}_2\text{FeSi}$  and the extrinsic lattice strain in  $\text{Co}_2\text{FeSi}$  in a simple model. Here, the extrinsic lattice strain is imposed through the in-plane lattice vectors  $a$  and  $b$  of the conventional 16-atom unit cell, as shown in the inset of Fig. 6a. Figure 6a shows the magnetocrystalline anisotropy energy (MAE) estimated by first-principles calculations for  $\text{Co}_2\text{FeSi}$ , together with  $\text{Fe}_3\text{Si}$  as a reference, as a function of  $b/a$ , where  $b/a$  is obtained by changing the lattice vector  $a$  while optimizing the  $b$  vector. The MAE of  $\text{Co}_2\text{FeSi}$  changes linearly with  $b/a$ , where the tetragonal in-plane lattice distortion results in in-plane magnetization pointing to the elongated axis: the positive and negative MAEs for  $b/a > 1$  and  $b/a < 1$ , respectively. In contrast,  $\text{Fe}_3\text{Si}$  shows relatively small changes in the MAE with the opposite sign compared to  $\text{Co}_2\text{FeSi}$ . This tendency supports that the value of  $\alpha_E$  for



**Fig. 5 Giant CME coupling coefficient.** **a** Plots of the CME coupling coefficient ( $\alpha_E$ ) versus  $E$  at room temperature for the polycrystalline  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure along the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions, where  $\alpha_E$  is estimated from the data in Fig. 3a, **b**  $\alpha_E$  versus  $E$  at room temperature for the polycrystalline  $\text{Fe}_3\text{Si}/\text{PMN-PT}(011)$  heterostructure along the  $\text{PMN-PT}[01\bar{1}]$  and  $\text{PMN-PT}[100]$  directions.

**Table 1 Giant  $\alpha_E$  for various multiferroic heterostructures.**

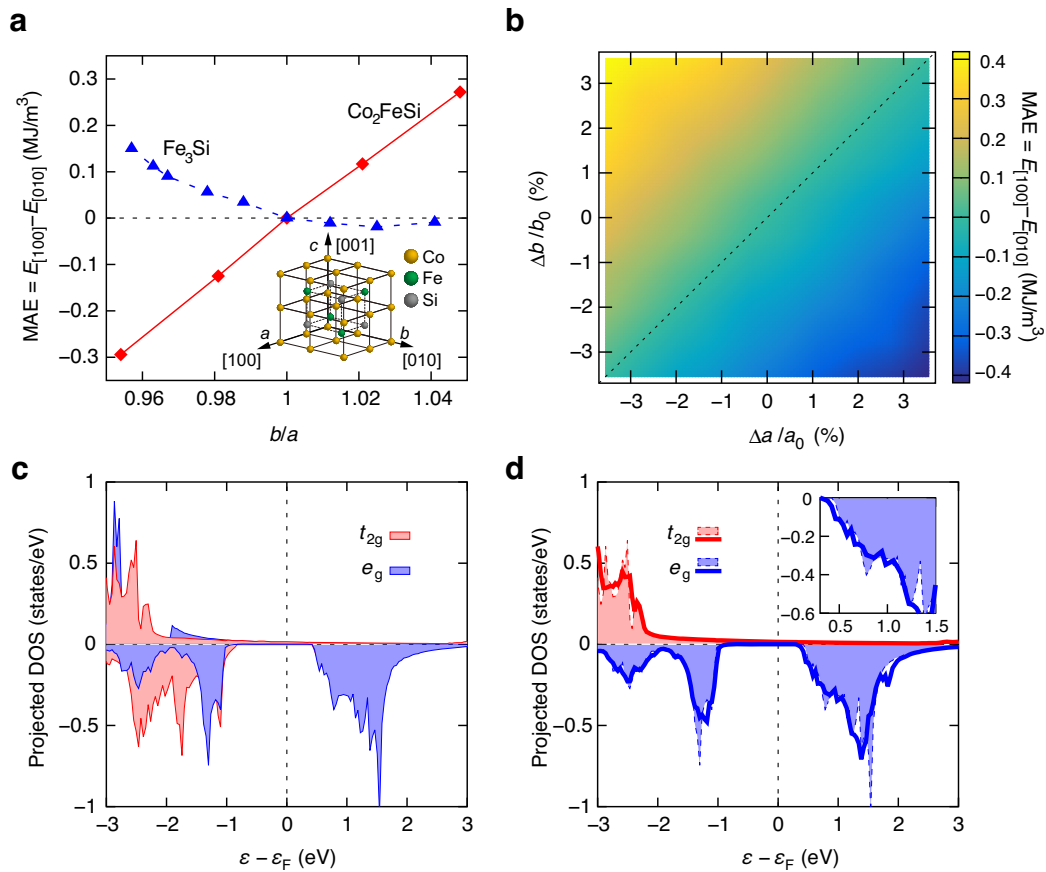
Heterostructure	Crystal quality	$\alpha_E$ (s/m)	Temperature (K)	Reference
$\text{Fe}_{50}\text{Rh}_{50}/\text{BaTiO}_3(001)$	Single crystal	$1.6 \times 10^{-5}$	385	22
$\text{Fe}_{80}\text{Ga}_{20}/\text{MgO}/\text{PMN-PT}(001)$	Single crystal	$1.5\text{--}4.5 \times 10^{-5}$	room temperature	34
$\text{Fe}_{70}\text{Ga}_{30}/\text{PMN-PT}(001)$	Single crystal	$1.5\text{--}2.0 \times 10^{-5}$	room temperature	35
$\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}/\text{PMN-PT}(011)$	Amorphous	$3.0\text{--}8.0 \times 10^{-6}$	room temperature	28
$\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$	Polycrystalline	$1.2\text{--}1.8 \times 10^{-5}$	room temperature	This work

the  $\text{Fe}_3\text{Si}/\text{PMN-PT}(011)$  heterostructure is smaller than that for the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructure. From these results, we interpret that the modulation of the lattice strain induced by the application of  $E$  causes changes in the MAE in  $\text{Co}_2\text{FeSi}$  and  $\text{Fe}_3\text{Si}$ . Even though the result in Fig. 6a is obtained with the constraint of  $c=a$  for simplicity, the behavior of the in-plane anisotropy favoring the

magnetization along the elongated axis remains unchanged for the case of full relaxation, as shown in Fig. 6b.

To elucidate the origin of strain-induced MAE modulation, we evaluated the orbital-resolved MAE for  $\text{Co}_2\text{FeSi}$  on the basis of perturbation theory (see Materials and methods). As we decompose the total MAE of  $\text{Co}_2\text{FeSi}$ , it is found that the dominant contribution to the MAE comes from Co atoms relative to those from Fe and Si atoms.





**Fig. 6** Strain-induced modulation in magnetocrystalline anisotropy energy (MAE). **a** MAE of the  $\text{Co}_2\text{FeSi}$  and  $\text{Fe}_3\text{Si}$  as a function of  $b/a$ . **b** MAE of the  $\text{Co}_2\text{FeSi}$  as a function of the interfacial strain ( $\Delta a/a_0$  and  $\Delta b/b_0$ ). The dashed line represents the case of uniform in-plane deformation, where the MAE becomes exactly zero. **c** Projected DOS of  $\text{Co}$  3d orbitals in  $\text{Co}_2\text{FeSi}$  without the strain. Relevant states ( $t_{2g}$  with up spins and  $e_g$  with down spins) for the strain-induced magnetic anisotropy are drawn as front. **d** Projected DOS per  $d$ -orbital of the dominant  $\text{Co}$  3d states for the magnetic anisotropy in  $\text{Co}_2\text{FeSi}$  for  $\Delta a/a_0 = 3.55\%$  and  $\Delta b/b_0 = -3.55\%$ . The case without strain is also shown as shades. In **a**, the ratio  $b/a$  is controlled by changing  $a$  while optimizing  $b$ , where  $c$  is fixed as  $a$  for simplicity. In contrast, vectors  $a$  and  $b$  were changed independently by optimizing  $c$  as the full relaxation for given strain states for **b**, **d**.

Figure 6c displays the projected density of states (DOS) of  $\text{Co}$  3d orbitals in  $\text{Co}_2\text{FeSi}$ . Here, the  $e_g$  ( $t_{2g}$ ) states consist of degenerate  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) states because the octahedral ligand field is valid due to the cubic structure. Even though the degeneracy is lifted by the interfacial strain, we also use this classification for the strain-perturbed states. With lateral strain, we find that the MAE is dominated by up spins in the occupied states and down spins in the unoccupied states, in particular,  $\langle t_{2g}, \uparrow | H_{\text{SO}} | e_g, \downarrow \rangle$  couplings, where the bra (ket) in the matrix element corresponds to occupied (unoccupied) states. These dominant orbitals are shown in Fig. 6d for  $\Delta a/a_0 = 3.55\%$  and  $\Delta b/b_0 = -3.55\%$ . Subtle changes are seen from the DOS that the unoccupied  $e_g$  orbital with the down spins shifts toward the Fermi level ( $\epsilon_F$ ) by the in-plane deformation. The change in the electronic structures contributes to the negative MAE favoring the magnetization in the  $a$  direction. It should be noted that changes in the occupied down spins in Fig. 6d

are irrelevant because the matrix element is small due to the very low density of states in unoccupied up-spin states. Therefore, the origin of the strain-induced MAE modulation in the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures is related to the modulation of the  $\text{Co}$ -3d orbitals occupied by up-spin states in  $\text{Co}_2\text{FeSi}$ .

In the field of next-generation spintronic nonvolatile memories such as MRAMs<sup>1–4</sup> and spintronic logic devices<sup>48,49</sup>, effective switching of the magnetization vector via spin transfer torque by using an electric current is one of the bottlenecks for low energy power consumption because of the heat dissipation process. In contrast, the CME effect in multiferroic heterostructures can provide a solution to overcome the heat dissipation of the magnetization switching at room temperature<sup>23–25</sup>. In this study, we have presented a giant CME effect in  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  multiferroic heterostructures with  $\alpha_E$  of more than  $1.0 \times 10^{-5} \text{ s/m}$  at room temperature. The value of giant  $\alpha_E$  is the

largest of the high-performance Heusler-based spintronic materials. We infer that the giant  $\alpha_E$  in the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  heterostructures is strongly related to the strain-induced in-plane magnetic anisotropy derived from the Co  $3d$  orbitals in  $\text{Co}_2\text{FeSi}$ , in addition to a relatively large  $M_S$ . Additionally, repeatable and nonvolatile magnetization vector switching without applying  $H$  has been demonstrated at room temperature. Thus, the present study provides a new solution for achieving magnetization switching with ultralow power consumption with hundreds of orders of magnitude of attoJoules in heat dissipation<sup>23–25</sup>.

Although the present study was performed by utilizing PMN-PT substrates, some technologies for PMN-PT films without the influence of substrate clamping, such as piezoelectric layers, have been demonstrated<sup>24,50</sup>. Furthermore, the giant CME effect based on the Co-based Heusler alloys/PMN-PT multiferroic heterostructures can be utilized for MTJs<sup>38,51</sup> and current-perpendicular-to-plane giant magnetoresistance (CPP-GMR) devices with polycrystalline Co-based Heusler alloy electrodes<sup>52</sup> and a new spintronic logic architecture, such as magnetoelectric spin-orbit devices<sup>23,53</sup>.

## Materials and methods

### Growth and characterization of $\text{Co}_2\text{FeSi}$ on PMN-PT(011)

The  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  multiferroic heterostructure was grown by molecular beam epitaxy (MBE). Prior to the growth of the  $\text{Co}_2\text{FeSi}$  film, heat treatment was performed at  $450^\circ\text{C}$  for 20 min to obtain a flat surface of the single-crystal PMN-PT(011) substrates with a size of  $5.0 \times 5.0 \times 0.5 \text{ mm}^3$ . After cooling to a growth temperature of  $300^\circ\text{C}$ , a 0.3-nm-thick Fe layer was grown on top of the cleaned PMN-PT(011) surface. When we did not use the 0.3-nm-thick Fe layer, the grown polycrystalline  $\text{Co}_2\text{FeSi}$  film became completely nonoriented. To improve the crystallinity of the  $\text{Co}_2\text{FeSi}$  film with an  $L2_1$ -ordered structure, the insertion of the 0.3-nm-thick Fe layer is essential. Thus, 30-nm-thick  $\text{Co}_2\text{FeSi}$  film was grown by co-evaporation using Knudsen cells, where we set the supplied atomic composition ratio of Co:Fe:Si to 2.0:1.0:1.0 during the growth<sup>29,45</sup>. Here, the heat treatment temperature of  $450^\circ\text{C}$  and the growth temperature of  $300^\circ\text{C}$  were lower than those described in the literature, showing a very high  $\alpha_E$  of  $1.5 - 4.5 \times 10^{-5} \text{ s/m}$ <sup>34</sup>. After growth, we characterized the  $\text{Co}_2\text{FeSi}/\text{PMN-PT}(011)$  multiferroic heterostructure. First, the multiferroic heterostructure was evaluated by X-ray diffraction (XRD) (Rigaku SmartLab) for out-of-plane and in-plane analyses. High-resolution transmission electron microscopy (HRTEM) and bright-field transmission electron microscopy (BF-TEM) were performed using an aberration-corrected JEOL 2200FS TEM, and nanobeam

diffraction was performed on a JEOL 2100+TEM. The specimen preparation for TEM analysis was performed using focused ion beam techniques.

To measure the conventional magnetic properties of the grown multiferroic heterostructures, we used a vibrating sample magnetometer (VSM) at room temperature, while magneto-optic Kerr ellipticity measurements using the LED with a wavelength of 670 nm were performed to examine the CME effect at room temperature. To apply an  $E$  to the PMN-PT substrate along the [011] direction, a  $\text{Au}(100 \text{ nm})/\text{Ti}(3 \text{ nm})$  electrode was deposited on the backside of the PMN-PT substrate, where the  $\text{Co}_2\text{FeSi}$  film was also utilized as a top electrode. Prior to the evaluation of the CME effect, we first applied an  $E$  of  $-0.8 \text{ MV/m}$ . Then, the amplitude of  $E$  was gradually changed from  $-0.8 \text{ MV/m}$  to  $+0.8 \text{ MV/m}$ , then back to  $E = -0.8 \text{ MV/m}$ . At each step, the Kerr-ellipticity magnitude was obtained by measuring the hysteresis loops as a function of  $H$  along the PMN-PT[011] or [100] direction.

### Computational details for first-principles calculations

We performed first-principles calculations on the basis of density functional theory by using the VASP code<sup>54</sup>, where the inner-core electrons were treated by the projector augmented-wave method<sup>55,56</sup>. The generalized gradient approximation parameterized by the Perdew-Burke-Ernzerhof functional was used for the exchange-correlation functional<sup>57</sup>. In addition, the DFT +  $U$  method with the effective Hubbard repulsion  $U_{\text{eff}} = 2.6 \text{ eV}$  and  $U_{\text{eff}} = 2.5 \text{ eV}$  was employed for the Co  $3d$  and Fe  $3d$  orbitals of  $\text{Co}_2\text{FeSi}$ , respectively<sup>58</sup>. The cutoff kinetic energy for the plane-wave basis set was set to 520 eV, and  $k$ -point grids were set to  $10 \times 10 \times 10$  and  $15 \times 15 \times 15$  for ionic relaxation and static calculations, respectively. The in-plane strain was generated by changing the in-plane lattice parameters  $a$  and  $b$ . Here, the strain was approximated with  $\Delta a/a_0$  and  $\Delta b/b_0$ , where  $\Delta a = a - a_0$ ,  $\Delta b = b - b_0$ , and  $a_0 (=b_0)$  is the equilibrium lattice constant without strain.

The MAE was evaluated as the total-energy difference obtained from calculations including the spin-orbit coupling for magnetization along the [100] and [010] directions while fixing the electron density that was obtained by the self-consistent collinear calculation. For the orbital-decomposed MAE, contributions from each atomic site  $\tau$  and couplings among atomic orbitals  $\mu$  were derived from second-order perturbation theory<sup>59,60</sup>:

$$E_{\text{SO}} = \sum_{\tau_1 \tau_2} \sum_{\mu_1 \mu_2} E_{\text{SO}}^{\tau_1 \tau_2 \mu_1 \mu_2} \quad (1)$$

$$E_{\text{SO}}^{\tau_1 \tau_2 \mu_1 \mu_2} \approx - \sum_i^{\text{occ.}} \sum_j^{\text{unocc.}} \sum_{\tau_3 \tau_4} \sum_{\mu_3 \mu_4} \frac{\langle i | \tau_1 \mu_1 \rangle \langle \tau_1 \mu_1 | H_{\text{SO}} | \tau_2 \mu_2 \rangle \langle \tau_2 \mu_2 | j \rangle \langle j | \tau_3 \mu_3 \rangle \langle \tau_3 \mu_3 | H_{\text{SO}} | \tau_4 \mu_4 \rangle \langle \tau_4 \mu_4 | i \rangle}{\varepsilon_j - \varepsilon_i} \quad (2)$$

where  $i$  and  $j$  are indices of occupied and unoccupied eigenstates with eigenenergies  $\varepsilon_i$  and  $\varepsilon_j$ , respectively. Note that the indices  $i$ ,  $j$ , and  $\mu$  include the spin index. The spin-orbit coupling is approximated as  $H_{\text{SO}} = \xi \mathbf{l} \cdot \mathbf{s}$ , where  $\xi$  is the coupling constant,  $\mathbf{l}$  is the orbital-angular momentum quantum number, and  $\mathbf{s}$  is the spin angular momentum quantum number. The values of  $\xi$  were compiled in a prior study<sup>61</sup>. In analyzing the MAE decomposition, electronic states obtained by the OpenMX code were used<sup>62</sup>. The  $x$ ,  $y$ , and  $z$  directions in the MAE decomposition were defined as along the  $a$ ,  $b$ , and  $c$  axes, respectively.

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#### Author details

<sup>1</sup>Department of Systems Innovation, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.

<sup>2</sup>Center for Spintronics Research Network, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. <sup>3</sup>Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan. <sup>4</sup>Department of Physics, University of York, York YO10 5DD, United Kingdom. <sup>5</sup>Department of Materials Science and Engineering, Tokyo Institute of Technology, J1-3, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8502, Japan. <sup>6</sup>Division of Spintronics Research Network, Institute for Open and Transdisciplinary Research Initiatives, Osaka University, Suita, Osaka 565-0871, Japan

#### Author contributions

K.H. proposed and supervised this study. The growth of the ferromagnetic films was conducted by S.F., T.U., S.Y., and K.H. The XRD and HRTEM measurements were performed by S.F. and T.U. and by A.K. and V.L., respectively. The magnetic properties and the CME effect were characterized by S.F., T.U., Y.S., R.N., and K.H. The strain was measured by T.K. The theoretical calculations were carried out by A.Y. and Y.G., and the data analyses were performed by A.Y., Y.G., T.O. All authors contributed to the discussion and interpretation of the results and preparation of the manuscript.

#### Competing interests

The authors declare no competing interests.

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