



Deposited via The University of York.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/240007/>

Version: Accepted Version

Article:

do Nascimento, Julio A., Nedelkoski, Zlatko, Kepaptsoglou, Demie et al. (2026) Atomic-scale origin of rotated epitaxy and its impact on spin-electronic properties at Co₂FeSi_{0.5}Al_{0.5}/Ge interface. APPLIED SURFACE SCIENCE. 166864. ISSN: 0169-4332

<https://doi.org/10.1016/j.apsusc.2026.166864>

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Atomic-Scale Origin of Rotated Epitaxy and its Impact on Spin-Electronic Properties at $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Ge}$ Interface

Julio A. do Nascimento ^a, Zlatko Nedelkoski ^b, Demie Kepaptsoglou ^{a,c}, Shinya Yamada ^{d,e}, Kohei Hamaya ^{d,e}, and Vlado K. Lazarov ^{a,f*}

^a School of Physics, Engineering, and Technology, University of York, Heslington, YO10 5DD, York, United Kingdom

^b Faculty of Technical Sciences, Mother Theresa University, 1669 11A, Skopje, North Macedonia

^c SuperSTEM, Sci-Tech Daresbury Campus, Daresbury, WA4 4AD, United Kingdom

^d Center for Spintronics Research Network, Graduate School of Engineering Science, The University of Osaka, 1-3 Machikaneyama, Toyonaka 560-8531, Japan

^e Spintronics Research Network Division, Institute for Open and Transdisciplinary Research Initiatives, The University of Osaka, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^f The York-JEOL Nanocentre, York Science Park, Heslington, York YO10 5BR, United Kingdom

*E-mail: vlado.lazarov@york.ac.uk

Abstract

Controlling interfacial atomic structure via epitaxial growth is essential for the spin polarization in half-metal/semiconductor heterostructures. Here, we use density functional theory to analyze a ‘rotated’ epitaxial relationship at the $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}/\text{Ge}(111)$ interface, experimentally realized on films grown by molecular beam epitaxy. The calculations indicate that a 180° -rotated epitaxy exhibits the lowest formation energy due to the bonding configuration of the initial Co layer. In this configuration, interfacial Ge atoms occupy positions corresponding to Si and Al sites in the extended $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ lattice. The lowest-energy atomic interface structure results in a bond angle change of the interfacial Ge dumbbell layer, which is confirmed by atomic-resolution electron microscopy. We also show that the interface structure of the observed 180° -rotated epitaxy reduces the formation energy and considerably increases the interfacial spin polarization, which is further enhanced by an energetically favorable Fe–Ge interface intermixing and selective Ge out-diffusion into the film. Furthermore, we demonstrate that the rotated epitaxy is preserved when $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ is grown on Si, despite the significant interdiffusion, and that such epitaxy should be preserved at the $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}/\text{GaAs}(111)$ interface, confirming the structural origin of the rotated epitaxy between Co-based Heusler alloys and Ge, Si, and GaAs substrates.

Keywords: Heusler alloy, $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$, interface, density functional theory, scanning transmission electron microscopy

1. Introduction

Co-based full Heusler alloys have been extensively investigated for the development of spintronic devices owing to their desirable spin-electronic properties [1–5]. Among them, $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (CFAS) [6–9] garners increasing interest for the fabrication of high-performance electronic and spintronic devices owing to its density functional theory (DFT)-predicted spin polarization of 100% at the Fermi level, high Curie temperature (~ 1000 K), abundant constituent elements (Co, Fe, Al, Si), and Fermi level in the middle of the band gap of the spin-down electrons, ensuring a more robust structure against the inevitable temperature effects. In addition, its 100% spin-polarized structure is crucial to overcome the conductivity mismatch issue [10] between the ferromagnet film and semiconductor substrate for an efficient spin injection, a problem that occurs if a standard ferromagnetic electrode such as Fe, Co, or CoFe is used.

The interface of the half-metallic CFAS with the conventional semiconductor Si suffers from a considerable lattice constant mismatch between CFAS and Si ($\sim 4.5\%$), strong out-diffusion of Si from the substrate into the film, and formation of secondary phases (Co and Fe silicides) in an ~ 3 nm thick region [11–13]. These issues can be overcome to a good extent by using Ge as a substrate [14–17], which ensures a negligible lattice mismatch (only 0.2%), largely reduced diffusion of substrate atoms into the film, and absence of undesirable secondary interfacial

phases. Therefore, the CFAS/Ge heterostructure is a promising platform for fabrication of spintronic devices with high performances.

Disorder, strain, and structural defects are among the factors responsible for lower measured performances of devices based on thin films composed of Heusler alloys including CFAS than those expected for ideal bulk-like structures [18–21]. The device properties can also be affected by effects originating from the interfaces between the thin films and between the thin films and substrate in the electronic devices [22–24]. Therefore, atomic control at the device interfaces is crucial to tailor electronic properties such as the spin polarization (SP), interface conductivity, and interfacial magnetism.

Electron microscopy measurements showed that both CFAS/Ge [14] and CFAS/Si(111) [12] interfaces exhibit a characteristic rotated epitaxial relationship of CFAS with Ge and Si. In other words, the [1-10] crystallographic direction of CFAS is parallel to the [-110] crystallographic direction of Ge or Si, in contrast to the expected simple nonrotated orientation of CFAS [1-10] and Ge/Si [1-10]. The aim of this study was to investigate the origin of the epitaxy rotation at the technologically important CFAS/Ge interface, and evaluate the effects of this rotation on the electronic properties at the interface, including the SP. Through DFT calculations, we show that the epitaxial rotation induced by the driving force of Ge to incorporate at Si, Al sites in the CFAS reduces the interface formation energy and notably increases the SP of the interface. In addition, as in the case of the [001]-oriented CFAS/Ge interface, the likely Fe–Ge intermixing and observed selective Ge out-diffusion into the film unexpectedly provide even higher interfacial SPs. Therefore, these naturally induced synergetic effects of epitaxy rotation and interdiffusion improve the properties of CFAS/Ge, and provide a promising heterostructural platform for spin injection applications.

2. Methods

We employed the CASTEP [25] software package for DFT calculations using supercells with dimensions of approximately $4.0 \times 6.9 \times 45 \text{ \AA}^3$, composed of two CFAS and two Ge unit cells interfaced on a (111) plane, with a vacuum region of approximately $14 \text{ \AA}$ along the [111] film growth direction. The vacuum region with such dimensions was introduced to ensure that the surface effects do not interfere with the interfacial properties [16]. In addition, these supercell dimensions ensure recovery of the bulk CFAS and Ge electronic structures in the interior parts of the film and substrate, respectively, i.e., enable a realistic analysis of the electronic structure of the CFAS/Ge interface. All constructed supercells are periodic in the in-plane directions. These supercell dimensions are sufficient for modelling of the interface properties, as further increase in the supercell size does not change the interfacial PDOS, as shown in Supplementary Figure S1. In all DFT calculations, we employed the Perdew–Burke–Ernzerhof (PBE) + U exchange–correlation functional with a Hubbard U of 2.1 eV for both d -block elements, Co and Fe [26], to open up the minority band gap, and approximately correct for the delocalization effect of self-

interaction [27]. We used ultrasoft PBE pseudopotentials with a plane wave cut-off energy of 500 eV. For visualization of the atomic structures, we employed the program VESTA [28]. Partial densities of states (PDOSs) were calculated with the OPTADOS software package with fixed Gaussian broadening [29].

Approximately 20 nm thick CFAS samples were prepared by codeposition of Co, Fe, Si, and Al on both Ge and Si substrates by low-temperature molecular beam epitaxy (MBE) using Knudsen cells [12,14]. After chemical cleaning of the Ge(111) surface with ultrasonic cleaning for 3 min in acetone, 3 min in ethanol, and 2 min in deionized water, followed by immersion for 5 min in an ~1 % diluted hydrofluoric acid solution, the Ge(111) surface was blow-dried with N₂. Subsequently, the substrate was loaded into an MBE chamber. A heat treatment at 550 °C for 20 min was then conducted in an ultrahigh vacuum (UHV) environment ($\sim 10^{-7}$ Pa) [30]. By in-situ reflection high-energy electron diffraction (RHEED) observations (Supplementary Figure S2), we confirmed a Ge(111)-(1 × 1) surface. Similarly, the Si(111) surface was chemically cleaned with ultrasonic cleaning for 3 min in acetone, 3 min in ethanol, 2 min in an NH₃:H₂O₂ solution, and 2 min in deionized water, followed by immersion for 5 min in an ~1 % diluted hydrofluoric acid solution [31]. After blow-drying the Si(111) surface, a heat treatment at 450 °C for 20 min was conducted in the UHV environment. The in-situ RHEED pattern (Supplementary Figure S2) after the annealing demonstrates the Si(111)-(1×1) surface.

To achieve stoichiometric Co₂FeSi_{0.5}Al_{0.5} films, a nonstoichiometric deposition technique was employed to suppress Si substrate diffusion and compensate for Al loss. We initially optimized the Co₂FeAl composition by increasing the Al flux and reducing the Co:Fe flux ratio to 1.8:1. Consequently, a quaternary Co₂FeSi_{0.5}Al_{0.5} was grown using a specific flux ratio of Co:Fe:Si:Al = 1.8:1:0.5:1. This approach yielded the desired stoichiometry while maintaining two-dimensional epitaxial growth at room temperature [32,33].

Cross-sectional transmission electron microscopy samples were prepared by focused ion beam. Electron microscopy images were acquired using a Nion UltraSTEM 100 microscope, operated at 100 kV, with a convergence angle of 30 mrad. The inner detector angle for high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) imaging was 76 mrad. HAADF STEM image simulations were performed using the multislice method with the QSTEM software package [34].

3. Results and Discussion

First, we investigate the possible sharp interface atomic structures of CFAS/Ge(111). Along the [111] crystallographic direction, the CFAS unit cell is composed of 12 alternating atomic planes, i.e., three structural motifs of –Co–Fe–Co–(Si,Al)–, as illustrated in the right panels in Figure 1. The DOS showing the half-metallic nature of this alloy is presented in the left panel in Figure 1. CFAS can be represented by the general X₂YZ formula unit, with nonmagnetic elements occupying

the Z sites. It has a cubic crystal structure with a space group of $Fm\bar{3}m$ (no. 225) with a lattice parameter of 5.68 Å. It is an intermetallic compound with a lattice that can be considered as four interpenetrating face-centred cubic sublattices. Two of these sublattices are populated by Co atoms, one by Fe, and the fourth is shared by both Si and Al. The Wyckoff positions of the atoms are: Fe at $4a$ (0, 0, 0), Si/Al at $4b$ (1/2, 1/2, 1/2), and Co at $8c$ (1/4, 1/4, 1/4). The two interpenetrating face-centered cubic Co sublattices yield a simple cubic Co sublattice. Structural models of bulk CFAS and constructed atomically sharp interfaces along different viewing directions are presented in Supplementary Figure S3. The combination of Si and Al enables the Fermi level to be positioned around the middle of the band gap of the minority spin-down electrons, which makes this structure robust upon inevitable structural deviations, strain effects, temperature effects, etc., in real application scenarios, as mentioned above. The electronic structure of CFAS is robust against Si/Al disorder effects, as shown in Supplementary Figure S4. Despite the variations in Si and Al distributions, we obtained identical DOS, lattice constant, and magnetic moment of the bulk CFAS cell.

The lattice constants of the CFAS film and Ge substrate are very similar, with a mismatch of only 0.2%, which is conducive to a desirable interface with a well-defined epitaxial relationship, and minimal interface strain. Hence, it is expected that strain-driven defects such as misfit dislocations, diffusion, and disorder are minimal.

We consider the possible atomically sharp interfaces between CFAS and Ge. Besides Si and Al as nonmagnetic elements in the Co-based Heusler alloy, Ge is used as a substrate, which fits well at the Z sites of the L_{21} structure of CFAS. Hence, an interface that follows the atomic stacking where the top Ge layer is structurally shared by both film and substrate is expected. In other words, the interface sites present in both structures would represent a smooth transition within the heterostructure, as shown in the right panel in Figure 1. The terminating Ge(111) plane of the substrate is placed at the atom positions of the (Si, Al) plane, as the (Si, Al) atomic Z-sites are the expected sites of Ge in the CFAS Heusler alloy. The CFAS/Ge interface is formed on the (111) plane, as illustrated in Figure 1, showing models along the $[-110]$ orientation of Ge.

The (111)-terminated CFAS and Ge allow two distinctive interfaces, rotated by 180° with respect to each other, as shown in the right panels in Figure 1. We denote them as rotated and nonrotated (111) interfaces. For the nonrotated interface (NRI), the epitaxial relationship is CFAS $[-110]$ || Ge $[-110]$ and CFAS $[111]$ || Ge $[111]$, while, for the rotated interface (RI), the epitaxial relationship is CFAS $[1-10]$ || Ge $[-110]$ and CFAS $[111]$ || Ge $[111]$.

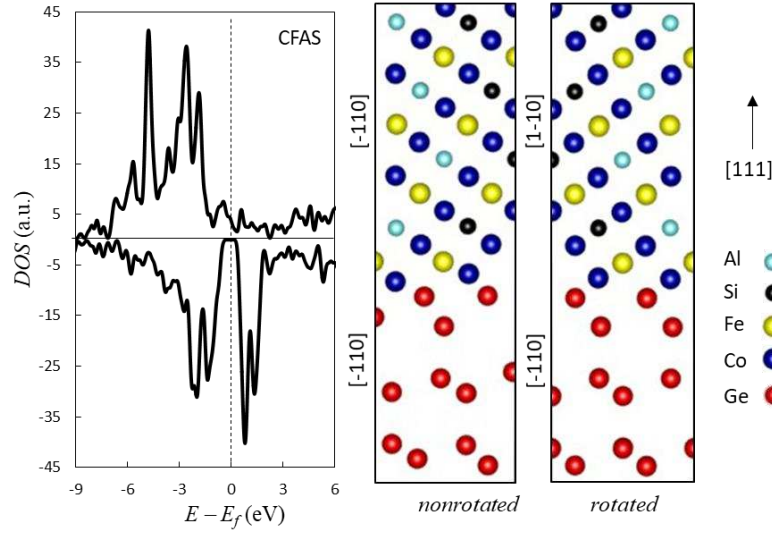


Figure 1. Calculated DOS of bulk CFAS and geometrically optimized structural models of Co-terminated CFAS/Ge NRI and RI. The Fermi level is indicated by the dashed line. The top and bottom panels show the DOSs for the spin-up and spin-down electrons, respectively. The color coding of the atoms is presented in the legend. The [111] growth direction is indicated by the arrow. The viewing directions of both CFAS and Ge in both models are also indicated.

We geometrically optimized the two interface structural models (NRI and RI) and calculated their total energies to analyze their stability, i.e., their likeliness to form at the CFAS–Ge interface. After the geometry optimization (Figure 1, right panels), the energy difference between the two models is 0.41 eV/supercell in favor of formation of RI, which agrees with the experimentally observed epitaxial relationship between CFAS and Ge (Figure 2) [14].

To provide insights into the initial stage of growth, we also performed calculations for supercells with only one structural motif of $-\text{Co}-\text{Fe}-\text{Co}-(\text{Si}, \text{Al})-$, i.e., one third of the CFAS unit cell (Supplementary Figure S5). We obtained an energy difference between RI and NRI of 0.13 eV/supercell, again in favor of formation of RI at the interface. In the first set of calculations with the larger supercells, there are no significant influences of the surface effects (CFAS/vacuum interface) on the CFAS–Ge interface, as those effects vanish after several atomic planes [16], while, in the second set of calculations, due to surface effects, a different energy difference between RI and NRI is obtained, as expected. However, the trend is consistent, i.e., RI is more likely to form in both cases.

Furthermore, we evaluated the energies of only the first Co atomic plane on Ge in both NRI and RI cases, as shown in Supplementary Figure S6. When we place the Co atomic plane at the sites that correspond to the RI, we obtained a stable interface, with a lower energy than that when the Co plane is placed at sites corresponding to the NRI before the interdiffusion of Co in the substrate during the geometry optimization, which occurred only in the NRI case. Although all

atomic species should be simultaneously considered in the simulations as the growth is performed by MBE codeposition, the lower initial energy of the single Co atomic plane in the RI case than that in the NRI case further indicates that the epitaxy rotation is guided by the first interface layers.

The experimentally observed interface atomic structure determined with a Co terminating plane ensures structural continuity and local symmetry preservation across the interface between CFAS and Ge. As the repeating stacking sequence of CFAS along the [111] growth direction is -Co-Fe-Co-Si/Al-, and, considering that the Si/Al sites are lowest-energy substitution sites for Ge in the CFAS structure, we “merge” the Ge substrate at a Si/Al (111) plane of CFAS, which yields a -Co-Fe-Co-Ge (substrate) atomic structure across the interface, with the interfacial Ge shared between the film and substrate. This structural continuity minimizes the formation energy of the interface, in comparison to the other considered configurations between CFAS and Ge.

To illustrate these energy-based considerations, we constructed a laterally shifted nonrotated model (Supplementary Figure S7), where the interfacial Ge occupies a site that would be populated by Co in the bulk CFAS. This model has a higher formation energy by 0.21 eV/supercell compared to the corresponding nonshifted model. We attribute the formation energy increase to the high energy of Ge-Co atomic swaps in the Heusler alloy, as discussed below.

Further, Supplementary Figure S8 shows a model where the Ge substrate is merged on an Fe (111) plane, so that the first (111) plane above Co is occupied by Si/Al. For completeness, we calculated the energy difference between the rotated and nonrotated models for such interface structure, and obtained that the rotated model has a lower energy by 0.41 eV/supercell, which is in line with the previous results.

Although the structural continuity is not realized with Fe and Si/Al terminations at the interface, for completeness, besides the above supercells with the Co termination plane, we also constructed supercells with Si/Al and Fe terminations of the CFAS Heusler alloy film, shown in Supplementary Figure S9 after the geometry optimization for both rotated and nonrotated epitaxy cases.

In the case of a Si/Al termination plane, we obtained an energy difference of 0.81 eV/supercell in favor of formation of the rotated epitaxy, as for the case with the Co termination. In the cases with the Fe termination plane, the energy difference between the rotated and nonrotated epitaxy supercells was very small, within 0.1 eV. However, in the case of the nonrotated Fe-terminated interface, the interfacial Fe atoms after the geometry optimization are largely displaced to sites that do not follow the CFAS lattice. This is not consistent with the experimental results, where the CFAS interface plane follows the Ge lattice, as indicated in Figure 2a, and discussed below. Therefore, the formation of such interface is unlikely. The low formation probability of an Fe-terminated interface is also expected from the energy-based structural continuity considerations. In this case, the interfacial Ge would occupy sites that would be

populated by Co in bulk CFAS. Such Ge-Co substitutions have a very high energy, as discussed below.

Although we rule out Fe and Si/Al terminations at the CFAS/Ge interface based on the above arguments, the rotated models in these cases exhibit lower energies than their NRI counterparts. This demonstrates that the epitaxy rotation would not depend on the type of termination plane. However, considering the HAADF STEM experimental results showing the Co termination of the CFAS/Ge interface, our further analysis is focused only on Co-terminated models.

This calculation prediction is in line with the results of our electron microscopy imaging of cross-sectioned film/substrate interfaces. A measured HAADF STEM image of CFAS grown on Ge is presented in Figure 2a, while Figures 2(b, c) show simulated HAADF STEM images for the NRI and RI models of CFAS/Ge. According to these images, the RI model corresponds to the observed epitaxial relationship of CFAS with Ge, as indicated by the (001) Co atomic planes, outlined with the white dashed rectangles. The RI epitaxial relationship is further confirmed by the presented fast Fourier transform (FFT) patterns for regions selected in the Ge substrate and CFAS film in both experimental and simulated images. Therefore, the HAADF STEM imaging demonstrates the rotated epitaxial relationship of CFAS and Ge.

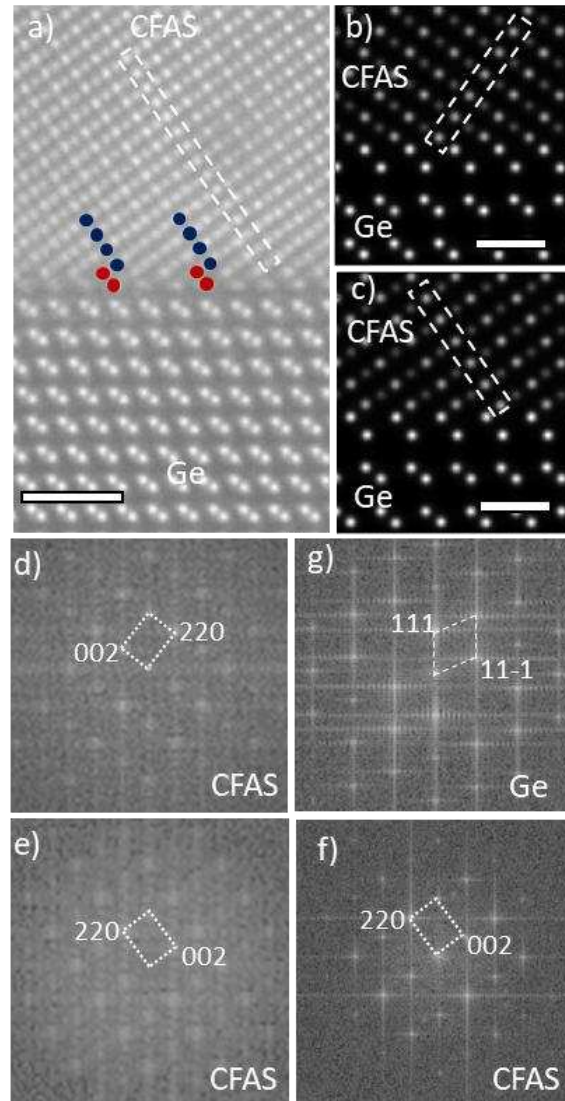


Figure 2. a) Experimental HAADF STEM image of the CFAS/Ge heterostructure, with an overlaid schematic showing the positions of several Co (blue) and Ge (red) atoms (scale bar: 1 nm). Simulated HAADF STEM images of CFAS/Ge with the b) nonrotated and c) rotated epitaxial relation between the film and substrate (scale bars: 0.5 nm). The dashed rectangles indicate a (001) Co plane to demonstrate the orientation matching in the RI case between the measured and simulated images. (d, e) FFT patterns of the CFAS film obtained by the simulated images in (b) and (c), respectively. FFT patterns of f) CFAS and g) Ge obtained from the experimental image in (a). The main crystallographic reflections for both CFAS and Ge are indicated.

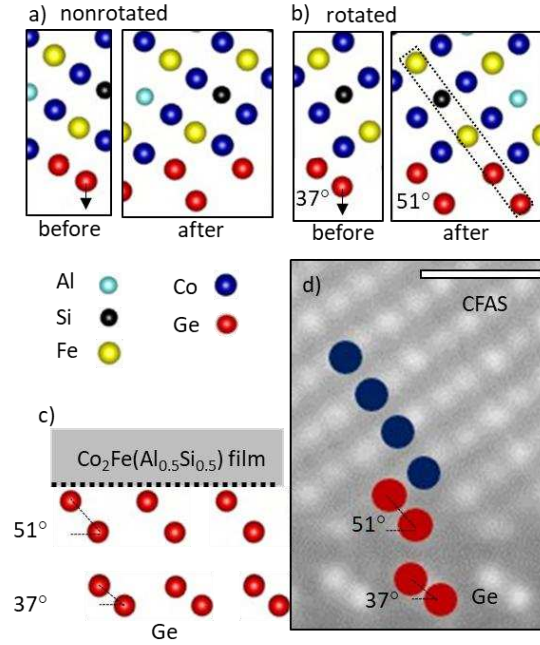


Figure 3. Structural models for the a) NRI and b) RI before and after geometry optimization at the interface region showing the displacements of the interfacial Ge atoms during the optimization from their bulk-like positions, as indicated by the arrows. The dashed rectangle in b) shows that the interfacial Ge atoms align in the Fe-Si/Al plane of CFAS after the geometry optimization. c) Tilting of the Ge dumbbells at the RI from 37° in the bulk-like interior of the substrate to 51° at the interface with respect to the interface plane. The dumbbell angles are defined with respect to the Ge (111) atomic plane. d) Magnified view of the experimental STEM image at the interface region of CFAS/Ge, with measured Ge dumbbell angles of $37^\circ \pm 1^\circ$ and $51^\circ \pm 1^\circ$ in the Ge substrate and at the interface, respectively, showing the excellent matching with the optimized RI model (scale bar: 0.5 nm).

Further, we investigate the origin of the epitaxy rotation from NRI to RI. In Figures 3(a, b), we show the structural models for NRI and RI, respectively, before and after the geometry optimization. As discussed above, the terminating Ge plane matches with a (Si, Al) atomic plane of CFAS, for both models. With this setting, for NRI, as shown in Figure 3a, the second-nearest Ge at the interface is positioned around a site that would be populated by Co in the CFAS structure. However, such Co–Ge swaps are very unlikely due to their high swapping energy [14]. In this regard, the CFAS structure “chooses” a different epitaxial relationship (RI) with the substrate to minimize the formation energy of the interface, which may be guided even by the first CFAS Co atomic plane, as discussed above.

In contrast, in the RI case, the second-nearest Ge is positioned around a site that would be occupied by an Fe atom of CFAS, and therefore only a slight displacement to such site occurs during the geometry optimization. Such Fe–Ge swaps are considerably more likely to occur than

Ge–Co swaps owing to their lower swapping energies [14]. The displacement of the second-nearest Ge from its initial substrate bulk-like position to the Fe site of CFAS results in a change in the [1-10]-projected bond angle between the nearest Ge and second-nearest Ge from 37° to 51° with respect to the interface plane, as shown in Figure 3c, in agreement with the experimental STEM image shown in Figure 3d.

Such repositioning of the Ge “dumbbell” pair was experimentally observed [14], and is further illustrated in Figure 2a and Figure 3d. The above analysis indicates that the Ge substrate guides the epitaxy of the CFAS film by positioning at the lower-energy Si/Al sites during the initial stage of growth. This agreement between the simulation and experiment on the fine structural changes at the interface region confirm the validity of our modelling of this heterostructure, and show that the epitaxial rotation results in a structural ordering at the interface.

To further demonstrate the structural ordering-induced origin of the epitaxy rotation, we grew and analyzed a CFAS film on a Si substrate. The formation of the same rotated epitaxy is also observed at the CFAS/Si interface (Figure 4a), where Si shares the same structural lattice as that of Ge. Therefore, the observation of the same epitaxy further confirms the structural lattice-origin of the epitaxy rotation.

In addition, we computed the energy difference between geometrically optimized CFAS(111) films on a GaAs(111) substrate with nonrotated and rotated epitaxial relationships. We obtained that the energy difference between the rotated and nonrotated models is 0.75 eV/supercell, in favor of epitaxy rotation (Figure 4b), in line with the epitaxial relationships observed for both Ge and Si substrates. The geometry optimization shows that the GaAs dumbbell pairs at the interface also tilt to fit in the Heusler lattice, as observed and discussed above when CFAS is grown on Ge.

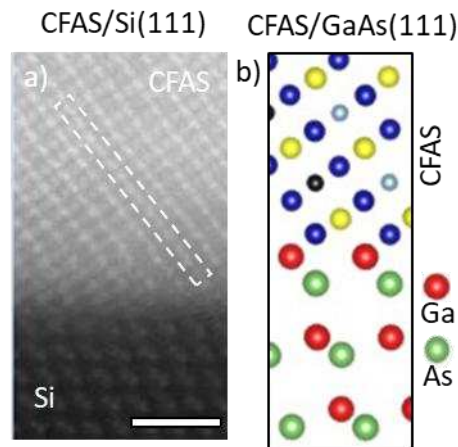


Figure 4. a) Experimental HAADF STEM image of a CFAS/Si heterostructure showing the same rotated epitaxial relation between the film and substrate, as indicated by the Co plane outlined by the dashed rectangle (scale bar: 1 nm). b) Geometrically optimized CFAS/GaAs interface with a rotated epitaxial relationship between the film and substrate.

Further, we investigate the electronic structures of RI and NRI on Ge. Figure 5 presents PDOSs for a relatively thin interface region (the dimensions of this region are specified in the caption) and those of the nearest Co and Fe atomic planes for both models, RI (dotted lines) and NRI (solid lines). The electronic structures are modified for both models, compared to those in the bulk CFAS (Figure 1). Both structures preserve the metallic state for the majority spin up electrons. However, the band gap of the minority spin down electrons present in the bulk CFAS is destroyed, due to the introduction of states at the spin-down channel around the Fermi level, as shown in Figure 5.

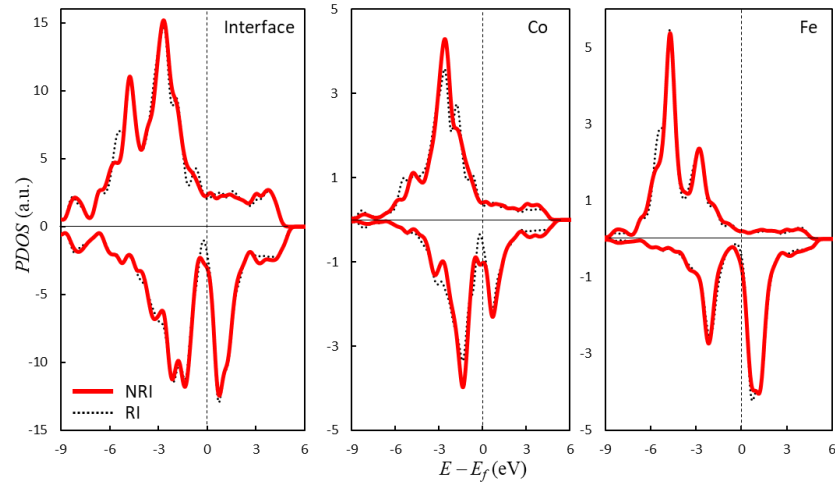


Figure 5. Calculated PDOSs for (left panel) a relatively thin interface region covering all element species (three nearest Co (111) planes, first nearest Fe (111) plane, first nearest (Al, Si) (111) plane, and nearest two Ge (111) planes), (middle panel) first nearest Co (111) plane, and (right panel) first nearest Fe (111) plane. The solid red and dotted black lines represent the results for the NRI and RI, respectively. The top and bottom panels show the PDOSs for the spin-up and spin-down electrons, respectively.

The extent of destruction of the band gap can be expressed by the SP, defined as $SP = (PDOS_u - PDOS_d) / (PDOS_u + PDOS_d)$, where $PDOS_u$ and $PDOS_d$ are the PDOSs for the majority spin-up and minority spin-down electrons at the Fermi level, respectively. The calculated SPs for NRI and RI for the interface region as well as those for the nearest single Co and Fe atomic planes are presented in Table 1.

Table 1. Calculated SPs of the nearest Co plane, nearest Fe plane, and interface region (Figure 5) for the NRI and RI.

Model	Co	Fe	Interface
Rotated	-24%	-46%	0%

Nonrotated	-43%	-57%	-14%
------------	------	------	------

As shown in Table 1, NRI consistently exhibits lower SPs than RI. The interface region for RI is depolarized, while that of NRI is inversely polarized (-14%). Regarding the single Co plane, the SP of RI is almost twice better than that of NRI. Although the SP change for the single Fe nearest plane is smaller, the trend that RI is better than NRI in terms of interfacial SP is still observed. These results suggest that the CFAS/Ge orders with a RI orientation, rather than with the “expected” NRI orientation, and that this epitaxial relationship improves the interfacial electronic structure and SP. This natural “reorganization” of the CFAS/Ge toward a better SP further confirms its high potential for spintronic applications.

Further, we consider the intermixing effect on both models by Ge–Fe and Ge–Co atomic swaps within the interface region of the supercells, as well as the effects of a selective Ge out-diffusion along Fe–Si/Al columns, observed previously by energy-dispersive spectroscopy [14].

Our set of calculations for RI show that the model with a Ge–Fe swap (model M3 in Figure 6) has a lower energy than the bulk-like-terminated CFAS/Ge RI (by 0.29 eV). This shows that Fe–Ge interdiffusion is likely to occur at the interface. Such behavior has also been demonstrated for the CFAS/Ge interface along the [001] growth direction [16]. As in the [001]-oriented growth case, for the [111] growth direction considered in this study, this likely interdiffusion unexpectedly improves the electronic structure at the interface, as shown in Figure 6 (model M3), with a positive interfacial SP of 15%. In contrast, for RI, the Ge–Co swapping energy is 0.78 eV, showing that such swaps are very unlikely to occur, which is desirable, as any changes in the Co sublattice could largely reduce the interfacial SP of the CFAS [21]. In the case of NRI, both Ge–Fe and Ge–Co swaps are favored, with swapping energies of 0.15 and 0.05 eV, respectively. This suggests that, even if this interface is formed, it would suffer from a considerable interdiffusion affecting both Co and Fe sublattices, and thus yielding reduced performances of such interface.

The models denoted as M1 and M2 in Figure 6 are obtained by substituting the first and first two Fe–Si/Al planes of CFAS with Ge in the energetically more favored RI model, respectively, according to the previously observed selective out-diffusion of Ge [14]. Their interfacial SPs are 32% and 19%, respectively. Therefore, all three considered models M1–M3 involving Ge diffusion across the energetically favored RI demonstrate an unexpected beneficial effect of the diffusion on the interfacial SP.

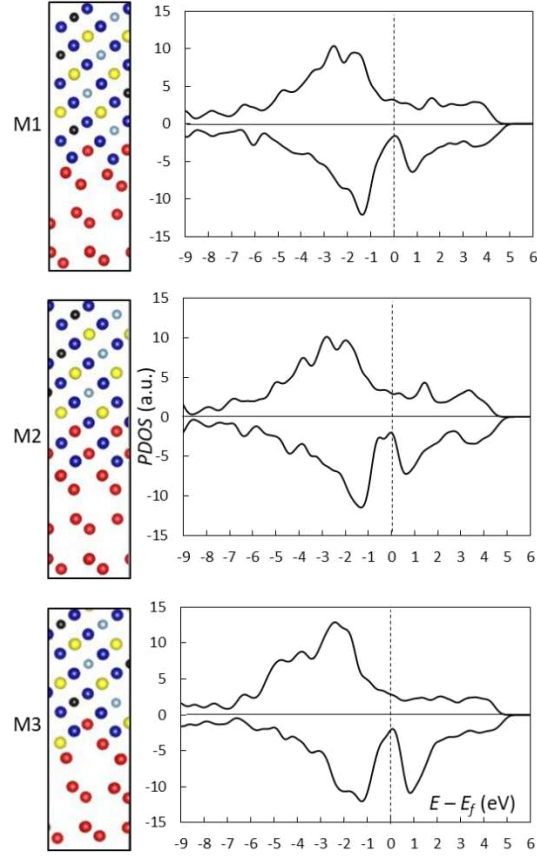


Figure 6. Calculated PDOSs for an interface region with the same dimensions as that in Figure 5 for RI models with a local Ge diffusion (illustrated in the left panels). Models M1 and M2 are obtained by substituting the first and first two Fe-Si/Al planes of CFAS with Ge, respectively, according to the observed selective out-diffusion of Ge. Model M3 is obtained by swapping Fe and Ge across the interface. The Fermi level is indicated by the dashed line.

4. Conclusions

The half-metal/semiconductor interfaces are crucial for hybrid spintronic devices. The epitaxial growth approach enables control of atomic structure and ultimately provides desired electronic properties including an improved SP. We investigated the origin of the rotated epitaxial relationship at the interface between the half-metallic CFAS grown by MBE and Ge, and effects of the epitaxy rotation on the interfacial spin-electronic properties. The DFT calculations demonstrated that the 180°-rotated epitaxy has a lower formation energy, due to the initial bonding configuration of the Co layer, which results in a significant change in the bond angle of the interfacial Ge dumbbell layer, in an excellent agreement with experimental data. In addition, we showed that the interfacial layer of Ge is incorporated to fit the atomic stacking of Si, Al sites

in the CFAS film. This atomic arrangement decreases the interface formation energy and considerably increases the interfacial SP. Furthermore, we showed that the low-energy Fe–Ge intermixing and observed selective Ge out-diffusion into the film could provide even higher interfacial SPs. The rotated epitaxy is preserved when CFAS is grown on Si even in the presence of the significant interface intermixing. These findings suggest that the CFAS/Ge interface achieves a largely improved electronic structure through epitaxial rotation and interdiffusion, which could guide the design of novel optimized spintronic heterostructures through interfacial atomic structure control.

Acknowledgement

We acknowledge the support by EPSRC [EP/S033394/1]. The Viking cluster was used during this project, which is a high-performance compute facility provided by the University of York. We are grateful for the computational support from the University of York, IT Services and Research IT team. We also acknowledge SuperSTEM, the UK National Research Facility for Advanced Electron Microscopy supported in part by the Engineering and Physical Sciences Research Council (EPSRC) under Grant No. EP/W021080/1.

Conflicts of Interest

The authors have no conflicts to disclose.

Author Contributions

Julio A. do Nascimento: Data curation, Formal analysis, Writing – original draft, Writing – review and editing; **Zlatko Nedelkoski:** Data curation, Formal analysis, Writing – original draft, Writing – review and editing; **Demie Kepaptsoglou:** Data curation, Formal analysis, Resources, Writing – review and editing; **Shinya Yamada:** Data curation; **Kohei Hamaya:** Data curation, Formal analysis, Resources, Writing – review and editing; **Vlado K. Lazarov:** Conceptualization, Formal analysis, Resources, Writing – original draft, Writing – review and editing.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] M.I. Katsnelson, V.Y. Irkhin, L. Chioncel, A.I. Lichtenstein, R.A. de Groot, Half-metallic ferromagnets: from band structure to many-body effects, *Rev. Mod. Phys.* 80 (2008) 315.
- [2] A. Hirohata, D.C. Lloyd, Heusler alloys for metal spintronics, *MRS Bull.* 47 (2022) 593.
- [3] Y. Xie, S.-Y. Zhang, Y. Yin, N. Zheng, A. Ali, M. Younis, S. Ruan, Y.-J. Zeng, Emerging ferromagnetic materials for electrical spin injection: towards semiconductor spintronics, *npj Spintronics* 3 (2025) 10.
- [4] K. Kudo, M. Yamada, S. Honda, Y. Wagatsuma, S. Yamada, K. Sawano, K. Hamaya, Room-temperature two-terminal magnetoresistance ratio reaching 0.1% in semiconductor-based lateral devices with L_{21} -ordered Co_2MnSi , *Appl. Phys. Lett.* 118 (2021) 162404.
- [5] K. Oki, S. Ueda, T. Usami, S. Fujii, S. Kikuoka, K. Yamamoto, K. Hamaya, Room-temperature spin transport through band-to-band tunneling at semiconductor p-n junctions, *Phys. Rev. Appl.* 23 (2025) L051005.
- [6] B. Achinuq, Y. Fujita, M. Yamada, S. Yamada, A.M. Sanchez, P.J. Hasnip, A. Ghasemi, D. Kepaptsoglou, G. Bell, K. Sawano, K. Hamaya, V.K. Lazarov, Correlation between spin transport signal and Heusler/semiconductor interface quality in lateral spin-valve devices, *Phys. Rev. B* 98 (2018) 115304.
- [7] R. Shan, H. Sukegawa, W.H. Wang, M. Kodzuka, T. Furubayashi, T. Ohkubo, S. Mitani, K. Inomata, K. Hono, Demonstration of half-metallicity in Fermi-level-tuned Heusler alloy $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ at room temperature, *Phys. Rev. Lett.* 102 (2009) 246601.
- [8] T. Naito, R. Nishimura, M. Yamada, A. Masago, Y. Shiratsuchi, Y. Wagatsuma, K. Sawano, R. Nakatani, T. Oguchi, K. Hamaya, Significant effect of interfacial spin moments in ferromagnet-semiconductor heterojunctions on spin transport in a semiconductor, *Phys. Rev. B* 105 (2022) 195308.
- [9] Y. Fujita, M. Yamada, M. Tsukahara, T. Oka, S. Yamada, T. Kanashima, K. Sawano, K. Hamaya, Spin transport and relaxation up to 250 K in heavily doped n-type Ge detected using $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ electrodes, *Phys. Rev. Appl.* 8 (2017) 014007.
- [10] G. Schmidt, D. Ferrand, L.W. Molenkamp, A.T. Filip, B.J. van Wees, Fundamental obstacle for electrical spin injection from a ferromagnetic metal into a diffusive semiconductor, *Phys. Rev. B* 62 (2000) R4790.
- [11] Z. Nedelkoski, D. Kepaptsoglou, A. Ghasemi, B. Kuerbanjiang, P.J. Hasnip, S. Yamada, K. Hamaya, Q.M. Ramasse, A. Hirohata, V.K. Lazarov, Controlling the half-metallicity of Heusler/Si(1 1 1) interfaces by a monolayer of Si-Co-Si, *J. Phys.: Condens. Matter* 28 (2016) 395003.
- [12] B. Kuerbanjiang, Z. Nedelkoski, D. Kepaptsoglou, A. Ghasemi, S.E. Glover, S. Yamada, T. Saerbeck, Q.M. Ramasse, P.J. Hasnip, T.P.A. Hase, G.R. Bell, K. Hamaya, A. Hirohata, V.K. Lazarov,

The role of chemical structure on the magnetic and electronic properties of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}/\text{Si}(111)$ interface, *Appl. Phys. Lett.* 108 (2016) 172412.

[13] S.E. Glover, T. Saerbeck, A. Ghasemi, D. Kepaptsoglou, Q.M. Ramasse, S. Yamada, K. Hamaya, T.P.A. Hase, V.K. Lazarov, G.R. Bell, Magnetic and structural depth profiles of Heusler alloy $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ epitaxial films on $\text{Si}(1\ 1\ 1)$, *J. Phys.: Condens. Matter* 30 (2018) 065801.

[14] Z. Nedelkoski, B. Kuerbanjiang, S.E. Glover, A.M. Sanchez, D. Kepaptsoglou, A. Ghasemi, C.W. Burrows, S. Yamada, K. Hamaya, Q.M. Ramasse, P.J. Hasnip, T. Hase, G.R. Bell, A. Hirohata, V.K. Lazarov, Realisation of magnetically and atomically abrupt half-metal/semiconductor interface: $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Ge}(111)$, *Sci. Rep.* 6 (2016) 37282.

[15] K. Hamaya, M. Yamada, Semiconductor spintronics with Co_2 -Heusler compounds, *MRS Bull.* 47 (2022) 584.

[16] Z. Nedelkoski, J.A. Nascimento, K. Hamaya, V.K. Lazarov, Effects of atomic structures at $\text{Co}_2\text{Fe}(\text{Al}_{0.5}\text{Si}_{0.5})/\text{Ge}$ interfaces on spin-electronic properties, *J. Phys. D: Appl. Phys.* 58 (2025) 245301.

[17] M. Yamada, F. Kuroda, M. Tsukahara, S. Yamada, T. Fukushima, K. Sawano, T. Oguchi, K. Hamaya, Spin injection through energy-band symmetry matching with high spin polarization in atomically controlled ferromagnet/ferromagnet/semiconductor structures, *NPG Asia Mater.* 12 (2020) 47.

[18] Z. Nedelkoski, A.M. Sanchez, A. Ghasemi, K. Hamaya, R.F.L. Evans, G.R. Bell, A. Hirohata, V.K. Lazarov, The antiphase boundary in half-metallic Heusler alloy $\text{Co}_2\text{Fe}(\text{Al},\text{Si})$: atomic structure, spin polarization reversal, and domain wall effects, *Appl. Phys. Lett.* 109 (2016) 222405.

[19] S. Picozzi, A.J. Freeman, Polarization reduction in half-metallic Heusler alloys: the effect of point defects and interfaces with semiconductors, *J. Phys.: Condens. Matter* 19 (2007) 315215.

[20] Y. Sakuraba, T. Iwase, K. Saito, S. Mitani, K. Takanashi, Enhancement of spin-asymmetry by $L2_1$ -ordering in $\text{Co}_2\text{MnSi}/\text{Cr}/\text{Co}_2\text{MnSi}$ current-perpendicular-to-plane magnetoresistance devices, *Appl. Phys. Lett.* 94 (2009) 012511.

[21] P. Hasnip, C. Loach, J. Smith, M. Probert, D. Gilks, J. Sizeland, L. Lari, J. Sagar, K. Yoshida, M. Oogane, A. Hirohata, V. Lazarov, The effect of cobalt-sublattice disorder on spin polarisation in $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ Heusler alloys, *Materials* 7 (2014) 1473.

[22] V.K. Lazarov, K. Yoshida, J. Sato, P.J. Hasnip, M. Oogane, A. Hirohata, Y. Ando, The effect of film and interface structure on the transport properties of Heusler based current-perpendicular-to-plane spin valves, *Appl. Phys. Lett.* 98 (2011) 242508.

[23] Z. Nedelkoski, P.J. Hasnip, A.M. Sanchez, B. Kuerbanjiang, E. Higgins, M. Oogane, A. Hirohata, G.R. Bell, V.K. Lazarov, The effect of atomic structure on interface spin-polarization of half-metallic spin valves: $\text{Co}_2\text{MnSi}/\text{Ag}$ epitaxial interfaces, *Appl. Phys. Lett.* 107 (2015) 212404.

- [24] M. Yamada, Y. Shiratsuchi, H. Kambe, K. Kudo, S. Yamada, K. Sawano, R. Nakatani, K. Hamaya, Effect of Fe atomic layers at the ferromagnet–semiconductor interface on temperature-dependent spin transport in semiconductors, *J. Appl. Phys.* 129 (2021) 183901.
- [25] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, M.C. Payne, First principles methods using CASTEP, *Z. Kristallogr.* 220 (2005) 567.
- [26] S. Chadov, G.H. Fecher, C. Felser, J. Minár, J. Braun, H. Ebert, Electron correlations in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler compounds, *J. Phys. D: Appl. Phys.* 42 (2009) 084002.
- [27] P.J. Hasnip, J.H. Smith, V.K. Lazarov, Ab initio studies of disorder in the full Heusler alloy $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$, *J. Appl. Phys.* 113 (2013) 17B106.
- [28] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.* 44 (2011) 1272.
- [29] A.J. Morris, R.J. Nicholls, C.J. Pickard, J.R. Yates, OptaDOS: a tool for obtaining density of states, core-level and optical spectra from electronic structure codes, *Comput. Phys. Commun.* 185 (2014) 1477.
- [30] K. Ueda, K. Hamaya, K. Yamamoto, Y. Ando, T. Sadoh, Y. Maeda, M. Miyao, Low-temperature molecular beam epitaxy of a ferromagnetic full-Heusler alloy on Ge(111), *Appl. Phys. Lett.* 93 (2008) 112108.
- [31] K. Hamaya, K. Ueda, Y. Kishi, Y. Ando, T. Sadoh, M. Miyao, Epitaxial ferromagnetic $\text{Fe}_3\text{Si}/\text{Si}(111)$ structures with high-quality heterointerfaces, *Appl. Phys. Lett.* 93 (2008) 132117.
- [32] K. Tanikawa, S. Oki, S. Yamada, M. Kawano, M. Miyao, K. Hamaya, High-quality $\text{Co}_2\text{FeSi}_{0.5}\text{Al}_{0.5}/\text{Si}$ heterostructures for spin injection in silicon spintronic devices, *Thin Solid Films* 557 (2014) 390.
- [33] S. Oki, S. Yamada, T. Murakami, M. Miyao, K. Hamaya, Influence of Al co-deposition on the crystal growth of Co-based Heusler-compound thin films on Si(111), *Thin Solid Films* 520 (2012) 3419.
- [34] C.T. Koch, Determination of core structure periodicity and point defect density along dislocations, Ph.D. thesis, Arizona State University (2002).