Fast Track Communication

Correlations between atomic structure and giant magnetoresistance ratio in Co$_2$(Fe,Mn)Si spin valves

L Lari$^{1,2}$, K Yoshida$^3$, P L Galindo$^4$, J Sato$^5$, J Sizeland$^1$, D Gilks$^1$, G M Uddin$^1$, Z Nedelkoski$^1$, P J Hasnip$^1$, A Hirohata$^{6,7}$, M Oogane$^5$, Y Ando$^5$ and V K Lazarov$^1$

$^1$ Department of Physics, University of York, Heslington, York, YO10 5DD, UK
$^2$ York JEOL Nanocentre, Helix House, Science Park, Heslington, York, YO10 5BR, UK
$^3$ Nanostructures Research Laboratory, Japan Fine Ceramics Centre, 2-4-1 Matsumo, Atsuta-ku, Nagoya, 456–8587, Japan
$^4$ Departamento de Lenguajes y Sistemas Informáticos, CASEM, Universidad de Cádiz, Campus Río San Pedro, s/n, 11510 Puerto Real, Cádiz, Spain
$^5$ Department of Applied Physics, Graduate School of Engineering, Tohoku University, Aoba-yama 6-6-05, Aramaki, Aoba-ku, Sendai 980–8579, Japan
$^6$ Department of Electronics, University of York, Heslington, York, YO10 5DD, UK
$^7$ PRESTO, Japan Science and Technology Agency, Kawaguchi, Saitama 332-0012, Japan

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

Received 6 May 2014, revised 12 June 2014
Accepted for publication 23 June 2014
Published 18 July 2014

Abstract

We show that the magnetoresistance of Co$_2$Fe$_x$Mn$_{1-x}$Si-based spin valves, over 70% at low temperature, is directly related to the structural ordering in the electrodes and at the electrodes/spacer (Co$_2$Fe$_x$Mn$_{1-x}$Si/Ag) interfaces. Aberration-corrected atomic resolution Z-contrast scanning transmission electron microscopy of device structures reveals that annealing at 350 °C and 500 °C creates partial B$_2$/L$_2$ and fully L$_2$ ordering of electrodes, respectively. Interface structural studies show that the Ag/Co$_2$Fe$_x$Mn$_{1-x}$Si interface is more ordered compared to the Co$_2$Fe$_x$Mn$_{1-x}$/Si/Ag interface. The release of interface strain is mediated by misfit dislocations that localize the strain around the dislocation cores, and the effect of this strain is assessed by first principles electronic structure calculations. This study suggests that by improving the atomic ordering and strain at the interfaces, further enhancement of the magnetoresistance of CFMS-based current-perpendicular-to-plane spin valves is possible.

Keywords: Heusler alloys, half-metals, thin films, spintronics materials

(Some figures may appear in colour only in the online journal)
a Co$_2$FeAl$_{0.5}$Si$_{0.5}$/Ag/Co$_2$FeAl$_{0.5}$Si$_{0.3}$ structure [12]. The MR is usually expected to be enhanced by improving the ordering of the Heusler alloy electrodes (from A2 and B2 to L2$_1$) since the ordering improves the half-metallicity and thus enhances the asymmetric spin scattering across the layers. Another important factor is the spin polarization at the interface between the electrodes and metallic spacers. Theoretical approaches have shown [13–16] that even at atomically abrupt interfaces spin polarization can be lost which would potentially reduce the MR of devices.

Recently, in Co$_2$Fe$_x$Mn$_{1-x}$Si (CFMS) it has been shown that both the Gilbert damping constant and the half-metallic band gap can be tailored with respect to Co$_2$MnSi (CMS) and Co$_2$FeSi (CFS) [7]. Furthermore, structural studies of CFMS have shown that a relatively well-ordered L2$_1$ phase can be achieved, in comparison to CMS [17]. These properties result in CFMS-based CPP-SVs outperforming devices based on CMS and Co$_2$MnGe in terms of magnetoresistance [10, 17, 18].

In this work we correlate the atomic structure of the electrodes and spacer-electrode interfaces with magnetotransport properties of Co$_2$Fe$_x$Mn$_{1-x}$Si/Ag/Co$_2$Fe$_x$Mn$_{1-x}$Si (CFMS/Ag/CMS) CPP-SVs. In addition we show that the improved properties of CFMS/Ag/CFMS CPP-SVs when compared with CMS/Ag/CMS CPP-SVs can be directly correlated with the improved atomic structure of both the electrode and the electrode/spacer interface of the former CPP-SV (CFMS).

The CPP-SV structure was deposited on a MgO(001) substrate, and consist of the following layers: Ru(10)/CFMS(5)/Ag(5)/CFMS(20)/Ag(50)/Cr(20)/MgO, all layer thicknesses are given in nm. The CFMS layers were deposited using Co–Fe–Mn–Si alloyed targets (Co: 45.2%, Fe: 9.7%, Mn: 16.8%, Si: 28.3%) which result in Co$_2$Fe$_{0.4}$Mn$_{0.6}$Si layers. In order to improve the CFMS crystallinity, in situ annealing has been performed. After the deposition of the bottom electrode (CFMS, 20 nm) the structure was annealed at 500°C. Similarly after the deposition of the top electrode (CFMS, 5 nm) the whole structure was annealed at 350°C. The lower annealing temperature of the final structure was chosen in order to minimize the atomic interlayer diffusion.

Atomic structure studies were performed by aberration-corrected scanning transmission electron microscopy (STEM) using high angle annular dark field (HAADF) techniques which are Z-contrast (where Z is atomic number) sensitive. These experiments were performed on JEOL ARM and JEOL 2200FS microscopes. Cross-sectional microscope specimens were prepared by conventional methods including mechanical thinning/polishing and low energy Ar ion milling to electron transparency [19]. Strain-mapping was performed using geometrical phase analysis techniques [20]. The magnetoresistance measurements were performed using a conventional dc 4-probe method from 20 K to room temperature with an applied magnetic field of up to 1 kOe.

Magnetoresistance measurements in figure 1(a) show 78% MR at 1 kOe at 20 K which gradually decreases with temperature to a value of 20% at 1 kOe at room temperature. In comparison CMS-based CPP-SVs show 20% MR at 20 K and 14% at room temperature [17]. These results show the advantage of CFMS compared to CMS electrodes.

In order to understand the cause of the better performance of the CFMS CPP-SVs, it is necessary to study its structure on the atomic level. Figure 1(b) shows a cross-sectional view of the CPP-SV structure using HAADF. All the layers, including the substrate, are clearly distinguished due to the Z-contrast characteristic of HAADF imaging clearly shows the seed layers (Cr, Ag), device layers (CFMS, Ag, CFMS) and the Ru capping layer.

All the layers in the junction are epitaxially related and have single crystal structure. The following epitaxial crystallographic relation between the CFMS and Ag are observed: CFMS(1 1 0)||Ag(1 0 0) and CFMS(0 0 1)||Ag(0 0 1). This epitaxy, with a 45° in-plane rotation of the CFMS crystal structure with respect to the Ag layer is expected as this minimizes the mismatch between Ag and CFMS to 2%. Atomic resolution imaging figure 2(a), from the CFMS/Ag/CFMS trilayer shows that both electrodes are in [1 1 0] direction while the Ag spacer layer in [1 0 0] viewing direction, this is confirmed by the digital diffractograms (not shown). The [1 1 0] viewing direction is particularly useful because each of the atomic species on the four FFC sublattices of the Heusler alloy e.g. Co, Fe/Mn and Si are projected...
Figure 2. (a) Z-contrast atomic resolution of the CFMS/Ag/CFMS layers in the [1 1 0] direction, showing the abrupt interface structure of the electrodes with Ag, and the L2₁ ordering of the bottom electrode. (b) The top CFMS/Ag interface showing partial ordering in the top electrode, with B2 and L2₁ regions. Atomic models of B2 and L2₁ ordering (c) and (d) and simulated HAADF images (e) and (f) showing the origin of the contrast change in Mn/Fe and Si atomic columns.

along individual atomic columns. Therefore the intensity in the HAADF images can be directly correlated to the atomic species as illustrated in figures 2(c)–(f) with the brightest columns corresponding to Co and darkest to Si. The presence of the low scattering atomic columns (Si) is clearly seen in the bottom electrode, followed by the Fe/Mn, and the most intense Co columns. This indicates the L2₁ ordering of the bottom electrode. In contrast to the bottom electrode the top electrode shows partial ordering (figures 2(a) and (b)), which is evident from the loss of variation in intensity between the Fe/Mn and Si atomic sites, as shown in the right-hand region of figure 2(b). Due to the significant difference in atomic number between Si and Fe/Mn atoms, these columns are clearly distinguished in the L2₁ phase, but when mixing between those two atomic columns is present (the B2 phase) the intensity of the nominal Fe/Mn and Si sites becomes uniform, as illustrated in figures 2(d) and (f). This disordering of the top electrode reduces the spin polarization of the top electrode by up to 20% compared to the fully ordered L2₁ phase, as shown by previous PBE +U simulations of Co₂Fe₃₋ₓMnₓSi for x = 0.5 [21].

It is interesting to note that the energy of Mn-Si and Fe-Si mixing in CFMS is similar, and in general slightly lower than in CMS (by ~0.002 eV/atom), but slightly higher (by ~0.01 eV/atom) than in CFS [22, 23]. Due to the relatively low energy of the (Fe/Mn)-Si disorder, the 500 °C annealing temperatures fully removes the B2 disorder, as shown for the bottom electrode.

Next we focus on the interface structure of the Ag/CFMS (spacer/bottom electrode) and CFMS/Ag interfaces (top electrode/spacer). Despite the relatively low lattice mismatch (2%), and the low thickness of the Ag layer and top CFMS electrode, misfit dislocations in both layers have been observed. Figure 3(a) shows an atomic resolution HAADF image of the Ag/CFMS interface. It can be observed that in the middle interface region, figure 3(a), the contrast of Ag atomic columns is reduced due to the presence of an edge misfit dislocation, as clearly outlined by the Bragg-filtered (2 2 0) atomic planes, figure 3(b). We note that the dislocation core is about 2–3 atomic layers above the interface plane, indicating that the strain field is mainly in the Ag layer. Full quantification and strain mapping around the dislocation core is shown as an inset in figure 3(b). As expected, around the dislocation core the strain field varies from positive (expansion of the atomic columns’ separation) to negative (compression of the atomic columns), towards the bottom electrode. This strain field would change the electronic properties of the spacer locally, but the overall effect can be neglected since the dislocation(s) in Ag are neither charged nor magnetic, and hence have only a localized effect.

The top electrode also contains a network of misfit dislocations, as illustrated in figures 3(c)–(e). From figure 3(c) one can observe that the terrace steps at the CFMS/Ag interface (top) are more frequent than those at the bottom Ag/CFMS interface. The Bragg filtering analysis in figures 3(d) and (e) shows a pair of misfit dislocations nucleated at a step edge, with Burgers vectors perpendicular to each other. We note that at the lower interface strain is released by single edge misfit dislocations.

In contrast to the bottom interface, the misfit dislocations for the top CFMS/Ag interface occur in the Heusler electrode, not the Ag spacer. The strain field associated with each dislocation is likely to modify the spin polarization of even fully L2₁-ordered electrodes, in addition to the effect of any chemical disorder. Since the atomic distances are far from the
Figure 3. (a) Atomic resolution image of Ag/CFMS-bottom electrode interface showing a region with misfit dislocation, outlined by Bragg filtering of (220) atomic planes in (b). (c) Region of the top-electrode CFMS/Ag interface at surface step edge showing two misfit dislocations, outlined by Bragg filtering the (2 2 0) reflection in (d) and the (0 0 2) planes in (e).

equilibrium, the effect is expected to be towards decreasing the spin polarization around the dislocation regions.

This effect of the strain can be simulated approximately by computing the electronic structure of the material under isotropic strain. First principles density-of-states calculations with the Castep program [24] using PBE + U with $U = 2.1$ eV [25] show that whilst the unstrained CFMS is half-metallic, the half-metallicity does not persist under isotropic strain. Under compression (negative strain) the spin polarization at the Fermi level decreases smoothly from fully polarized at the equilibrium lattice constant to completely depolarized at a strain close to $-10\%$. For larger compressive strains the spin polarization at the Fermi-level reverses, becoming slightly negative, indicating that there are more minority spin states at the Fermi-level than majority states. Under tension (positive strain) the Fermi-level polarization decreases more rapidly, with the material depolarizing at strains close to $+5\%$; larger strains cause the spin polarization at the Fermi-level to reverse.

In summary, we have shown that single-crystal CPP-SVs based on CFMS show better MR compared to analogous CMS-based devices. A critical improvement over the CMS electrodes when used in combination with Ag spacer is the lower ordering temperatures for CFMS, as well as the atomically sharper interface of both the bottom and top electrodes with the spacer layer. An interface analysis of the top and bottom interfaces has shown the presence of misfit dislocations in Ag and the top electrode layer. First principles calculations of isotropically strained CFMS indicate that these dislocations would have a detrimental effect on the spin polarization at the Fermi level. Due to the strain induced in the upper interface as a result of step edge misfits this region is expected to be the most significantly affected, this is expected to reduce the overall MR of the device. Finally, this study has demonstrated that the structural properties of the CFMS CPP-SV devices can in principle be improved further, in particular the ordering of the top electrode, and this will enable CFMS-based devices with larger MR.

Acknowledgment

This work has been supported by Engineering and Physical Sciences Research Council, grant number EP/K03278X/1.

References

[1] Felser C, Fecher G H and Balke B 2007 Spintronik: eine Herausforderung für Materialwissenschaften und Festkörperchemie Angew. Chem. 119 680–713
[2] Sakuraba Y et al 2006 Direct observation of half-metallic energy gap in Co$_2$MnSi by tunneling conductance spectroscopy Appl. Phys. Lett. 89 192508
[3] Ishikawa T et al 2006 Spin-dependent tunneling characteristics of fully epitaxial magnetic tunneling junctions with a full-Heusler alloy Co2MnSi thin film and a MgO tunnel barrier Appl. Phys. Lett. 89 192505

[4] Tsunegi S et al 2008 Large tunnel magnetoresistance in magnetic tunnel junctions using a Co2MnSi Heusler alloy electrode and a MgO barrier Appl. Phys. Lett. 93 112506

[5] Hirohata A et al 2013 Heusler-alloy films for spintronic devices Appl. Phys. A 111 423–30

[6] Ishida S et al 1995 Search for half-metallic compounds in Co2MnZ (Z = IIIb, IVb, Vb element) J. Phys. Soc. Japan 64 2152

[7] Kubota T et al 2009 Half-metallicity and Gilbert damping constant in Co2Fe,Mn1−xSi Heusler alloys depending on the film composition Appl. Phys. Lett. 94 122504

[8] Furubayashi T et al 2008 Current-perpendicular-to-plane giant magnetoresistance in spin-valve structures using epitaxial Co2FeAl0.5Si0.5/Ag/Co2FeAl0.5Si0.5 trilayers Appl. Phys. Lett. 93 122507

[9] Iwase Y et al 2009 ‘All-Heusler alloy’ current-perpendicular-to-plane giant magnetoresistance Appl. Phys. Lett. 94 222501

[10] Nikolaev K et al 2009 Enhancement of spin-asymmetry by L21-ordering in fully epitaxial Co2MnSi/Cr/Co2MnSi current-perpendicular-to-plane magnetoresistive devices Appl. Phys. Express 2 067003

[11] Sakuraba Y et al 2009 Enhancement of spin-asymmetry by L21-ordering in Co2MnSi/Cr/Co2MnSi current-perpendicular-to-plane magnetoresistive devices Appl. Phys. Lett. 94 012511

[12] Nakatani T M et al 2010 Bulk and interfacial scatterings in current-perpendicular-to-plane giant magnetoresistance with Co2Fe(Al0.5Si0.5) Heusler alloy layers and Ag spacer Appl. Phys. Lett. 96 212501

[13] Nagao K, Miura Y and Shirai M 2006 Half-metallicity at the (1 1 0) interface between a full Heusler alloy and GaAs Phys. Rev. B 73 104447

[14] Yoshio M et al 2007 Coherent tunnelling conductance in magnetic tunnel junctions of half-metallic full Heusler alloys with MgO barriers J. Phys.: Condens. Matter 19 365228

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

[16] Picozzi, S., Continenza A and Freeman A J 2004 Role of structural defects on the half-metallic character of Co2MnGe and Co2MnSi Heusler alloys Phys. Rev. B 69 094423

[17] Lazarov V K et al 2011 The effect of film and interface structure on the transport properties of Heusler based current-perpendicular-to-plane spin valves Appl. Phys. Lett. 98 242508

[18] Carey M J et al 2011 Co2MnGe-based current-perpendicular-to-the-plane giant-magnetoresistance spin-valve sensors for recording head applications J. Appl. Phys. 109 093912

[19] Lari L et al 2012 Ferromagnetic InMnSb multi-phase films study by aberration-corrected (scanning) transmission electron microscopy J. Appl. Phys. 111 07C311

[20] Hýtch M J, Snoeck E and Kilaas R 1998 Quantitative measurement of displacement and strain fields from HREM micrographs Ultramicroscopy 74 131–46

[21] Hasnip P J, Smith J H and Lazarov V K 2013 Ab initio studies of disorder in the full Heusler alloy Co2Fe,Mn1−xSi J. Appl. Phys. 113 17B106

[22] Hasnip P J et al 2014 B2 Atomic Disorder in Co2Fe,Mn1−xSi Heusler Alloys J. Magn. Soc. Jpn 38 50–5

[23] Hasnip P J et al 2014 The effect of cobalt-sublattice disorder on spin polarisation on Co2Fe,Mn1−xSi Heusler alloys Materials 7 1473–82

[24] Clark S J et al 2005 First principles methods using CASTEP Z. Kristallogr. 220 567

[25] Chadov S et al 2009 Electron correlations in Co2Mn1−xFe2-x Si Heusler compounds J. Phys. D: Appl. Phys. 42 084002