Evolution of the interfacial perpendicular magnetic anisotropy constant of the Co$_2$FeAl/MgO interface upon annealing

A Conca$^1$, A Niesen$^2$, G Reiss$^2$ and B Hillebrands$^1$

$^1$ Fachbereich Physik and Landesforschungszentrum OPTIMAS, Technische Universität Kaiserslautern, 67663 Kaiserslautern, Germany
$^2$ Physics Department, Center for Spinelectronic Materials and Devices, Bielefeld University, 33615 Bielefeld, Germany

E-mail: conca@physik.uni-kl.de

Received 23 January 2018, revised 8 March 2018
Accepted for publication 12 March 2018
Published 28 March 2018

Abstract
We investigate a series of films with different thickness of the Heusler alloy Co$_2$FeAl in order to study the effect of annealing on the interface with a MgO layer and on the bulk magnetic properties. Our results reveal that while the perpendicular interface anisotropy constant $K^\perp_S$ is zero for the as-deposited samples, its value increases with annealing up to a value of $1.14\pm0.07\text{ m J m}^{-2}$ for the series annealed at 320 °C and of $2.01\pm0.7\text{ m J m}^{-2}$ for the 450 °C annealed series owing to a strong modification of the interface during the thermal treatment. This large value ensures a stabilization of a perpendicular magnetization orientation for an extrapolated thickness below 1.7 nm. The data additionally shows that the in-plane biaxial anisotropy constant has a different evolution with thickness in as-deposited and annealed systems. The Gilbert damping parameter $\alpha$ shows minima for all series for a thickness of 40 nm and an absolute minimum value of $2.8\pm0.1\times10^{-3}$. The thickness dependence is explained in terms of an inhomogeneous magnetization state generated by the interplay between the different anisotropies of the system and by the crystalline disorder.

Keywords: Heusler, PMA, interface, CFA, perpendicular magnetization, damping, FMR

(Some figures may appear in colour only in the online journal)
MgO interface, by measuring different thickness series. Since the in-plane anisotropies and the Gilbert damping parameter change with varying thickness and annealing temperature, also their evolution is reported. The relevance of the study is not limited to Co$_2$FeAl but it is a model for all TMR systems with Co-based Heusler alloys and an interface with a MgO tunneling barrier.

2. Sample preparation

Thickness series (7–80 nm) of Co$_2$FeAl (CFA) epitaxial films were prepared and a microstrip-based VNA-FMR setup was used to study their magnetic properties. The dependence of the in-plane anisotropies and the Gilbert damping parameter on the thickness and the determination of the interface perpendicular anisotropy constant $K_S$ for the CFA/MgO interface is presented for as-deposited samples and for two different values of the annealing temperature.

The stack layer structure is MgO(1 0 0)(subs)/ MgO(5)/ CFA($d$/)/MgO(7)/Ru(2) with $d = 7, 9, 11, 15, 20, 40$ and $80$ nm. Rf-sputtering was used for the MgO deposition and dc-sputtering for the rest. The values of the annealing temperature for the two series with thermal treatment are 320 °C and 450 °C. The layer stacking is symmetrical around CFA so that a similar interface is expected for both sides. The samples were all deposited at room temperature and annealed afterwards under vacuum conditions.

3. X-ray characterization

Crystallographic properties of the CFA thin films were determined using x-ray diffraction (XRD) measurements in a Philips X’Pert Pro diffractometer equipped with a Cu anode. The (0 0 2) superlattice and the fundamental (0 0 4) peak of the CFA can be observed (see figure 1) already for the as-deposited state. In-plane performed $\phi$ scan measurements reveal the absence of the (1 1 1) superlattice reflection in these films. Therefore, partial $B2$ crystalline order is verified. Epitaxial, 45° rotated growth, relative to the MgO buffer layer, was verified using a $\phi$ scan of the reflection from the (2 0 2) planes (not shown here). The epitaxial relationship CFA (0 0 1)(1 0 0) // MgO(0 0 1)(1 1 0) was therefore confirmed for these films, i.e. CFA grows with the same crystalline orientation as the substrate but the unit cell is rotated 45° in plane respect to the MgO unit cell.

X-ray reflectometry (XRR) has been performed on the 20 nm thick films and it is shown in figure 2. The estimation of the RMS value is only possible with a certain uncertainty due to the number of layers which increases the number of fitting parameters (layers thickness, interface roughness and material refractive index) but it is possible to say that it lays around 0.1–0.3 nm for the three samples when analyzing fits performed with GenX 2.4.10. In any case, it is evident that the interface is very smooth in all cases and that the annealing is not modifying the roughness properties. In [8] AFM data on very similar CFA samples provide a value of 0.3 nm for the roughness of the CFA surface prior to the deposition of the top layer which is compatible with the estimated roughness range. In any case, the exact value of the roughness is less relevant that the fact that a low roughness is guaranteed and the morphology remains unchanged with annealing as evidenced by the similarity of the curves for the three cases.

4. Results and discussion

From the dependence of $H_{\text{FMR}}$ on the resonance frequency $f_{\text{FMR}}$, the effective magnetization $M_{\text{eff}}$ is extracted using a fit to Kittel’s formula [23]. For a more detailed description of the FMR measurement and analysis procedure please see [24]. $M_{\text{eff}}$ is related to the saturation magnetization of CFA by [25–27]

$$M_{\text{eff}} = M_s - H_K^+ = M_s - \frac{2K_S}{\mu_0 M_s d}$$

Figure 3 shows the dependence of $M_{\text{eff}}$ on 1/d for the three CFA series. The lines are a fit to equation (1). Let us
first discuss the case of the as-deposited series shown in figure 3(a). An almost constant value for $M_{\text{eff}}$ is observed for the low thickness range (15–7 nm) where the interface properties should become dominating. The fit gives a value for $K_S^\perp$ of 0.03 ± 0.1 mJ m$^{-2}$ compatible with zero (hollow values in figure 3 not considered for the fit). This implies that it is not possible to obtain a stable perpendicular magnetization orientation for any thickness value based only on the interface effect. However, it has to be commented that a non-vanishing volume perpendicular anisotropy has also been reported for CFA [20] which may indeed stabilize an out-of-plane orientation. Concerning the relative decrease of $M_{\text{eff}}$ for large thicknesses, we attribute this to an inhomogeneous magnetization state which is sometimes observed in thick films [32]. This point will be later commented when analyzing the damping properties.

Figures 3(b) and (c) show the evolution of the situation when the annealing step is applied. The interface properties change with the thermal treatment and $K_S^\perp$ increases to a value of 1.14 ± 0.07 mJ m$^{-2}$ for the 320 °C case and of 2.07 ± 0.7 mJ m$^{-2}$ for 450 °C. The larger error bar in the later value is due to a larger scattering of values for $M_{\text{eff}}$. A recent study of the perpendicular anisotropy properties on CFA thin films has been published where a novel TiN buffer layer is employed [8]. In- and out-of-plane hysteresis loops are used to determine the value of $K_S^\perp$ instead of the FMR measurements used here. However, the largest obtained values for $K_S^\perp$ are in both cases in accordance with ours (0.86 ± 0.16 mJ m$^{-2}$). For comparison it has to be taken into account that due to the presence of two CFA/MgO interfaces, the values presented here are expected to be a factor of two larger. Both values are then in good agreement. The different annealing temperature range does not allow for a comparison of the evolution of $K_S^\perp$ with that parameter but a remarkable difference can be found in the as-deposited samples. A comparatively smaller but, contrary to our case, non-zero value is reported. This reveals the role of the TiN buffer layer in improving the interface quality.

Although it cannot be quantified with XRD, the existence of a certain level of stress in the films cannot be excluded. This stress is changing upon annealing together with the crystalline order at the interface and therefore it is reasonable to admit that it plays a role in the evolution of $K_S^\perp$. However, it is not possible to separate the contribution to the evolution of the PMA due to these two effects. First principle calculations of $K_S^\perp$ for stress-free CFA/MgO interfaces [34] has provided a value for $K_S^\perp$ of 1.31 mJ m$^{-2}$ for Co-terminated interfaces while FeAl-termination does induce in-plane orientation. This value is compatible with our results for the 450 °C case taking into account that our samples have two CFA/MgO interfaces. In any case, our results are more compatible with a Co-termination at the MgO interfaces following this calculation. Other experimental results using XMCD attribute, contrarily to the previous calculation, a PMA contribution to the Fe atoms at the interface [35]. The exact atomic origin of the PMA is then still under discussion and therefore also the actual impact of stress.

As already shown in figure 2, the roughness remains unchanged after the annealing process. The increase of $K_S^\perp$ is then due to a more subtle change of the atomic ordering at the immediate interface and is not connected to a roughness modification, or at least not in a large degree.

The theoretical studies [34] show that for the interface-originated PMA properties, the termination of the Heusler film (Co- or FeAl-termination) and the strength of the hybridization of certain orbitals in ordered interfaces are critical. By locally improving the crystalline order, the hybridization of the orbitals is modified and also the termination can be changed due to the fact that thermal energy is required for formation of a certain termination. All these changes are related to the very last atomic layers and are therefore invisible in the XRD signal, which is mainly originated in the bulk.

By setting $d = \infty$ in equation (1) it is possible to extract a value for $M_s$ of 1140 ± 30 kA m$^{-1}$ from the linear fit for the as-deposited samples. This value is larger than the ones reported in [21, 28] (1000–1030 kA m$^{-1}$) but similar to a FMR study [31] on very thick (140 nm) CFA polycrystalline films providing a value of $M_s = 1200$ kA m$^{-1}$.

The saturation magnetization $M_s$ for TiN buffered CFA, deposited and investigated by the same group, was measured.
to be 1140 ± 60 kA m⁻¹, which is in excellent agreement with the value obtained from the FMR data. The saturation magnetization for TiN buffered CFA was obtained using alternating gradient magnetometer (AGM) measurements and verified using vibrating sample magnetometer (VSM) on a 10 nm thin CFA layer [8].

The value of $M_S$ also increases upon annealing up to 1213 ± 8 kA m⁻¹ for the 320 °C series and 1340 ± 70 kA m⁻¹ for the 450 °C one. This increase can be attributed to an improvement of the crystalline order with annealing.

From the extrapolation of the linear fits to $M_{sat} = 0$ it is possible to extract the thickness at which the interfacial perpendicular anisotropy is able to stabilize an out-of-plane configuration by overcoming the demagnetization field and allowing the magnetic easy axis to be out-of-plane. This thickness is 1.2 nm and 1.7 nm for 320 °C and 450 °C annealing temperature, respectively. The relative difference between both values for the critical thickness is smaller than the relative difference for $K_S^\perp$ for the respective temperature values. This is explained by the larger $M_S$ value for the 450 °C case for which a larger demagnetizing field must be overcome to achieve PMA.

Belmeguenai et al presented data very similar to the one shown in figure 3(a) for (110)-oriented textured films [21] and for (100)-oriented epitaxial films grown on MgO(100) substrates [22]. The annealing temperature is 600 °C. The data is given for thickness values not smaller than 10 nm. However, the interpretation of the data is completely opposite to ours, resulting in a negative value $K_S^\perp = -1.8$ mJ m⁻². The negative value indicates that the interface anisotropy is favoring an in-plane orientation of the magnetization. PMA with Ta/CFA/MgO (or Cr or Ru) systems have been indeed achieved [20, 29, 30] with values of $K_S^\perp = +0.6$ mJ m⁻² for the Ta case, +1.0 mJ m⁻² for Cr and +2.0 mJ m⁻² for Ru. This shows how sensitive $K_S^\perp$ is to the exact growth properties which are modified by the different seed layer. The values reported in this work for both annealed series are very similar to the Cr and Ru buffered systems. The fact that $K_S^\perp$ vanishes in the as-deposited series shows also how important the annealing step is for adjusting the interface properties.

Figure 4 shows the dependence of the Gilbert damping parameter $\alpha$ on the thickness $d$ for three sample series: as-deposited, annealed at 320 °C, and annealed at 450 °C. The inset shows the dependence of the linewidth $\Delta H$ on the frequency for the 80 nm samples. The lines are a linear fit used to extract the damping parameter $\alpha$.

Belmeguenai et al presented data very similar to the one shown in figure 3(a) for (110)-oriented textured films [21] and for (100)-oriented epitaxial films grown on MgO(100) substrates [22]. The annealing temperature is 600 °C. The data is given for thickness values not smaller than 10 nm. However, the interpretation of the data is completely opposite to ours, resulting in a negative value $K_S^\perp = -1.8$ mJ m⁻². The negative value indicates that the interface anisotropy is favoring an in-plane orientation of the magnetization. PMA with Ta/CFA/MgO (or Cr or Ru) systems have been indeed achieved [20, 29, 30] with values of $K_S^\perp = +0.6$ mJ m⁻² for the Ta case, +1.0 mJ m⁻² for Cr and +2.0 mJ m⁻² for Ru. This shows how sensitive $K_S^\perp$ is to the exact growth properties which are modified by the different seed layer. The values reported in this work for both annealed series are very similar to the Cr and Ru buffered systems. The fact that $K_S^\perp$ vanishes in the as-deposited series shows also how important the annealing step is for adjusting the interface properties.

Figure 4 shows the dependence of the Gilbert damping parameter $\alpha$ on the thickness $d$ for three sample series: as-deposited, annealed at 320 °C, and annealed at 450 °C. The inset shows the dependence of the linewidth $\Delta H$ on the frequency for the 80 nm samples. The lines are a linear fit used to extract the damping parameter $\alpha$.
is the in-plane azimuthal angle and $\varphi$ may be at different angles. The lines in figure 5(a) are contributions, i.e. the easy axis of both constants $K_b$ and $K_u$ allow for a misalignment of the uniaxial $\varphi$. Figure 5(a) shows exemplarily this dependence for a thickness of 11 nm in the range 0–180° at 18 GHz for the as-deposited and the 450 °C annealed one. An overall four-fold anisotropy, as expected from the cubic lattice of CFA and the (100) growth direction is observed. The easy axes correspond to 0° and 90°. Overimposed to this, an additional weaker two-fold uniaxial anisotropy is also observed ($H_{\text{FMR}}$) at 0° and 90°). The uniaxial anisotropy may be induced by stress in the film or by the vicinal structure in the substrate surface induced by miscut.

In order to extract the anisotropy fields the following formula was used:

$$H_{\text{FMR}} = H_b + H_b \cos(4\phi) + H_u \cos(2\phi + \varphi).$$

Here $H_b$ and $H_u$ are the biaxial and uniaxial anisotropy fields, $\phi$ is the in-plane azimuthal angle and $H_{\text{FMR}}$ is the averaged value. The angle $\varphi$ allows for a misalignment of the uniaxial and biaxial contributions, i.e. the easy axis of both contributions may be at different angles. The lines in figure 5(a) are fits to this formula. These field values are related to the anisotropy constants $H_{\text{FMR}} = 2K_b/M_s$.

The results for $K_b$ and $K_u$ from the fits are plotted in figure 5(b). For the calculation of the anisotropy constant the magnetization values obtained from the fits in figure 3 are used. For $K_b$ we observe a different thickness dependence for the as-deposited series and the series annealed at 320 °C compared to the series annealed at 450 °C. The value of $K_b$ shows minor variation for the as-deposited samples with a small reduction for the thinner films. The evolution is similar for the 320 °C case. In contrast, the anisotropy constant increases continuously and strongly with decreasing thickness in the annealed series. However, the values converge for thick films and for 80 nm the difference vanishes. This points to an important role of the stress in the films, which normally relaxes with thickness, in the evolution of $K_u$. The absolute values are in agreement with literature data [22]. The values of $K_u$ are an order of magnitude smaller and the absolute values and the thickness dependence are very similar for the three cases.

5. Conclusions

In summary, we measured the evolution of the interface induced perpendicular anisotropy for epitaxial CFA/MgO interfaces and we observed a strong increase with the annealing temperature up to a value of $K_u = 2.01 \pm 0.7 \text{ mJ m}^{-2}$ for an annealing temperature of 450 °C. A stabilization of a perpendicular magnetization orientation is then expected for films thinner than 1.7 nm. We studied the thickness dependent magnetic properties of CFA for as-deposited and annealed series. We obtained minimum values for $\alpha$ for a thickness of 40 nm for all series and a different evolution with annealing for thinner or thicker films. We correlate this with interface and bulk changes upon annealing, respectively. The study of the in-plane anisotropy constant shows a much larger thickness dependence on the annealed samples compared to the as-deposited ones.

Acknowledgments

Financial support by M-era.Net through the HEUMEM project is gratefully acknowledged.

ORCID iDs

A Conca https://orcid.org/0000-0002-4206-1288

References

[1] Tsunegi S, Sakuraba Y, Oogane M, Takahashi K and Ando Y 2008 Appl. Phys. Lett. 93 112506

[2] Tezuka N, Ikeda N, Sugimoto S and Inomata K 2007 Japan J. Appl. Phys. 46 L454

[3] Wang W, Sukegawa H, Shan R, Mitani S and Inomata K 2009 Appl. Phys. Lett. 95 182502

[4] Ishikawa T, Hakamata S, Matsuda K, Uemura T and Yamamoto M 2008 J. Appl. Phys. 103 07A919

[5] Ebke D, Drewello V, Schäfers M, Reiss G and Thomas A 2009 Appl. Phys. Lett. 95 232510
[6] Drewello V, Ebke D, Schäfers M, Kugler Z, Reiss G and Thomas A 2012 *J. Appl. Phys.* **111** 07C701

[7] Bainsla L, Suzuki K Z, Tsujikawa M, Hiroki Tsuchiura, Shirai M and Mizukami S 2018 *Appl. Phys. Lett.* **112** 052403

[8] Niesen A, Ludwig J, Glas M, Silber R, Schmalhorst J-M, Arenholz E and Reiss G 2017 *J. Appl. Phys.* **121** 223902

[9] Takamura Y, Suzuki T, Fujino Y and Nakagawa S 2014 *J. Appl. Phys.* **115** 17C732

[10] Kamada T, Kubota T, Takahashi S, Sonobe Y and Takanashi K 2014 *IEEE Trans. Magn.* **50** 2600304

[11] Kamada T, Kubota T, Takahashi S, Sonobe Y and Takanashi K 2014 *IEEE Trans. Magn.* **50** 2600304

[12] Ludbrook B M, Ruck B J and Granville S 2016 *J. Appl. Phys.* **120** 013905

[13] Ludbrook B M, Ruck B J and Granville S 2017 *Appl. Phys. Lett.* **110** 062408

[14] Oogane M, Yilgin R, Shinano M, Yakata S, Sakuraba Y, Ando Y and Miyazaki T 2007 *J. Appl. Phys.* **101** 09J501

[15] Cinchetti M, Wüstenberg J-P, Sánchez Albaneda M, Steeb F, Conca A, Jourdan M and Aeschlimann M 2007 *J. Phys. D: Appl. Phys.* **40** 1544

[16] Conca A, Jourdan M and Adrian H 2007 *J. Phys. D: Appl. Phys.* **40** 1534

[17] Wen Z, Sukegawa H, Mitani S and Inomata K 2007 *J. Phys. D: Appl. Phys.* **40** 1534

[18] Cinchetti M, Wüstenberg J-P, Sánchez Albaneda M, Steeb F, Conca A, Jourdan M and Aeschlimann M 2007 *J. Phys. D: Appl. Phys.* **40** 1544

[19] Conca A, Jourdan M and Adrian H 2007 *J. Phys. D: Appl. Phys.* **40** 1534

[20] Wen Z, Sukegawa H, Mitani S and Inomata K 2007 *J. Phys. D: Appl. Phys.* **40** 1534

[21] Belmeguenai M, Tuzcuoglu H, Gabor M, Petrisor T, Tiusan C, Berling D, Zighem F and Chérif S M 2015 *J. Magn. Magn. Mater.* **373** 140

[22] Belmeguenai M, Tuzcuoglu H, Gabor M S, Petrisor T Jr, Tiusan C, Berling D, Zighem F, Chérif S M and Moch P 2013 *Phys. Rev.* **B** 87 184431

[23] Kittel C 1948 *Phys. Rev.* **73** 155

[24] Conca A, Keller S, Mihalceau L, Kehagias T, Dimitrakopoulos G P, Hillebrands B and Papaioannou E T 2016 *Phys. Rev.* **B** 93 134405

[25] Liu X, Zhang W, Carter M J and Xiao G 2011 *J. Appl. Phys.* **110** 033910

[26] Nascimento V P, Saitovitch E B, Pelegrini F, Figueiredo L C, Biondo A and Passamani E C 2006 *J. Appl. Phys.* **99** 08C108

[27] Beaujour J-M L, Chen W, Kent A D and Sun J Z 2006 *J. Appl. Phys.* **99** 08N503

[28] Ortiz G, Gabor M S, Petrisor T Jr, Boust F, Isaac F, Tiusan C, Henn M and Bobo J F 2011 *J. Appl. Phys.* **109** 07D324

[29] Gabor M S, Petrisor T Jr, Tiusan C and Petrisor T 2013 *J. Appl. Phys.* **114** 063905

[30] Wen Z C, Sukegawa H, Furubayashi T, Koo J, Inomata K, Mitani S, Hadorn J P, Ohkubo T and Hono K 2014 *Adv. Mater.* **26** 6483

[31] Yadav A and Chaudhary S 2014 *J. Appl. Phys.* **115** 133916

[32] Chen Y, Hung D, Yao Y, Lee S, Ji H and Yu C 2007 *J. Appl. Phys.* **101** 09C104

[33] Schebaum O, Ebke D, Niemeyer A, Reiss G, Moodera J S and Thomas A 2010 *J. Appl. Phys.* **107** 09D717

[34] Vadapoo R, Hallal A, Yang H and Chshiev M 2016 *Phys. Rev. B* 94 104418

[35] Wen Z, Hadorn J P, Okabayashi J, Sukegawa H, Ohkubo T, Inomata K, Mitani S and Hono K 2017 *Apppl. Phys. Express* **10** 013003

[36] Usov N A and Serebryakova O N 2017 *J. Appl. Phys.* **121** 133905