Magnetic and structural properties of CoFeB thin films grown by pulsed laser deposition

Geet Awana, Chris Cox, Laura Stuf, Guru Venkat, Kelly Morrison, Zhaoxia Zhou and Dirk Backes

1 Department of Physics, Loughborough University, Loughborough LE11 3TU, United Kingdom
2 Loughborough Materials Characterisation Centre (LMCC), Department of Materials, Loughborough University, Loughborough LE11 3TU, United Kingdom
3 Diamond Light Source, Harwell Campus, Didcot OX11 0DE, United Kingdom
E-mail: dirk.backes@diamond.ac.uk

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Abstract
The emergence of thin film CoFeB has driven research and industrial applications in the past decades, with the magnetic random access memory (MRAM) the most prominent example. Because of its beneficial properties, it fulfills multiple functionalities as information-storing, spin-filtering, and reference layer in magnetic tunnel junctions. In future, this versatility can be exploited beyond the traditional applications of spintronics by combining with advanced materials, such as oxide-based materials. Pulsed laser deposition (PLD) is their predominant growth-method, and thus the compatibility of CoFeB with this growth technique will be tested here. This encompasses a comprehensive investigation of the structural and magnetic properties. In particular, we find a substantial ‘dead’ magnetic layer and confirm that it is caused by oxidation employing the x-ray magnetic circular dichroism (XMCD) effect. The low damping encountered in vector network analyzer-based ferromagnetic resonance (VNA-FMR) renders them suitable for magnonics applications. These findings demonstrate that CoFeB thin films are compatible with emergent, PLD-grown materials, ensuring their relevance for future applications.

1. Introduction

Thin films of CoFeB have been central for the advancement of spintronics, a promising candidate for future data storage and processing technologies beyond Moore’s Law. They are essential parts of magnetic tunnel-junctions (MTJs) [1] with high tunneling magnetoresistance (TMR) and synthetic antiferromagnets [2, 3], both of which are important components of magnetic random access (MRAM) devices [4]. They act as spin-polarizing layers in spin-transfer torque MRAM [5–7] and spin-torque oscillators [8]. The discovery of perpendicular magnetic anisotropy (PMA) in iron-rich CoFeB has facilitated a higher storage density in MRAMs [9, 10]. Employing electric fields instead of charge transport, magnetisation reversal was demonstrated in CoFeB-based MTJs, reducing the energy required compared to current-induced switching considerably [11, 12].

To maintain the same degree of advancement and innovation in future, it will be crucial to integrate CoFeB with different classes of materials. An example are complex oxide materials such as perovskites, showing interfacial ferromagnetism [13]. Combining such materials with CoFeB could pave the way to devices with better performance or new functionality. Currently, such heterostructures are studied by depositing CoFeB on top of complex oxide substrates using sputtering [14, 15]. For spintronic applications though, multilayers will need to incorporate thin layers of both CoFeB and complex oxides. This requires one deposition technique compatible with both CoFeB and complex oxides, in order to maintain the properties of the respective single layers.

Pulsed laser deposition (PLD) is the preferred deposition technique for complex oxide compounds [16]. This is mainly because the stoichiometry of the target material can be readily achieved in the ablated films [17].

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Despite first attempts to grow CoFeB thin films with PLD [18, 19], a comprehensive study of their structural and magnetic properties is still missing.

The purpose of this work is to provide a detailed analysis of the structural and magnetic properties of PLD-grown CoFeB. We employ a range of techniques to explore the crystalline structure, composition, and morphology of the thin films. The magnetisation, determining the degree of spin polarization which can be achieved, is revealed using vibrating sample magnetometry (VSM) and synchrotron-based x-ray magnetic circular dichroism (XMCD) for elemental selectivity. The damping, determining the time-scale magnetodynamical processes can be sustained, is elucidated by ferromagnetic resonance (FMR).

2. Sample preparation

Thin films of CoFeB were deposited using pulsed laser deposition (PLD) at a base pressure of $1.3 \times 10^{-9}$ mbar. A Nd:YAG laser (Quanta Ray GCR series) with a fluence of $\sim 2.2 \text{ J cm}^{-2}$ and 10 Hz pulse rate was employed, operating at a wavelength of 532 nm. No external magnetic field nor any heating was applied during deposition. A 5 nm thick CoFeB layer was ablated from a target consisting of 20% Co, 60% Fe and 20% B. The layers were likely to be composed of packed nanosized grains. To elucidate the crystallinity further electron diffraction was not available the growth parameters for the target layer thickness was derived from a calibration sample. The actual layer thickness was determined after deposition using x-ray reflectivity (XRR) and transmission electron microscopy (TEM).

3. Structural characterisation

The film structure was confirmed from x-ray diffraction (XRD) using the K$_\alpha$ line (see figure 1(a)). Very weak and broad peaks found can be attributed mainly to the substrate and oxidised Ta-seed layers. Only a Fe$_3$B [201] peak can be related to the magnetic layer. Overall, the XRD-scan is commensurate with an amorphous layer in the as-grown state [21]. Annealing is known to cause Boron to migrate out of the amorphous CoFeB layer [18], leading to a crystallized CoFe layer with a bcc texture [21, 22]. High tunnel magnetoresistance has been demonstrated in CoFeB/MgO/CoFeB-based tunnel junctions where MgO constitutes the tunnel barrier [23, 24]. Finding a process for crystallization of PLD-grown samples was not part of this study, but it can be expected that the necessary growth conditions will be very similar while compatible with complex oxide growth at the same time [25, 26].

In figure 1(b) the x-ray photoelectron spectroscopy (XPS) spectra for B, Fe, and Co are shown. Peaks at 186 eV, 707 eV, and 778 eV correspond to B1s, Fe 2p$_{3/2}$, and Co 2p$_{3/2}$ transitions, respectively [27–31]. Additional peaks are found at slightly higher energy. These are pointing at the formation of oxides, which we will later corroborate using x-ray absorption spectroscopy (XAS). The Ta spectrum shows oxidation peaks commensurate with Ta$_2$O$_5$, not surprising since the Ta capping layer is exposed to air. As will be seen later, the capping layer is thinner than intended and seems not to prevent the oxidation of the underlying CoFeB. A thicker Ta layer or alternative materials such as gold are likely to prevent such oxidation effects. Another potential source for Ta oxidation is the glass substrate, consisting of amorphous SiO$_x$. By choice of a silicon wafer as substrate and surface treatment of the thin, natural surface oxide layer a cleaner interface could be achieved.

Transmission electron microscopy (TEM) imaging and chemical analysis of the CoFeB film were performed using a FEI Tecnai F20 field emission gun scanning transmission electron microscope (FEGSTEM) equipped with an Oxford Instrument X-Max 80 windowless x-ray detector for energy dispersive x-ray spectroscopy (EDS) (see figure 2). TEM specimens were prepared using a FEI Nova 60 nanoLab focused ion beam/scanning electron microscope (FIB-SEM). A carbon layer was sputtered onto the film prior to the standard Pt deposition in the FIB as surface protection to preserve the outermost structure of the film. The carbon layer has an additional role to provide a gap between the Pt and the extremely thin Ta layers, improving accuracy of chemical analysis by minimizing the ambiguity of the two heavy metal layers. Furthermore, a Mo support grid instead of standard Cu was used to mount the FIB lift-out lamella in order to mitigate the x-ray energy overlapping issue in the films with the Cu K$_\alpha$ (8.041 kV) and Ta L$_\alpha$ (8.145 kV) transitions.

The thickness of the bottom Ta, CoFeB, and top Ta-layers are 3.1 nm, 3.7 nm, and 4.5 nm, respectively. The interfaces to the glass slide at the bottom and Pt coating on the top, applied for TEM imaging, exhibit considerable roughness. The bottom Ta layer appears to consist of discrete nano-grains of between 1 and 4 nm in size. Although the top Ta layer was deposited by the same parameters, it has a more uniform thickness and is denser than the bottom Ta layer. Many frames over the cross section area were taken to ascertain whether the three layers are crystallized or amorphous. None of the layers showed columnar grain structure suggesting that the layers are likely to be composed of packed nanosized grains. To elucidate the crystallinity further electron
Diffraction was performed using both convergent beam nano-diffraction on the thin film (∼10 nm) and parallel beam selecting a 100 nm diameter area. No diffraction spots were observed while the halos are typical for an amorphous sample. Improvement can be envisioned by substituting Ta with TaN as seed layer, known to result in smoother and better defined interfaces in sputtered samples and an enhancement of their magnetic properties [32].

While TEM provides local information about the thickness and interface quality of the layers, x-ray reflectivity (XRR) delivers a global perspective by averaging over a larger area (see figure 1(c)). The fitting program GenX [33] was employed to fit the data with the layer thickness, density and roughness as fitting parameters (see table 1). The goodness of fit LogFOM was 0.068 where a value ≤ 1 indicates a good agreement between measured and simulated XRR. As already observed in TEM images, the measured thicknesses are thinner than the nominal ones, with the CoFeB layer 2.3 nm and the total of Ta layers, encompassing also intermixing and oxidised layers, between 2.0 and 3.0 nm thick. The intermixing layers are situated between the CoFeB and Ta layers while the oxidised Ta layers can be found at the interface to the substrate and at the top surface of the sample. They are between 0.5 and 1.5 nm thick and difficult to discern in TEM images, explaining the discrepancy of the thickness information received between the two techniques.

The intermixed zone was examined in more detail using energy-dispersive x-ray spectroscopy (EDS). Maps of Ta Lα, Fe Kα, and Co Kα visualise the position of the Fe-rich CoFeB layer sandwiched between the two Ta layers (see figure 2(c)). Since the Si Kα transition at 1.740 kV overlaps with the Ta Mα transition at 1.711 kV, the Ta Lα was used. While Co sits well-defined between the two Ta-layers, it appears that Fe diffuses into the bottom Ta layer. The large grain size found using TEM seems to promote diffusion due to the enlarged surface area. In contrast, the top Ta-layer is denser and constitutes an effective barrier against both Co and Ta diffusion towards

Figure 1. (a) XRD, (b) XPS and (c) XRR measurements of the 5 nm CoFeB sample. The energy regions in (b) correspond to Ta, B, Fe and Co. The logarithmic figure of merit (LogFOM) of the XRR fit is 0.068.
the upper layers. Hence, improving the layer stack should target the optimisation of the seed layer. The oxygen content measured using the $K_{\alpha}$ transition is shown in the second panel from the right in figure 2(c). While oxygen can be found in the substrate and in the Ta layers, it is largely absent in the CoFeB layer. A concentration can be found at the interface to the Ta bottom and top layers, constituting the magnetically dead layers.

4. Magnetic characterization

Room temperature hysteresis measurements have been carried out to determine the magnetisation and coercivity of PLD-grown thin films (see figure 3(a)). Saturation was reached at in-plane magnetic fields of around 100 mT. Using the CoFeB-thickness from the TEM images of 3.7 nm and the lower value of 2.3 nm obtained from XRR resulted in a saturation magnetisation $M_s$ of 579 emu/cc and 931 emu/cc, respectively.

The discrepancy in thickness and magnetisation, respectively, is most likely caused by oxidation and intermixing at the interface between CoFeB and Ta\textsuperscript{[34]}. Oxidation of Co, Fe, and B can clearly be seen in XPS measurements (see figure 1(b)) while a certain degree of alloying with Ta can be expected from EDS maps (see figure 2(c)). Nevertheless, these effects do not lead to a markable change in contrast and can thus not be distinguished from CoFeB in TEM cross sections (see table 1). The fit to the measurement is sensitive to small changes in density of the intermixing layers, associated with alloying and oxidation (see figure 1(c)).

It stands to assume that the intermixing layers are magnetically ’dead’, i.e. not contributing to the magnetisation. A common method to determine its thickness and to obtain an accurate value for $M_s$ is to

![Figure 2. (a) TEM images of a cross section, (b) typical electron diffraction pattern of the film and substrate, and (c) EDS maps of the cross section.](image_url)

![Table 1. Structural fitting parameters for the thickness, density and roughness. Values which were kept constant are shown without error.](table_url)
measure the magnetic moment per area as function of the CoFeB thickness [35]. Unfortunately, such a study could not be carried out because the necessary systematic, incremental variation of the CoFeB thickness well below 5 nm was not possible in our PLD-chamber. Our best estimation for the magnetisation of CoFeB relies on the CoFeB-thickness from XRR, while the one measured by TEM represents a lower boundary of the magnetisation.

The range of 579 to 931 emu/c.c. for $M_s$ is lower than the 1130 emu/c.c. reported in the literature for sputtered layers of similar thickness [36]. In the following we will employ element-specific and non-intrusive polarized synchrotron radiation to study in more detail how Co and Fe and their oxides contribute to the magnetisation. For this purpose, x-ray absorption spectra (XAS) at positive and negative circular polarisation were taken at the Branchline of beamline I06 at Diamond Light Source Ltd and the XMCD calculated. A saturating magnetic field of 6 Tesla was applied perpendicular to the sample surface, coinciding with the direction of the x-rays. Both total electron yield (TEY) and fluorescence yield (FY) were recorded. They both show similar results, hence only the TEY data is displayed here. All measurements were taken at room temperature.

The Fe L$_{2,3}$ peaks of the XAS spectrum exhibit two features (see figure 4(a)). A peak at 710.5 eV (723.6 eV) of the L$_3$ (L$_2$) edge stems from metallic Fe while a peak at 711.7 eV (725.3 eV) hints at an oxidised state, respectively. In the Co-spectrum such a feature is less obvious (see figure 4(b)). When comparing to the respective XPS measurements, a pronounced FeO$_x$ peak is visible while the CoO$_x$ peak is recognizable but broader compared to...
the Co-peak (see figure 1(b)). Bearing this in mind, a closer look at the Co-L₃ peak at 781.6 eV reveals an asymmetry at slightly higher energy, broadening the peak structure.

The impact of pure and oxidised Fe and Co was studied in element-specific XMCD spectra (see figures 4(c) and (d)). They are obtained when XAS spectra of opposite helicity are subtracted (see red and blue curves in figures 4(a) and (b)). Both Fe and Co show a strong XMCD signal, indicating that both contribute to the magnetisation. No contribution to the magnetisation arises from Fe-oxide. This can be easily seen from the structure of the XMCD signal, commensurate to elementary Fe. The double-peak structure of Co in both XAS and XMCD spectra is less pronounced, indicating a lesser degree of oxidation. In total, these measurements tightly string together the presence of Fe- and Co-oxide, already known from XPS (see figure 1(b)), with the formation of a magnetically dead layer. This finding promotes the choice of the CoFeB-thickness from XRR for the calculation of the magnetisation, since it omits the oxidised parts which do not contribute to the magnetisation.

Lastly, we want to address the suitability of PLD-grown CoFeB as platform for magnetodynamical processes. The most important figure is the damping parameter α, proportional to the slope of the peak width dependence on the frequency in ferromagnetic resonance (FMR) spectra (see figure 3(b)). Here, lower damping means that dynamic processes can be sustained over longer times. This is crucial for many spintronics applications such as ultra-fast switching [4] and propagation of spin-waves in magnonic crystals [37]. FMR is the method of choice [38] to quantify the damping. A home-built vector-network analyzer (VNA) setup probes the absorption of an rf signal applied to the sample as a function of frequency and magnetic field. A thin film sample is directly attached to a coplanar waveguide, fabricated using sputtering and a lift-off technique for patterning. The peak width dependence on the frequency was fit to

\[ \Delta H(f) = \Delta H_0 + \frac{4\pi\alpha f}{\gamma} \]

where \( \Delta H_0 \), the inhomogeneous broadening, is independent of the frequency \( f \), while the second term, the intrinsic broadening, is proportional to the damping parameter \( \alpha \). \( \gamma = g \mu_B / h \) is the gyromagnetic ratio with \( g \) the g-factor [39]. A value of 2.04 ± 0.04 for \( g \) was determined from the dispersion relation of the same sample.

A very low \( \alpha \) of 0.008 is found and in line with damping in as-grown, sputtered CoFeB [40]. A spin-pumping effect into the Ta layers [41] cannot be excluded because Ta acts as a strong spin-scatterer for a spin-current, generated by spin-precession in the CoFeB-layer. Without such Ta layers embedding the CoFeB-layer the damping could be reduced even further.

The FMR measurements present another opportunity to determine the magnetisation of the CoFeB-layer from the FMR dispersion relation [38, 39]. Its accuracy hinges on a perpendicular anisotropy \( H_K \) to be small or absent which for thicknesses larger than 1 nm is a valid assumption. The \( M \), thus obtained is 995 emu/cc, larger when compared to the values obtained from combined VSM and TEM or VSM and XRR measurements, respectively. The 12% reduction from the literature value [36] could be evidence for the onset of perpendicular magnetic anisotropy [9, 10]. Tuning the thickness towards 1 nm will reveal if out-of-plane magnetization in PLD-grown CoFeB can be achieved.

5. Conclusions

In summary, we have investigated the structural and magnetic properties of CoFeB thin films grown with PLD. In its as-grown state and with the seed layer not optimized, it has a magnetisation between 579 and 995 emu/cc, and low damping of 0.008. Our findings suggest that optimizing the seed layers and growth conditions will be necessary to achieve similar magnetic properties as have been reported in the literature. The results presented here are encouraging though and could be the starting point to investigate combinations of CoFeB with PLD-grown materials, such as complex oxides. This could lead to energy-efficient devices made of CoFeB/complex oxide-heterostructures with improved or new functionality.

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ORCID iDs

Chris Cox @ https://orcid.org/0000-0003-2889-9751
Kelly Morrison @ https://orcid.org/0000-0001-5672-3310
Dirk Backes @ https://orcid.org/0000-0002-1019-3323

References

[1] Moodera J S, Kinder L R, Wong T M and Meservey R 1995 Phys. Rev. Lett. 74 3273
[2] Wiese N, Dimopoulos T, Kührig M, Wecker J, Brückl M and Reiss G 2004 Appl. Phys. Lett. 85 2020
[3] Hayakawa J, Ikeda S, Lee Y M, Sasaki R, Meguro T, Matsukura F, Takahashi H and Ohno H 2006 Jpn. J. Appl. Phys. 45 1057
[4] Liu H, Bedau D, Backes D, Katine J A and Kent A D 2012 Appl. Phys. Lett. 101 032403
[5] Myers E B, Ralph D C, Katine J A, Louie R N and Buhrman R A 1999 Science 285 867
[6] Hayakawa J, Ikeda S, Matsukura F, Takahashi H and Ohno H 2005 Jpn. J. Appl. Phys. 44 587
[7] Koch R H, Katine J A and Sun J Z 2004 Phys. Rev. Lett. 92 088302
[8] Houshang A et al 2018 Nat. Commun. 9 4374
[9] Ikeda S, Miura K, Yamamoto H, Mizunuma K, Gan H D, Endo M, Kanai S, Hayakawa J, Matsukura F and Ohno H 2010 Nature Mater. 9 721
[10] Worledge D C, Hu G, Abraham D W, Sun J Z, Trouilloud P L, Nowak J, Brown S, Gaidis M C, O’ Sullivan E J and Robertazzi R P 2011 Appl. Phys. Lett. 98 022501
[11] Kanai S, Yamamoto M, Ikeda S, Nakatani Y, Matsukura F and Ohno H 2015 Appl. Phys. Lett. 101 122403
[12] Kato Y, Saito Y, Yoda H, Inokuchi T, Shiratori S, Shimomura N, Oikawa S and Tiwari A 2018 Phys. Rev. Appl. 10 044011
[13] Liu Y and Ke X 2015 J. Phys. Condens. Matter 27 373003
[14] Brandt F, Franke K J, Lahtinen T H, van Dijken S and Grundler D 2014 Sol. Stat. Commun. 198 13
[15] Wang J, Pesquera D, Mansell R, van Dijken S, Cowburn R P, Ghidini M and Mathur N D 2019 Appl. Phys. Lett. 114 094041
[16] Koster G, Huijbens M and Rijnders G 2015 Epitaxial Growth of Complex Metal Oxides (Amsterdam: Woodhead Publishing) (https://doi.org/10.1016/0025-0005-04499-9)
[17] Cox C D, Caruana A J, Cropper M D and Morrison K 2020 J. Phys. D: Appl. Phys. 53 035005
[18] Swamy G V, Pandey H, Srivastava A K, Dalai M K, Maurya K K R and Rakshit R K 2013 Appl. Phys. Lett. 102 022501
[19] Caricato A P, Fernández M, Frait Z, Fraitova D, Luby S, Luches A, Majkova E, Majni G, Malych R and Mengucci P 2004 Appl. Phys. A 79 1251
[20] Cao Z H, Hu K and Meng X K 2009 J. Appl. Phys. 106 113513
[21] You C Y, Ohkubo T, Takahashi Y and Hono K 2008 J. Appl. Phys. 104 033517
[22] Yuasa S, Suzuki Y, Katayama T and Ando K 2005 Appl. Phys. Lett. 87 242503
[23] Djayapravicz D T, Tsunezuka K, Nagai M, Maehara H, Yamagata S, Watanabe N, Yuasa S, Suzuki Y and Ando K 2005 Appl. Phys. Lett. 86 92502
[24] Hayakawa J, Ikeda S, Lee Y M, Matsukura F and Ohno H 2006 Appl. Phys. Lett. 89 232510
[25] Feng G, van Dijken S and Croy J M 2006 Appl. Phys. Lett. 89 162501
[26] Liu C, Cheng Y B and Ge Z 2020 Chem. Soc. Rev. 49 1653
[27] Jang Y, Nam C, Lee K S, Cho B K, Cho Y J, Kim K S and Kim K W 2007 Appl. Phys. Lett. 91 102104
[28] Saravanamurthi L, Raja M M, Prabhu D and Therese H A 2018 J. Mater. Sci. Mater. Electron. 29 336
[29] Moudler J F, Stickle W F, Sobol P E and Bomben K D 1992 Handbook of X-Ray Photoelectron Spectroscopy—Elen-Prairie, Perkin-Elmer
[30] Li M, Lu J, Yu G, Li X, Han G, Chen X, Shi H, Yu G, Amiri P K and Wang K I 2016 AIP Adv. 6 45107
[31] Kaveev A K, Sokolov N S, Suturin S M, Zhiltsov N S, Golyashov V A, Kohk K A, Prosvirin I P, Tereshchenko O E and Sasawada M 2018 Cryst. Eng. Commun. 20 3419
[32] Sinha I et al 2013 Appl. Phys. Lett. 102 242405
[33] Bjorka M and Andersson G 2007 J. Appl. Phys. 104 401174
[34] Nanib V B, Meng H and Shiba R 2012 AIP Adv. 2 042182
[35] Jang S Y, Lim S H and Lee S R 2010 J. Appl. Phys. 107 96707
[36] Wang W G, Li M, Hageman S and Chien C L 2012 Nat. Mater. 11 64
[37] Kruglyak V V, Demokritov S O and Grundler D 2010 J. Phys. D: Appl. Phys. 43 264001
[38] Backes D, Bedau D, Liu H, Langer J and Kent A D 2012 J. Appl. Phys. 111 07C721
[39] Beaujour J M, Chen W, Krycka K, Kao C C, Sun J Z and Kent A D 2007 Eur. Phys. J. B 59 475
[40] Bilzer C, Devolder T, Kim J V, Couril G, Chappert C, Cardoso S and Freitas P 2006 J. Appl. Phys. 100 053903
[41] Tserkovnyakov Y, Brataas A and Bauer G E 2002 Phys. Rev. Lett. 88 117601