Spectroscopic ellipsometry and magneto-optical Kerr effect spectroscopy study of thermally treated Co$_{60}$Fe$_{20}$B$_{20}$ thin films

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Abstract
We report the optical and magneto-optical properties of amorphous and crystalline Co$_{60}$Fe$_{20}$B$_{20}$ films with thicknesses in the range of 10 nm to 20 nm characterized using spectroscopy ellipsometry (SE) and magneto-optical Kerr effect (MOKE) spectroscopy. We derived the spectral dependence of the dielectric tensor from experimental data for samples prior and after annealing in vacuum. The features of the dielectric function can be directly related to the transitions between electronic states and the observed changes upon annealing can be ascribed to an increase of the crystalline ordering of CoFeB.

Keywords: CoFeB, spectroscopic ellipsometry, magneto-optical Kerr effect spectroscopy, x-ray diffraction

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction
In recent years, CoFeB films have been extensively investigated due to the interest in understanding spin-dependent phenomena [1, 2] and their suitability for applications such as magnetic recording media, sensors or microwave applications [3–5]. In the particular case of tunneling magnetoresistance (TMR) devices, large magnetoresistance (MR) yields were predicted [6] and observed [7] in magnetic tunnel junctions (MTJs) using (001)-textured MgO as a tunnel barrier. The amorphous nature of sputtered CoFeB allows a smooth growth of these films on the MgO barrier with minimal roughness, and a near-epitaxial relationship between MgO and CoFeB can be achieved upon a post-deposition thermal treatment [8]. In this process, the (001)-textured MgO serves as a template for the crystallization of the CoFeB layers, resulting in high TMR values.

As the current trends in spintronic devices demand new physical principles to provide scalability, there has been an increasing interest in the interaction between magnetism in CoFeB films and light. This includes studies of the optical driven magnetization dynamics on very short-time scales [9] or the development of all-optical switching mechanisms for spin-transfer-torque magnetic random-access memory [10]. As such, there is significant interest in studying the optical properties of CoFeB.

Spectroscopic ellipsometry (SE) in combination with magneto-optical Kerr effect (MOKE) spectroscopy can provide...
significant information on the electronic structure, as well as the crystallographic orientation and magnetization direction. There are a number of experimental and theoretical studies focusing on the optical properties of elemental Co and Fe [11–15] and also a few dedicated to Co-Fe alloys [16–18]. However, only limited attention has been paid to CoFeB, regarding solely the ellipsometry evaluation of its optical constants [19] or the comparison of optical and magneto-optical properties of granular nanostructures [20].

In this work, the optical and magneto-optical properties of Co_{60}Fe_{20}B_{20} thin films, with thicknesses below and equal to 20 nm grown on Si covered with thermally grown SiO_{2}, are investigated after annealing in vacuum by SE and MOKE spectroscopy. The changes observed in the dielectric function upon thermal annealing can be correlated to the crystallization of the films, while the increase in the MOKE signal indicates an increase in the magnetization driven by the annealing process.

2. Materials and methods

2.1. Sample preparation and structural characterization
Co_{60}Fe_{20}B_{20} thin films with nominal thicknesses (determined using a quartz crystal microbalance) ranging from 10 nm to 20 nm covered by a 3 nm gold passivation layer were deposited by dc magnetron sputtering on thermally oxidised silicon substrates. The depositions were performed at room temperature (RT) with a base pressure below 2 × 10^{-4} Pa and a working pressure of 0.35 Pa. The samples were annealed for 30 min in vacuum at 350 °C and subsequently again for 30 min at 400 °C. The first annealing step was performed at 350 °C as the transformation of the film from amorphous into a crystalline bcc Co–Fe phase is expected to occur above 325 °C [21]. The characterization of the samples with the methods described below, was performed in the as-deposited state and repeated after each of the subsequent annealing steps.

X-ray reflectivity (XRR) and x-ray diffraction (XRD) measurements were performed on a 3000 PTS diffractometer from SEIFERT-FPM (today GE INSPECTION Technologies GmbH), allowing the film thickness and crystallinity to be assessed, independently of the ellipsometric model described below. The thickness of every single layer was determined through a simulation based on the experimental XRR data with the open-source software GenX [22]. In order to probe the crystallization of Co_{60}Fe_{20}B_{20} as-deposited and post-annealed layers x-ray diffractograms were recorded.

The surface of the samples was studied by atomic force microscopy (AFM) in AC mode with an Agilent 5500 Scanning Probe Microscope, using reflective Si AFM probes with a guaranteed tip radius below 10 nm, and scanning electron microscopy (SEM) on a ZEISS Supra 60 workstation.

2.2. Spectroscopic ellipsometry
SE data were recorded with a J A Wollam Co., Inc. M-2000 ellipsometer between 0.74 eV and 5.03 eV at incidence angles of 50°, 55°, 60°, 65°, and 70°. The experimentally measured SE data ψ and Δ, are related to the ratio of amplitudes of p- and s-polarized components of the light reflected on the sample and their phase difference, respectively:

\[ \rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}. \] (1)

The optical constants for each sample were determined through a Kramers–Kronig consistent regression modelling of the ellipsometric parameters ψ and Δ [23]. In the optical layer stack model, the layer thicknesses obtained from the XRR measurements were used as input parameters for the fitting and kept fixed throughout the study. On top of the Au layer, a surface roughness layer (where the dielectric function of the cap layer is mixed with 50% void) based on the RMS roughness values obtained from the AFM measurements was used. For the dielectric function, a multi-sample analysis based on a parametric model consisting of one Drude free electron model and a series of five Gauss-Lorentz oscillators was employed in order to represent the fine structure of the optical dispersion in the Co_{60}Fe_{20}B_{20} in the entire investigated spectral range. In the multi-sample analysis, the dielectric function of the samples with thicknesses from 10 nm to 20 nm was considered to be identical. This model was then further adjusted to respond to the structural changes induced by the annealing steps. The data evaluation for all ellipsometry experiments was performed using the software WVASE32™.

2.3. MOKE spectroscopy
The polar Kerr rotation θ_K and ellipticity η_K spectra were measured with an indigenous developed MOKE spectrometer. The spectrometer measures simultaneously both rotation and ellipticity of the light reflected on the sample at near normal incidence by means of a polarization modulation method using a piezo-birefringent modulator also known as photelastic modulator (PEM). A detailed discussion of this measurement technique can be found elsewhere [24]. All the spectra were measured at RT in a photon energy range of 1.5 eV–5 eV with a magnetic field of ~1 T applied perpendicularly to the plane of the layers.

3. Results and discussion

3.1. Structural characterization
The thickness of the Co_{60}Fe_{20}B_{20}/Au bilayers was initially verified using XRR measurements on the as-deposited samples, yielding differences below 1 nm with respect to the nominal values. The best fit simulation results for the Co_{60}Fe_{20}B_{20} (20 nm)/Au (3 nm) sample are shown in figure 1.

The layers were further characterized using XRD before and after annealing at 350 °C, and 400 °C and the x-ray diffractograms are shown in figure 2. For the as-deposited state of the sample, only the Au (1 1 1) and Si (substrate) peaks at 38.2° and 69.1°, respectively, were observed, indicating that the Co_{60}Fe_{20}B_{20} film is amorphous. Even after annealing at 350 °C, no peak corresponding to the CoFe crystalline phase was detected, suggesting that the Co_{60}Fe_{20}B_{20} layer is still in
an amorphous phase or that the eventually formed crystallites are not large enough to be detected by our XRD equipment. A further annealing step at 400°C resulted in the occurrence of a well distinguishable peak around 45°, characteristic for the CoFe(1 1 0) crystalline phase. For this peak, a crystallites size of (8.9 ± 2.0) nm was calculated using the Scherrer formula [25].

The values of the root-mean-square (RMS) roughness were obtained from the AFM data, before and after annealing, as any changes in this parameter need to be accounted for in the ellipsometric modelling. The initial roughness was measured to be around 0.5 nm, and a substantial increase was registered upon annealing to 1.5 nm (350°C) and 2 nm (400°C). These changes in the roughness and grain structure upon annealing were further confirmed by SEM images.

3.2. Optical and magneto-optical properties

The measured ψ and Δ spectra and the fitted spectra at an angle of incidence (AOI) of 60° for all the samples before annealing are shown in figure 3. For the fitting, the layer thicknesses of CoFeB and Au were kept constant at the values determined by XRR (see table 1) and the thickness of SiO₂
was kept at 103.8 nm, as determined before the deposition with ellipsometry.

In addition, the known dielectric functions of gold [26], SiO2 [27] and Si [28] were used, leaving only the optical constants of Co20Fe60B20 as the fit parameters. The quality of the fit was evaluated based on the mean square error (MSE) values, calculated from N, C and S parameters (Mueller matrix components for isotropic material) [29], along with the agreement between experimental values and simulated curves. MSE values of less than ten were achieved for all results presented in this work.

The changes found in the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function of Co60Fe20B20 obtained from the SE measurements, before and after annealing, are shown in Figure 4. As mentioned previously, all thicknesses as well as the optical constants of the substrate (Si/SiO2) and capping layer (Au) were kept constant throughout the modelling, considering only a change in the surface roughness upon annealing, as measured by AFM. Hence, only the optical constants of CoFeB were fitted.

For the as-deposited films, the dielectric function relates well to the typical line shape of the optical function reported for amorphous Co20Fe60B20 films with thicknesses between 10 nm and 40 nm grown on Si/SiO2 (1000 nm), i.e. with very broad features [19]. It should be noted that thicker films of Co60Fe20B20 as the fit parameters. The quality of the fit was evaluated based on the mean square error (MSE) values, calculated from N, C and S parameters (Mueller matrix components for isotropic material) [29], along with the agreement between experimental values and simulated curves. MSE values of less than ten were achieved for all results presented in this work.

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The electronic origin of the observed spectral features is discussed in the following. At low photon energies (NIR and visible), the optical spectra are expected to relate mostly to intraband transitions. At higher photon energies (UV) the features in the spectra relate to interband transitions, namely transitions from the occupied $d$-bands to unoccupied ones. A broad pronounced feature at ~2.6 eV was previously observed for Fe–Co alloys in the bcc phase [17, 18] and ascribed to direct interband transitions in the minority-spin bands between occupied $d$- and unoccupied $p$-states [13]. It is worth mentioning that the response may also be influenced by interband transitions from gold typically found around 2.5 eV [33] or by plasmonic effects in Au or even in CoFeB. While the interband transitions are taken into account by the optical constants for gold [26] used in our model, the plasmonic effects were not taken into account [34]. Since in our case we have an additional degree of complexity relating to the B content of our alloy, it is not straightforward to compare to simple Co–Fe alloys, and since the complete removal of the Au signature at
2.5 eV by the optical model used cannot be warranted, any comparison should be taken with care. The energy range above 3 eV is dominated by the interband transitions typical of the Fe–Co sites, including d transitions of the Fe p as well as d transitions above 3 eV.

In the context of pure bcc-Fe, the peaks at 2.8 eV and 4 eV are ascribed to transitions along high symmetry points of the crystal lattice [35]. It can be assumed that this is also the case for a CoFeB alloy, suggesting that the observed transitions are likely to be consistent with the presence of a bcc crystalline phase, in agreement with the presence of the CoFe (1 1 0) peak in the diffractogram of the 400 °C annealed sample. In any case, because the major plasmonic effects due to gold are expected at energies below the plasma edge (2.5 eV) [34], the observed changes in the spectra are more likely to be due to the crystallization of CoFeB.

Next, we compare the change in the Kerr spectra before and after annealing in figure 5. A broad feature centred at about 2.5 eV is in this case also very pronounced, becoming clearly narrower upon annealing.

The spectra compare well with previous studies on Co–Fe alloys [18], suggesting that the B content in our alloy may have a minimal influence on the magneto-optical response transitions in the studied energy range. The amplitude of the signal improves with the annealing, similarly to the previously reported case of FePt alloys [36]. Following the interpretation in [36], the enhancement of the MOKE signal can be regarded as a sign of improvement in the magnetic ordering of the films.

4. Conclusions

In this work, the optical and magneto-optical properties of Co60Fe20B20 were investigated by means of ellipsometry and MOKE spectroscopy, before and after annealing in vacuum. The dielectric function of the Co60Fe20B20 layers (diagonal elements) was determined from a multi-sample analysis of layers with thickness from 10 nm to 20 nm. The dielectric function of the layers after annealing is consistent with previous experimental and theoretical studies on Co–Fe alloys with a bcc crystalline structure, indicating the formation of this crystalline phase in the present alloy already after an annealing step of 30 min at 350 °C. The crystallization of the films was also confirmed by XRD for films annealed at 400 °C. This study shows that the optical and magneto-optical spectra are sensitive to the crystallization of the Co60Fe20B20 layers already at initial stages that are not yet detectable by XRD.

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References

[1] Tsymbal E Y, Mryasov O N and LeClair P R 2003 Spin-dependent tunnelling in magnetic tunnel junctions J. Phys.: Condens. Matter 15 R109–42
[2] Brataas A, Kent A D and Ohno H 2012 Current-induced torques in magnetic materials Nat. Mater. 11 372–81
[3] Ikeda S, Miura K, Yamamoto H, Mizunuma K, Gan H D, Endo M, Kanai S, Hayakawa J, Matsukura F and Ohno H 2010 A perpendicular-anisotropy CoFeB–MgO magnetic tunnel junction Nat. Mater. 9 721–4
[4] Chen J Y, Feng J F and Coey J M D 2012 Tunable linear magnetoresistance in MgO magnetic tunnel junction sensors using two pinned CoFeB electrodes Appl. Phys. Lett. 100 142407
[5] Costa J D, Serrano-Guisan S, Borme J, Deepak F L, Tarequzzaman M, Paz E, Ventura J, Ferreira R and Freitas P P 2010 Impact of MgO thickness on the performance of spin-transfer torque nano-oscillators IEEE Trans. Magn. 51 1401604
[6] Mathon J and Umerski A 2001 Theory of tunneling magnetoresistance of an epitaxial Fe/MgO/Fe(001) junction Phys. Rev. B 63 220403
[7] Djayaprawira D D, Tsunekawa K, Nagai M, Maehara H, Yamagata S, Watanabe N, Yuasa S, Suzuki Y and Ando K 2005 230% room-temperature magnetoresistance in CoFeB/MgO/CoFeB magnetic tunnel junctions Appl. Phys. Lett. 86 92502
[8] Ikeda S, Hayakawa K, Ashizawa Y, Lee Y M, Miura K, Hasegawa H, Tsunoda M, Matsukura F and Ohno H 2008 Tunnel magnetoresistance of 604% at 300 K by suppression of Ta diffusion in CoFeBMgOCoFeB pseudo-spin-valves annealed at high temperature Appl. Phys. Lett. 93 082508
[9] Bonetti S, Hoffmann M C, Sher M J, Chen Z, Yang S-H, Samant M G, Parkin S S P and Durr H A 2016 THz-driven ultrafast spin-lattice scattering in amorphous metallic ferromagnets Phys. Rev. Lett. 117 087205

Figure 5. Comparison of Kerr rotation θK (black) and ellipticity ηK (red) for Si/SiO2(100 nm)/Co60Fe20B20(20 nm)/Au(3 nm) before and after annealing.
[10] Chen J Y, He L, Wang J-P and Li M 2017 All-optical switching of magnetic tunnel junctions with single subpicosecond laser pulses Phys. Rev. Appl. 7 021001

[11] Halilov S V and Uspenskii Y A 1990 Effects of degeneracy removal on optical and magneto-optical properties of 3d ferromagnetic metals J. Phys.: Condens. Matter 2 6137

[12] Oppeneer P M, Maurer T, Sticht J and Kübler J 1992 Ab initio calculated magneto-optical Kerr effect of ferromagnetic metals: Fe and Ni Phys. Rev. B 45 10924–33

[13] Kim K J, Leung T C, Harmon B N and Lynch D W 1994 Calculation of optical properties and self-energy shifts for ferromagnetic Ni, Co and Fe J. Phys.: Condens. Matter 6 5069–79

[14] Oppeneer P M, Kraft T and Eschrig H 1995 Anisotropic magneto-optical Kerr effect of hcp and fcc Co from first principles Phys. Rev. B 52 3577–80

[15] Kuneck J and Novák P 1999 Full-potential linearized augmented-plane-wave calculation of the magneto-optical Kerr effect in Fe, Co and Ni J. Phys.: Condens. Matter 11 6301–9

[16] Kim K J, Lee S J and Lynch D W 2000 Study of optical properties and electronic structure of ferromagnetic FeCo Solid State Commun. 114 457–60

[17] Kim K J, Lee S J and Park J M 2002 Electronic structure of DO$_3$-ordered Fe$_x$Co and Co$_x$Fe studied by spectroscopic ellipsometry J. Magn. Magn. Mater. 241 40–46

[18] Kumar M, Nautiyal T and Auluck S 2010 Optical and magneto-optical properties of 3d ferromagnetic metals J. Phys.: Condens. Matter 2 6137

[19] Halilov S V and Uspenskii Y A 1990 Effects of degeneracy removal on optical and magneto-optical properties of 3d ferromagnetic metals J. Phys.: Condens. Matter 2 6137