Co-sputtered PtMnSb thin films and PtMnSb/Pt bilayers for spin–orbit torque investigations

Jan Krieft⁷, Johannes Mendig⁵, Myriam H. Aguirre⁶,⁴, Can O. Avci⁵, Christoph Klewe⁴, Karsten Rott¹, Jan-Michael Schmalhorst¹, Günter Reiss¹, Pietro Gambardella², and Timo Kuschel¹,⁷

¹ Center for Spinelectronic Materials and Devices, Department of Physics, Bielefeld University, 33615 Bielefeld, Germany
² Department of Materials, ETH Zürich, Hönggerbergstrasse 64, 8093 Zürich, Switzerland
³ Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain
⁴ Instituto de Nanociencia de Aragón (INA) & Laboratorio de Microscopias Avanzadas (LMA), Universidad de Zaragoza, 50018 Zaragoza, Spain
⁵ Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
⁶ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
⁷ Physics of Nanodevices, Zernike Institute for Advanced Materials, University of Groningen, 9747 AG Groningen, The Netherlands

Received 21 December 2016, revised 21 January 2017, accepted 31 January 2017
Published online 7 February 2017

Keywords PtMnSb, Pt, half-Heusler alloys, spin–orbit torques, magnetron sputtering, thin films

* Corresponding author: e-mail jkrieft@physik.uni-bielefeld.de

The manipulation of the magnetization by spin–orbit torques (SOTs) has recently been extensively studied due to its potential for efficiently writing information in magnetic memories. Particular attention is paid to non-centrosymmetric systems with space inversion asymmetry, where SOTs emerge even in single-layer materials. The half-metallic half-Heusler PtMnSb is an interesting candidate for studies of this intrinsic SOT. Here, we report on the growth and epitaxial properties of PtMnSb thin films and PtMnSb/Pt bilayers deposited on MgO(001) substrates by dc magnetron co-sputtering at high temperature in ultra-high vacuum. The film properties were investigated by X-ray diffraction, X-ray reflectivity, atomic force microscopy, and electron microscopy. Thin PtMnSb films present a monocristalline C1b phase with (001) orientation, coexisting at increasing thickness with a polycrystalline phase with (111) texture. Films thinner than about 5 nm grow in islands, whereas thicker films grow ultimately layer-by-layer, forming a perfect MgO/PtMnSb interface. The thin PtMnSb/Pt bilayers also show island growth and a defective transition zone, while thicker films grow layer-by-layer and Pt grows epitaxially on the half-Heusler compound without significant interdiffusion.

1 Introduction Spin–orbit torques (SOTs) in ferromagnet/heavy metal bilayers can be utilized to electrically manipulate and switch the magnetization in the magnetic layer [1–5]. In these systems, the spin Hall effect [6, 7] in the heavy metal layer and electron scattering at the interface [8] induce a spin current from the heavy metal to the adjacent magnetic layer, which gives rise to SOT. This has been demonstrated for ferromagnetic semiconductors [9] and, more recently, for the room-temperature ferromagnet half-Heusler compound NiMnSb [10] and the antiferromagnet CuMnAs [11]. The family of half-metal Heusler alloys with C1b structure is particularly interesting for SOT studies because of their robust magnetic properties and lack of inversion symmetry.

In this work, we prepare and investigate co-sputter-deposited thin films of the room-temperature ferromagnet PtMnSb, which belongs to the same Heusler class of materials [12, 13]. PtMnSb thin films were first investigated in the 1980s as magnetooptical recording media [14], due to their very large magnetooptical Kerr effect [15]. Half-
metallic alloy films have been prepared by rf sputtering from a sintered MnSb target with Pt sheets or from a mosaic target on a fused quartz or glass substrate followed by annealing [16, 17]. To investigate the possibility of using the ferromagnet PtMnSb in giant magnetoresistance applications, epitaxial PtMnSb(111) films on Al₂O₃(0001) have been produced with dc magnetron co-sputtering at 500 °C [18]. Epitaxial PtMnSb(001) films were also obtained by dc co-sputtering on an MgO(001) substrate, using an oriented W seed layer. This growth is accompanied by a modest in-plane strain insufficient to induce perpendicular magnetization through inverse magnetostriction [19]. Moreover, ordered thin films of PtMnSb can be produced by solid-state phase formation via thermal annealing of compositionally modulated thin multilayered Pt/Mn/Sb films. In this process, films consisting of the two phases PtMnSb and Mn₂Sb have been obtained [20]. Structurally related half-Heusler compounds such as NiMnSb can equally be grown by pulsed-laser deposition using low substrate temperature [21]. In addition, epitaxial NiMnSb(001) thin films can be fabricated on (In,Ga)As(001) by molecular-beam epitaxy (MBE) [22–24].

As mentioned in the prior paragraph, the successful growth of single-phase epitaxial PtMnSb films by dc magnetron co-sputtering was already reported in the 1990s [25]. We extended the investigation of this half-Heusler alloy by the detailed structural analysis of PtMnSb/Pt bilayers prepared as twin samples with bare PtMnSb films with explicit focus on the interface region. The quality of the bilayer interface is highly important for the study of heterostructures to realize spintronic devices based on the spin polarization in proximity to the PtMnSb. This provides an insight into ferromagnetic properties and SOT effects in PtMnSb films with or without an additional Pt layer. Ultimately, it allows for studying the SOT dependency on using an adjacent heavy metal layer and opens new possibilities for practical applications [26]. In addition, the preparation of PtMnSb and PtMnSb/Pt twin samples is particularly useful for the quantitative disentanglement of spin caloritronic effects such as spin Seebeck and anomalous Nernst effect in ferromagnet/heavy metal bilayers [27].

We prepared epitaxial PtMnSb thin films with varying film thickness on MgO(001) substrates at high temperatures without utilizing any seed layer and fabricated additional PtMnSb/Pt bilayers. In this Letter, we present a detailed X-ray technique analysis in combination with high resolution transmission electron microscopy (TEM) to characterize the film growth and quality. In future work electrical measurements on these single films and bilayers could be performed to ultimately study spin transport properties and SOTs [28, 29]. Furthermore, the spin polarization depth profile of the samples could be detected using X-ray resonant magnetic reflectivity [30–32]. We would expect a Pt spin polarization in the Pt film at the interface due to the magnetic proximity effect and, in addition, in the PtMnSb material itself which significantly would influence the transport phenomena.

2 Experimental

2.1 Sample growth The PtMnSb films are prepared by dc magnetron co-sputtering from three 3-inch sources in
an ultra-high vacuum chamber with a base pressure of 10^{-9} mbar. In each preparation cycle, two nominally identical PtMnSb(x nm) layers were grown on two polished MgO(001) substrates with a lattice mismatch of about 4%, one of them with Pt(x nm) on top. Sputter powers used for the elemental targets are 25 W for Pt, 38 W for Mn and 41 W for Sb with 10 sccm Ar gas flow at 1.9 \times 10^{-3} mbar to obtain the correct stoichiometry with a deposition rate of 0.11 nm/sec for the total thickness. The sources are confocally arranged and tilted towards the substrate at an angle of 35° with respect to surface normal. The substrates are rotated during deposition at 10 rpm to avoid inhomogeneous covering. Deposition temperature is 400 °C to achieve optimal growth followed by a cool down to room temperature in about 2 h. The structural analysis reveals that temperatures higher than 400 °C are incompatible with monocrystalline growth and not suitable for further investigation of the magnetic and transport properties due to increased granular character of the films.

Subsequently, the Pt layer is deposited at room temperature at 100 W with 10 sccm Ar gas flow at 1.9 \times 10^{-3} mbar and substrate rotation, with a Pt deposition rate of 0.09 nm/sec. For the twin sample fabrication with and without Pt top layer, the PtMnSb film on one MgO substrate is covered by a mask prior to the Pt deposition. Afterwards and prior to atmosphere exposure, the single PtMnSb layer is capped at room temperature by MgO(3 nm) to avoid ex-situ oxidation and by 2 nm of Al forming a passivating oxide to protect the hygroscopic MgO layer.

2.2 Methods After deposition, the composition of the films is determined by spectral energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) measurements are performed with a Philips X’Pert Pro diffractometer with a Cu Kα source in a Bragg Brentano configuration to analyze crystallographic properties of the samples. The film thickness and roughness are determined via X-ray reflectivity (XRR) in the same setup. A Bruker AFM Multimode is used for atomic force microscopy (AFM) of the surface topography utilizing Bruker FMV-A probes in tapping mode. The thin films crystallinity, structure and composition is analyzed by a scanning transmission electron microscope (STEM) with a high angular annular dark field (HAADF) detector in a FEI Titan G2 60–300 equipment with an aberration corrected probe. HAADF imaging is used to map the thin layer via STEM microscopy which is highly sensitive to element variations. The preparation of uniformly thin TEM lamellae is done by focused ion beam milling in a Dual Beam Helios 650 Nanolab. We visualize the atomic structure to check growth and layer roughness. The EDX analysis is performed by in-situ-STEM with an Oxford equipment.

3 Results and discussion Figure 1a shows the results of the XRD analysis. The PtMnSb(004) Bragg peak is clearly visible for all samples, while the (002), (222) and (333) only appear when the layer thickness exceeds about 15 nm. The (111) peak is visible for all PtMnSb thicknesses, except for the 5 nm sample where it is weakly expressed. Therefore, all films show at least a polycrystalline but textured structure with major epitaxial growth in the [001] direction, as can be concluded from the peak intensity ratios and complementary calculations of the structure factors. Off-specular XRD experiments using an electron probe confirm the crystalline growth of the PtMnSb with (001) orientation, which is reflected by the Bragg reflections. The Bragg reflections could not be found. Therefore, the specular PtMnSb(111) reflections belong to polycrystalline material with [111] texture, while the dominant PtMnSb(004) reflection is due to a monocrystalline PtMnSb phase.

Figure 1b shows the (004) Bragg peak intensity and full width at half maximum (FWHM) plotted against the PtMnSb film thickness. The flattening of the intensity increase between 15 nm and 25 nm points to an increasingly polycrystalline growth accompanied by a reduction of texture. Due to direct growth on the MgO substrate, for thin PtMnSb layers epitaxial growth of Pt in (111) and (001) orientation could be observed. With increasing thickness Pt is growing quasi-epitaxially on the ordered PtMnSb in (001) orientation, since corresponding sharp Bragg reflections can be detected. Off-specular Bragg reflections from the (111) orientation could not be found. Therefore, the specular PtMnSb(111) reflections belong to polycrystalline material with [111] texture, while the dominant PtMnSb(004) reflection is due to a monocrystalline PtMnSb phase.

Figure 2 shows the (004) Bragg peak intensity and full width at half maximum (FWHM) plotted against the PtMnSb film thickness. The flattening of the intensity increase between 15 nm and 25 nm points to an increasingly polycrystalline growth accompanied by a reduction of texture. Due to direct growth on the MgO substrate, for thin PtMnSb layers epitaxial growth of Pt in (111) and (001) orientation could be observed. With increasing thickness Pt is growing quasi-epitaxially on the ordered PtMnSb in (001) orientation, hence only the Pt(002) and (004) peaks are visible (cf. Fig. 4e).

The pronounced oscillations in the XRR scans shown in Fig. 2 verify relatively smooth surfaces for all layers exceeding 5 nm with roughnesses in the range of 0.7 nm to 1.2 nm. This nicely fits the roughness value obtained by additional AFM measurements shown in Fig. 3. The 1 µm × 1 µm scan reveals a locally smooth and homogeneous growth with granular character for thin films prepared at 400 °C (cf. Fig. 3a). We find larger grains and a
more distinct island growth for an increasing deposition temperature of 475 °C as exemplarily shown in Fig. 3b. The depth profile of the dispersion δ is simulated for the XRR fits by a layer-by-layer model which depends on the Heusler compound thickness and growth. Consequently, the density distribution is significantly affected by the island growth of PtMnSb (cf. TEM results in Fig. 4a) and the thickness dependent-transition zone between PtMnSb and Pt.

Figure 4 shows representative STEM images of PtMnSb/Pt bilayers for different thicknesses of PtMnSb. To separate both PtMnSb and Pt layers within the STEM pictures it is most convenient to refer to Fig. 4d and e where the PtMnSb half-Heusler and Pt fcc structure are easily separable by brightness, order and the labeled crystal directions. We find that the thinnest layer, PtMnSb(5 nm)/Pt (cf. Fig. 4a and b) grows epitaxially in a...
Volmer–Weber mode (PtMnSb on MgO) forming a sharp interface with MgO. Dark field images show the non-wetting elemental micro and granular structure of the PtMnSb. Structural coherence and epitaxy is found in large regions of 20–60 nm. The diffraction patterns correspond to the adjacent system layer and emphasis the local epitaxial growth on the MgO substrate. The red arrow indicates the structural coherence of the bilayer system in the direction of growth. In bilayers the Pt overlayer grows uniformly over the substrate, covering both PtMnSb islands and the bare MgO substrate in a uniform way. Therefore, in regions without PtMnSb, the Pt is growing directly on the MgO. The interface of PtMnSb(5 nm)/Pt is partially defective, as seen in Fig. 4b, showing a STEM-HAADF image of an island of the nominal 5 nm film with a height of up to 9.5 nm.

The intermediate thickness layer, PtMnSb(10 nm)/Pt (cf. Fig. 4c), shows a much smaller roughness and relatively homogeneous growth. This is due to the Frank–van der Merwe growth mode (PtMnSb on PtMnSb) which results in fully formed layers and is confirmed by TEM, but not shown here. A small transition zone manifests at the interface, where the Pt is forced into a disordered cubic structure. STEM-HAADF images indicate partially epitaxial films with a transition zone adjusting to both crystal structures. Areas with excess Pt tend to grow adopting the fcc structure instead of the half-Heusler structure. EDX linescans confirm that certain areas of PtMnSb(10 nm)/Pt(4 nm) exhibit a transition zone of about 2.5 nm with high Pt content on top of the stoichiometric PtMnSb. This can be seen in Fig. 4e as the large interface defect in gray color between the bright Pt and ordered PtMnSb area. In these intermediate layers we find misoriented grains, exemplary illustrated on the left side of Fig. 4c, where the lattice structure of PtMnSb cannot be resolved. Hence, these images reveal a defective quasi-amorphous interface between Pt and PtMnSb in half-Heusler structure.

Finally, the thickest PtMnSb(15 nm)/Pt layer (cf. Fig. 4d and e) exhibits ultimately layer-by-layer growth. Thereby the islands close up with growing thickness and the surface becomes smoother which resembles layer-by-layer growth at the final stage. The interface only shows some steps and dislocations for fitting the two lattices with an almost perfect match (cf. Fig. 4e). Consequently, we find that thin PtMnSb layers exhibit island growth and a defective PtMnSb/Pt transition zone, while thicker films show homogeneous epitaxial growth and high quality interfaces. Since the XRD analysis reveals polycrystalline properties in these thicker films, this homogeneous growth influenced by the thicker and therefore smoother half-Heusler structure is locally confined. However, these grains get significantly larger and more defect-free, as confirmed by additional TEM images. Figure 4f shows the transversal EDX linescans with drift correction, confirming the composition of the PtMnSb/Pt bilayer films.

Figure 5 presents exemplary room temperature SQUID magnetization measurements including a hysteresis loop of the PtMnSb(15 nm)/Pt(4 nm) bilayer (cf. Fig. 5a). The samples show an in-plane magnetization with a coercivity of about 150 Oe. An additional variance of 10% due to an upper bound for any SQUID related artifact such as sample shape is considered for the measurements of the saturation magnetization $M_S$ of PtMnSb(5 nm)/Pt(4 nm) bilayers as a function of thickness $t_{PtMnSb}$. The sample thickness was rechecked by STEM measurements to determine the magnetic volume. The determined values are about 30% below bulk values (570 kA/m [17, 33]).

4 Conclusion We have prepared highly textured PtMnSb thin films and PtMnSb/Pt bilayers on MgO(001) substrates by co-sputter deposition. PtMnSb films grow epitaxially with a thickness-dependent degree of coherence and texture. The crystal structure corresponds to that of a C1b Heusler alloy. In bilayer systems, Pt grows as a uniform polycrystalline fcc layer, in which the interface quality is significantly improving with the PtMnSb thickness. While thin PtMnSb films of 5 nm grow as separate islands, thicker films such as 15 nm and above show layer-by-layer growth. The Pt covers the PtMnSb and the MgO substrate between the islands on the PtMnSb(5 nm) thin films, whereas it grows epitaxially and flat on PtMnSb(15 nm) films. The interface quality highly increases with the thickness of PtMnSb, up to quasi-perfect matching. Locally, the Pt grows crystalline on the PtMnSb as seen in the STEM images, but on average the XRD analysis reveals the polycrystalline textured character for the whole PtMnSb/Pt film. While PtMnSb has a monoclinic phase with (001) orientation deduced from off-specular XRD measurements, a second polycrystalline phase with (111) texture is present. These results show that heterostructures based on the PtMnSb Heusler alloy are suitable to realize spintronic devices and study SOT in non-centrosymmetric systems.

Acknowledgements C.K. acknowledges financial support by the Alexander von Humboldt foundation.
References

[1] I. M. Miron, G. Gaudin, S. Auffret, B. Rodmacq, A. Schuhl, S. Pizzini, J. Vogel, and P. Gambardella, Nature Mater. 9(3), 230–234 (2010).
[2] I. M. Miron, K. Garello, G. Gaudin, P. J. Zermatten, M. V. Costache, S. Auffret, S. Bandiera, B. Rodmacq, A. Schuhl, and P. Gambardella, Nature 476(7359), 189–193 (2011).
[3] L. Liu, C. F. Pai, Y. Li, H. W. Tseng, D. C. Ralph, and R. A. Buhrman, Science 336(6081), 555–558 (2012).
[4] L. Neumann, D. Meier, J. Schmalhorst, K. Rott, G. Reiss, and M. Meinert, Appl. Phys. Lett. 109(14), 142405 (2016).
[5] C. O. Avci, A. Quindeau, C. F. Pai, M. Mann, L. Caretta, A. S. Tang, M. C. Onbasli, C. A. Ross, and G. S. Beach, Nature Mater., DOI: 10.1038/nmat4812 (2016).
[6] I. M. Dyakonov and V. I. Perel, Phys. Lett. A 35(6), 459–460 (1971).
[7] J. Sinova, S. O. Valenzuela, J. Wunderlich, C. Back, and T. Jungwirth, Rev. Mod. Phys. 87(4), 1213 (2015).
[8] V. P. Amin and M. D. Stiles, Phys. Rev. B 94(10), 104420 (2016).
[9] A. Chernyshov, M. Overby, X. Liu, J. K. Furdyna, Y. Lyanda-Geller, and L. P. Rochinson, Nature Phys. 5(9), 656–659 (2009).
[10] C. Ciccarelli, L. Anderson, V. Tsitillow, A. J. Ferguson, F. Gerhard, C. Gould, L. W. Molenkamp, J. Gayles, J. Železný, L. Smejkal, Z. Yuan, J. Sinova, F. Freimuth, and T. Jungwirth, Nature Phys. 12, 855–860 (2016).
[11] P. Wadley, B. Howells, J. Železný, C. Andrews, V. Hills, R. P. Campion, V. Novák, K. Olednjk, F. Maccherozzi, S. S. Dhesi, S. Y. Martin, T. Wagner, J. Wunderlich, F. Freimuth, Y. Mokrousov, J. Kuneš, J. S. Chauhan, M. J. Grzybowski, A. W. Rushforth, K. W. Edmonds, B. L. Gallagher, and T. Jungwirth, Science 351, 587–590 (2016).
[12] K. Watanabe, J. Phys. Soc. Jpn. 28(2), 302–307 (1970).
[13] R. A. De Groot, F. M. Mueller, P. G. Van Engen, and K. H. J. Buschow, Phys. Rev. Lett. 50(25), 2024 (1983).
[14] P. G. Van Engen, K. H. J. Buschow, R. Jongebreur, and M. Erman, Appl. Phys. Lett. 42(2), 202–204 (1983).
[15] H. Akasaka and M. Sato, Process and apparatus for simultaneous erasure and recording in magneto-optical recording, 1989, US Patent 4,853,912.
[16] R. Ohyama, T. Koyanagi, and K. Matsubara, J. Appl. Phys. 61(6), 2347–2352 (1987).
[17] E. Attaran and P. J. Grundy, J. Magn. Magn. Mater. 78(1), 51–55 (1989).
[18] M. C. Kautzky, F. B. Mancoff, J. F. Bobo, P. R. Johnson, R. L. White, and B. M. Clemens, J. Appl. Phys. 81(8), 4026–4028 (1997).
[19] M. C. Kautzky and B. M. Clemens, Appl. Phys. Lett. 66(10), 1279–1281 (1995).
[20] T. Matsui, N. Iketani, K. Morii, and Y. Nakayama, Mater. Chem. Phys. 36(1–2), 106–111 (1993).
[21] J. Giapintzakis, C. Grigorescu, A. Klini, A. Manousaki, V. Zorbas, J. Androulakis, V. Viskadourakis, and C. Fotakis, Appl. Phys. Lett. 80(15), 2716–2718 (2002).
[22] W. Van Roy, J. De Boeck, B. Bijis, and G. Borghs, Appl. Phys. Lett. 77(25), 4190–4192 (2000).
[23] P. Bach, A. S. Bader, C. Rüster, G. Schmidt, L. W. Molenkamp, W. Weigand, C. Kumpf, E. Umbach, R. Urban, G. Wolsiders, and B. Heinrich, Appl. Phys. Lett. 83(3), 521–523 (2003).
[24] F. Gerhard, C. Schumacher, C. Gould, and L. W. Molenkamp, J. Appl. Phys. 115(9), 094505 (2014).
[25] M. C. Kautzky and B. M. Clemens, Epitaxial growth of (001)-and (111)-oriented ptmnsb films and multilayers, in: MRS Proceedings, 1995, p. 109.
[26] Y. Xu, Y. Yang, K. Yao, B. Xu, and Y. Wu, Sci. Rep. 6, 26180 (2016).
[27] P. Bougiatioti, C. Klewe, D. Meier, O. Manos, O. Kuschel, J. Wollschläger, L. Bouchenoire, S. D. Brown, J. M. Schmalhorst, G. Reiss, and T. Kuschel, to be submitted (2017).
[28] R. A. Buhrman, Science 336(6081), 555–558 (2012).
[29] K. Garello, I. M. Miron, C. O. Avci, F. Freimuth, Y. Mokrousov, S. Blügel, S. Auffret, O. Boulle, G. Gaudin, and P. Gambardella, Nature Nanotechnol. 8(8), 587–593 (2013).
[30] C. O. Avci, K. Garello, A. Ghosh, M. Gabureac, S. F. Alva-rado, and P. Gambardella, Nature Phys. 11(7), 570–575 (2015).
[31] T. Kuschel, C. Klewe, J. M. Schmalhorst, F. Bertram, O. Kuschel, T. Schemme, J. Wollschläger, S. Francoual, J. Strempfer, A. Gupta, M. Meinert, G. Götz, D. Meier, and G. Reiss, Phys. Rev. Lett. 115(9), 097401 (2015).
[32] C. Klewe, T. Kuschel, J. M. Schmalhorst, F. Bertram, O. Kuschel, J. Wollschläger, J. Strempfer, M. Meinert, and G. Reiss, Phys. Rev. B 93(9), 214440 (2016).
[33] T. Inukai, M. Matsuoka, and K. Ono, Appl. Phys. Lett. 49(1), 52–53 (1986).