1. Introduction

The magnitude of the spin polarization of ferromagnetic materials is a key property for their application in spin transport-based electronics [1]. However, it is not the bulk, but the surface or interface electronic properties, which are relevant for most applications. Investigating epitaxial thin films of the Heusler compound Co$_2$MnSi [2–5] by spin resolved UV-photoemission spectroscopy (HAXPES), recently a high spin polarization was observed at room temperature in a wide energy range below the Fermi energy [9]. This resonance is related to a surface resonance in the majority electron spin band extending deep into the bulk of the material [9, 10]. Correspondingly, Co$_2$Fe$_x$Mn$_{1-x}$Si/Ag/Co$_2$Fe$_x$Mn$_{1-x}$Si spin valves show giant magnetoresistance (GMR) values up to 170 % at low temperatures [13]. However, the use of alternative non-magnetic spacer layers like thin Cr always resulted in strongly reduced GMR values [14] with unclear origin. In order to understand this behavior, we investigated Co$_2$MnSi interfaces with several metals typically used as spacer layers for spin valves. The high photon energy of HAXPES (typically 6–8 keV) corresponds to a relatively large inelastic mean free path of the photoelectrons of $\approx 10$ nm [15], which allows to probe electronic bulk states and buried interfaces. However, the small scattering cross sections in HAXPES result in general in a relatively small photoemission intensity. As spin-filtering typically is associated with an additional reduction of
layers demonstrated epitaxial growth of Ag(1 0 0) (figure 2, diffuse RHEED images indicating polycrystalline growth. Additionally, the calculated bulk density of states of Co2MnSi is shown [9].

The count rates by orders of magnitude, it is not available as a standard method [16].

Our previous HAXPES investigations (6keV photon energy) of Co2MnSi(100)/AlOx(2nm) thin films showed a characteristic shoulder feature near the Fermi edge. This feature is, based on comparison with HAXPES calculations considering a bare Co2MnSi(100) surface, associated with the highly spin-polarized surface resonance [9, 10] (figure 1). Here, we propose to use this HAXPES shoulder feature as a signature of high spin polarisation also for buried metal interfaces. First, the previously implied association of the AlOx(2nm) capping layer with a vacuum interface is reconsidered by investigations of Co2MnSi(100)/metal(2nm)/AlOx(2nm) trilayers, before other Co2MnSi(100)/metal(2nm)/AlOx(2nm) trilayers are discussed.

2. Sample preparation and characterization

The multilayer samples were prepared by radio-frequency (RF)-sputtering at room-temperature. Epitaxial Co2MnSi(100) layers with a typical thickness of 20 nm were deposited directly on MgO(100) substrates. After an in-situ annealing process at 550 °C, L21 order was obtained and verified by x-ray diffraction and in-situ electron diffraction (RHEED). The arrangement of the RHEED spots on semi-circles as shown in the upper panel of figure 2 indicates scattering on a 2-dimensional surface, which is consistent with the generally very smooth morphology of this type of Heusler thin films [12]. The alternating intensity of neighboring RHEED spots is characteristic for a L21 ordered surface. Co-Mn swapping disorder (B2 structure) would result in a vanishing of the weaker spots. After allowing the sample to cool down within 45 min to ≃100 °C in ultra high vacuum (≃10−10 mbar), either Al, Cr, Cu, or Ag layers (2nm) were deposited in-situ on top of the Co2MnSi thin films. The RHEED investigations of these layers demonstrated epitaxial growth of Ag(100) (figure 2, lower panel) and Cr(100), whereas Al and Cu layers showed diffuse RHEED images indicating polycrystalline growth.

3. Experimental HAXPES investigations

The multilayer samples described above were investigated ex-situ by HAXPES with a photon energy of 6keV at beamline P09 of the Deutsches Elektronen-Synchrotron (DESY), Hamburg [17]. The SPECS Phoibos 225HV spectrometer was operated in the transmission mode of the transfer lens which is optimized for high transmission at the expense of angular information. The entrance slit of the spectrometer with a size of 3 × 30 mm was aligned parallel to the in-plane [1 1 0]-direction of the Co2MnSi epitaxial thin film. The angular acceptance was ±15° and ±1.55° parallel and perpendicular to the entrance slit, respectively. The angle of x-ray incidence was 5° with respect to the surface normal. All experiments discussed were performed at room temperature.

In principle, the shoulder feature in the HAXPES intensity near the Fermi edge shown in figure 1 could result from metallic states of an underoxidized AlOx capping layer. For the investigation of such effects we compare the HAXPES spectrum shown in figure 3 obtained when measuring a Co2MnSi(100)/Al(2nm)/AlOx(2nm) trilayer with the spectrum from the Co2MnSi(100)/AlOx(2nm) sample shown in figure 1. It is obvious that with the insertion of the additional metallic Al layer the shoulder feature is completely suppressed, ruling out a simple capping layer related origin and thus corroborating the highly spin polarized surface resonance based theoretical interpretation given in our previous work [9, 10].

Next, the influence of various potential spacer layers of GMR devices on the HAXPES shoulder feature is studied by comparing all results shown in figure 3. Investigating the fully epitaxial Co2MnSi(100)/Ag(100) interface the obtained
HAXPES intensities are very similar to the Co$_2$MnSi(100)/AlO$_x$ case, which suggests the conversion of the surface resonance into an interface state for these samples.

In the HAXPES data obtained investigating the Co$_2$MnSi(100)/Cu (polycrystalline) interface the shoulder feature is strongly diminished, but still observable. Investigating epitaxial Co$_2$MnSi(100)/Cr(100) interfaces, as in the case of the Co$_2$MnSi(100)/Al (polycrystalline) interfaces described already above, no indication at all of the shoulder feature related to the surface resonance of Co$_2$MnSi(100) is found.

For the interpretation of the HAXPES results described above, it is important to estimate the contribution of the bulk electronic states of the 2 nm metal layers to the spectra. Experimentally, this is possible by investigating the metallic top layers separately without a Heusler thin film below. As HAXPES of 2 nm metal plus 2 nm AlO$_x$ capping deposited directly on MgO substrates resulted in charging of the samples, we investigated MgO/Al(10nm)/metal (2 nm)/AlO$_x$ samples. In figure 4, the spectra obtained with identical experimental settings are shown allowing for a comparison of the intensities measured at the Fermi edge. In the cases of 2 nm Ag and Cu metal layers as well as with metallic Al below the AlO$_x$ capping layer similar intensities were obtained. In the case of the 2 nm Cr layer, the intensity $\approx$1.5 eV below the Fermi-energy was much higher, which is to be expected due to the d-electron character at the Fermi level of this compound. Relating these intensities to the appearance or distinctiveness of the shoulder feature in HAXPES of the Heusler/metal (2 nm)/AlO$_x$ samples, it is obvious that the additional intensity near the Fermi level in the case of Co$_2$MnSi(001)/Ag(001) is not caused by bulk contributions of the Ag layer itself, rendering from a purely experimental point of view the observation of a specific surface resonance derived interface state possible.

4. Band structure and HAXPES calculations

To gain deeper insight into the electronic origin of the shoulder feature discussed above and its relation to the highly spin polarized surface resonance of bare Co$_2$MnSi(001), band structure and HAXPES calculations for the epitaxial Co$_2$MnSi(001)/Ag(001) system were performed. The experimentally investigated Co$_2$MnSi(001)/Al (or Cu) interfaces could not be considered theoretically, because the polycrystalline structure of the normal metals involved is not describable by our theoretical models. Also the HAXPES intensity for epitaxial Co$_2$MnSi(001)/Cr(001) interfaces was not calculated, in this case due to the unknown magnetic order of the 2 nm Cr layer, which is a complex topic by itself [18].

The self-consistent electronic structure calculations were performed within the framework of ab initio spin-density functional theory by use of the local density approximation. The electronic structure of six monolayers Ag on Co$_2$MnSi(001) was computed for a semi-infinite system using the fully relativistic screened Korringa–Kohn–Rostoker method as implemented in the Munich SPR-KKR package [19, 20]. All technical details can be found in [9, 10]. Corresponding to the experiments all calculations were performed assuming in-plane magnetized samples. Self-consistent potentials were used as input for angle-integrated HAXPES calculations of the Co$_2$MnSi(001)/Ag(001) surface. We accounted for the surface by use of a Rundgren–Malmström barrier potential [21], which was included as an additional layer in the photoemission analysis. This procedure is described in detail in [22] and accounts quantitatively for the energetics and dispersion of all surface-related features. Furthermore, the relative intensities of surface states and resonances are accounted for by calculating the corresponding matrix elements in the surface regime. As the LSDA does not consider the finite lifetime of the initial state, its effect was treated phenomenologically by including an imaginary part of the potential (0.03 eV). The impurity scattering of the final state and its inelastic mean free path was modeled by the imaginary part of the inner potential (10.0 eV) [23]. The chosen value results in a photocurrent that decays exponentially by one order of magnitude within the first 35 atomic layers. This was the bulk sensitivity is guaranteed.

In figure 5, we show the calculated spin-resolved total density of states (DOS) for six monolayers of Ag on top of the
C. Lidig et al.

A semi-infinite Co$_2$MnSi(0 0 1) surface, which was obtained by adding the averaged DOS of the Ag layers to the bulk DOS of Co$_2$MnSi(0 0 1). At the interface with Ag the spin polarisation at the Fermi level is slightly reduced due to interface and surface states found in the minority channel. However, as shown in figure 5, the Ag states are located far below the Fermi level and therefore contribute to the spectral features at the Fermi level not significantly.

As shown in our previous publications [9, 10], the close to 100% spin polarisation obtained by UV-photoemission experiments is ascribed to a surface resonance in the majority channel. As such resonances are typically hidden in the bulk continuum, they cannot be assigned directly from ground state-electronic calculations. However, matrix element effects enhance the spectral intensity of these features significantly. Similar states can be found by analyzing the ground state Bloch spectral function. These states are localized at the interface between Co$_2$MnSi(0 0 1) and Ag and are situated slightly above the Fermi level with high Co partial character. However, these interface resonances show very low spectral weight and it is difficult to identify them because they are found not only in the band gap but also disperse in the bulk continuum. Thus, additionally to our ground state electronic structure calculations, we performed angle-integrated HAXPES one-step model calculations, which are shown in figure 6 in comparison with the corresponding experimental data. The good agreement of both data sets, specifically concerning the spectral shoulder at $E - E_F \simeq -0.5$ eV, is obvious. From this, we conclude that a highly spin-polarized surface resonance exists at the Co$_2$MnSi(0 0 1)/Ag(0 0 1) interface as well.

The resonance discussed above is a specific feature of the fully epitaxial Co$_2$MnSi(0 0 1)/Ag(0 0 1) system. A necessary precondition for the development of interface resonances as discussed above is their coupling to dispersive states, which disappear in the polycrystalline case. This is consistent with the suppression of the HAXPES shoulder feature observed if the epitaxial Ag(0 0 1) layer is replaced by polycrystalline Al or Cu. In general, also the energetic position of the surface resonance depends on the specific metal deposited on top of the Co$_2$MnSi layer. This is because the electronic structure of the interface region depends on the adsorbate, and the resonance by definition has a significant bulk contribution. Thus, the surface resonance is sensitive in its dispersive behavior to the corresponding bulk states. Experimentally, we also observed for the epitaxial Co$_2$MnSi(0 0 1)/Cr(0 0 1) system a full suppression of the related HAXPES shoulder feature. However, as already mentioned above, the magnetic structure of the 2 nm thin Cr(0 0 1) on Co$_2$MnSi(0 0 1) is unknown. Thus, no attempt to calculate the corresponding HAXPES spectrum was made.

5. Summary

By experimental HAXPES investigations of Co$_2$MnSi(1 0 0)/Ag(1 0 0)/(2 nm)/AlO$_x$ (2 nm) trilayer samples and corresponding calculations, evidence for a highly spin polarized interface state close to the Fermi level of the Heusler compound is found. The corresponding shoulder like HAXPES feature is diminished for interfaces with polycrystalline Cu.

Figure 5. Spin resolved density of states (DOS) for the Co$_2$MnSi(0 0 1)/Ag(0 0 1) system. Upper panel: DOS of the majority charge carriers. Lower panel: DOS of the minority charge carriers. The total density of states obtained by averaging the contributions of Co$_2$MnSi(0 0 1) and Ag(0 0 1) is shown in black. Additionally, the Co$_2$MnSi-bulk-DOS (red) and the Ag-DOS (green) obtained by averaging six epitaxial Ag monolayers on top of the Heusler thin film are shown.

Figure 6. Comparison of the experimentally and theoretically obtained HAXPES intensities (photon energy 6 keV, energy resolution $\simeq$300 meV) investigating a Co$_2$MnSi(0 0 1)/Ag(0 0 1) (2nm)/AlO$_x$(2nm) sample.
and vanishes completely for interfaces with polycrystalline Al as well as with epitaxial Cr. These observations are consistent with the possibility to realize large GMR effects with Heusler/Ag interfaces, but not with alternative non-magnetic spacer layers and suggest a relation of the GMR with the existence/non-existence of a spin polarized interface state.

Acknowledgments

Financial support by the German Research Foundation (DFG) via project Jo404/9-1 is acknowledged. Funding for the HAXPES instrument at beamline P09 by the Federal Ministry of Education and Research (BMBF) under contracts 05KS7UM1 and 05K10UMA with Universität Mainz, 05KS7WW3, 05K10WW1 and 05K13WW1 with Universität Würzburg is gratefully acknowledged. We further thank for the support from CEDAMNF (CZ.02.1.01/0.0/0.0/15_003/0000358) of Czech ministry MSMT.

ORCID iDs

Martin Jourdan https://orcid.org/0000-0001-6785-0518

References

[1] Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnár S, Roukes M L, Chetchedkanaova A Y and Treger D M 2001 Science 294 1488
[2] Andrieu S, Neggache A, Hauet T, Devolder T, Hallal A, Chshiev M, Bataille A M, Le Fèvre P and Bertran F 2016 Phys. Rev. B 93 094417
[3] Galanakis I, Dederichs P H and Papanikolaou N 2002 Phys. Rev. B 66 174429
[4] Graf T, Felser C and Parkin S S P 2011 Prog. Solid State Chem. 39 1
[5] Ishida S, Fujii S, Kashiwagi S and Asano S 1995 J. Phys. Soc. Japan 64 2152
[6] Hahn M, Schönhense G, Arbelo Jorge E and Jourdan M 2011 Appl. Phys. Lett. 98 232503
[7] Kolbe M, Chadow S, Arbelo Jorge E, Schönhense G, Felser C, Elmers H J, Kläui M and Jourdan M 2012 Phys. Rev. B 86 024422
[8] Schönhense G, Medjanik K and Elmers H J 2015 J. Electron. Spectrosc. 200 94
[9] Jourdan M et al 2014 Nat. Commun. 5 3974
[10] Braun J et al 2015 Phys. Rev. B 91 195128
[11] Braun J and Donath M 2002 Europhys. Lett. 59 592
[12] Herbourt C, Arbelo Jorge E and Jourdan M 2009 Appl. Phys. Lett. 94 142504
[13] Sakuraba Y, Ueda M, Miura Y, Sato K, Bosu S, Saito K, Shirai M, Konno T J and Takanashi K 2012 Appl. Phys. Lett. 101 252408
[14] Yakushiji K, Saito K, Mitani S, Takanashi K, Takahashi Y K and Hon M 2006 Appl. Phys. Lett. 88 222504
[15] Tanuma S, Powell C J and Penn D R 2011 Surf. Interface Anal. 43 689
[16] Kozinaa X, Ikenaga E, Viol Barbosa C E, Ouardi S, Karel J, Yamamoto M, Kobayashi K, Elmers H J, Schönhense G and Felser C 2016 J. Electron Spectrosc. Relat. Phenom. 211 12
[17] Gloskovskii A et al 2012 J. Electron. Spectrosc. 185 47
[18] Zabel H 1999 J. Phys.: Condens. Matter 11 9393
[19] Ebert H et al 2017 The Munich SPR-KKR package, version 7.7 http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR
[20] Ebert H, Ködderitzsch D K and Minár J 2011 Rep. Prog. Phys. 74 096501
[21] Malmström G and Rundgren J 1980 Comput. Phys. Commun. 19 263
[22] Nuber A, Braun J, Forster F, Minár J, Reinert F and Ebert H 2011 Phys. Rev. B 83 165401
[23] Braun J 1996 Rep. Prog. Phys. 59 1267