Detection of the valence band in buried $Co_2MnSi-MgO$ tunnel junctions by means of photoemission spectroscopy

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This work reports on the detection of the valence band of buried Heusler compounds by means of hard x-ray photoemission spectroscopy. The measurements have been performed on the so-called "half" tunnel junctions that are thin films of Co_2MnSi underneath MgO. Starting from the substrate, the structure of the samples is MgO(buffer)$-Co_2MnSi-MgO(t_{MgO})-AlO_x$ with a thickness t_{MgO} of the upper MgO layer of 2 and 20 nm. The valence band x-ray photoemission spectra have been excited by hard x rays of about 6 keV energy. The valence band spectra have been used to estimate the mean free path of the electrons through the MgO layer to be 17 nm at kinetic energies of about 6 keV. In particular, it is shown that the buried Co_2MnSi films exhibit the same valence density of states as in bulk samples. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2931089]

The X_2YZ (X, Y=transition metal, Z=main group element) Heusler compounds have attracted scientific and technological interest for their potential use as materials for magnetoelectronic devices. The reason for this is the exceptional electronic structure found in particular in the Co_2YZ Heusler compounds (see Refs. 1 and 2, and references therein). Kübler *et al.*[3] concluded from *ab initio* calculations that Co_2 based compounds would have peculiar transport properties when they recognized that the minority-spin density at the Fermi energy ϵ_F vanishes in Co_2MnAl and Co_2MnSn. That means that those compounds exhibit a complete spin polarization at ϵ_F such that they behave like a metal for electrons of one spin direction and like an insulator for the other one. Therefore, these compounds are called half-metallic ferromagnets.[4]

One major research area where Co_2 based Heusler compounds are used is on tunneling magnetoresistive (TMR) junctions (see Ref. 5 for a review on other materials). For materials with complete spin polarization, an infinite TMR ratio is expected. Structural and magnetic properties of Co_2MnSi have been reported for films and single crystals[6–8] and the compound was suggested to be suitable for magnetic tunnel junctions (MTJs). For example, the end members of the series $Co_2Mn_{1-x}Fe_xSi$ (x=0 and 1) have been used for fabrication of MTJs.[9–11] Sakuraba *et al.* measured a high TMR ratio of 570% at 2 K (67% at room temperature) for junctions with Co_2MnSi films as both lower and upper electrodes and with an AlO_x tunnel barrier.[12] Some of the present authors recently developed fully epitaxial MTJs with a Co_2YZ thin film as a lower electrode and a MgO tunnel barrier.[13–15] At room temperature (RT), relatively high TMR ratios of 109% (317% at 4.2 K) for $Co_2Cr_{0.6}Fe_{0.4}Al/MgO/CoFe$ MTJs (Ref. 14) and 90% (192% at 4.2 K) for $Co_2MnSi/MgO/CoFe$ MTJs (Ref. 13) were reported. Furthermore, high TMR ratios of 179% at RT and 683% at 4.2 K were demonstrated for fully epitaxial MTJs with Co_2MnSi films as both lower and upper electrodes and MgO tunnel barrier.[16] The high quality of the interface in Co_2MnSi films with MgO barrier was proved by x-ray absorption spectroscopy and x-ray magnetic circular dichroism.[17]

To develop high performance spintronic devices with Co_2-based Heusler compound thin films as ferromagnetic electrodes, it is essential to clarify the electronic structures of these films in terms of the half-metallic nature. The purpose of the present study was to investigate the valence band electronic structure of Co_2MnSi thin films buried underneath a MgO barrier by means of hard x-ray photoemission spectroscopy (HAXPES).

For the present study, special multicomponent thin film arrangements were produced that correspond to half of a MTJ as used in TMR devices (see Refs. 18–20). In particular, the free electrode was modeled. The fabricated sample layer structure was as follows: MgO(001) substrate/MgO buffer layer (10 nm)/Co_2MnSi (50 nm)/MgO barrier (t_{MgO})/AlO_x(t_{AlO_x}) cap. t_{MgO}=2 nm, 20 nm and t_{AlO_x}=1 nm, 2 nm were chosen for the thickness of the MgO and AlO_x cap, respectively. The topmost AlO_x was used for protection of the MgO layer. Each layer in the sample layer structure was successively deposited in an ultrahigh vacuum chamber (base pressure: about 6×10^{-8} Pa) through the combined use of magnetron sputtering for Co_2MnSi and Al, and electron beam evaporation for MgO. The fabrication procedure was the same as in previous work.[13,16] The Co_2MnSi film was deposited at 300 K and subsequently annealed *in situ* at 870 K for 15 min. The MgO barrier (2 or 20 nm) was deposited at 300 K. X-ray pole figure measurements confirmed that the fabricated Co_2MnSi film was grown epitaxially and was a single crystal with the $L2_1$ structure.[18] It was also proved that the MgO barrier was grown epitaxially and was single crystalline from reflection high-energy electron diffraction patterns[18] and cross-sectional high-resolution trans-

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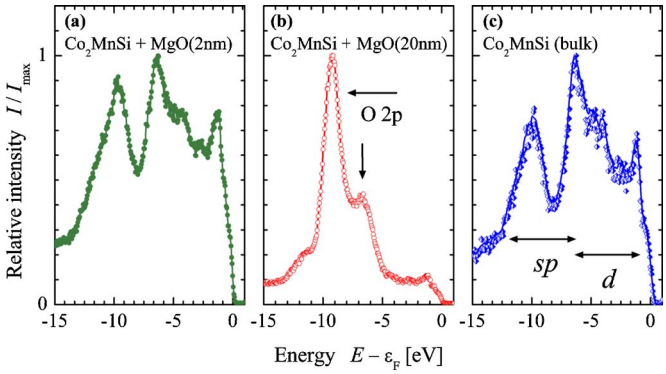

FIG. 1. (Color online) High kinetic energy photoemission spectra of buried Co_2MnSi. The spectra with different thickness 2 nm (a) and 20 nm (b) of the MgO interlayer with spectra from bulk material (c) are compared ($h\nu$=5.95 keV). Oxygen p states and Co_2MnSi valence bands are indicated by arrows in (b) and (c), respectively.

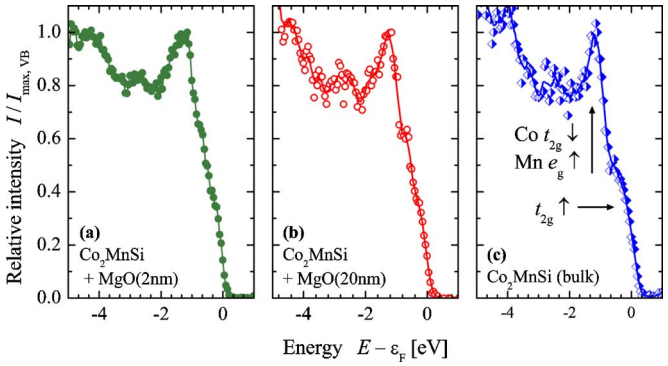

FIG. 2. (Color online) Comparison of the Co_2MnSi valence band spectra close to ϵ_F. Co_2MnSi d states with different character are indicated by arrows. [(a)–(c) like in Fig. 1.]

mission electron microscope lattice images.[13] The AlO_x cap was prepared by exposing the sputter-deposited Al layer to an O_2 atmosphere of ($\approx 1\times10^5$ Pa for 2 h). Al 1s core level spectra (not shown here) revealed that the 1 nm thick Al layer was completely oxidized to Al_2O_3, whereas the 2 nm layer had a remaining, small contribution of metallic Al. Polycrystalline bulk material was used for comparison. It was produced, prepared, and characterized as described in Ref. 21.

The HAXPES experiments were performed at the beamline BL15XU of SPring-8. The photon energy was fixed at 5.946 77 keV using a double crystal monochromator and a Si(333) postmonochromator. The photoemitted electrons were analyzed for their kinetic energy and detected by means of a hemispherical analyzer (Scienta). The overall energy resolution (monochromator plus analyzer) was set to 250 meV, as verified by spectra of the Au valence band at the Fermi energy (ϵ_F). Additionally, spectra close to the Fermi energy were taken with a resolution of 150 meV. The angle between the electron spectrometer and photon propagation is fixed at 90°. The photons are p polarized, that is, the electric field vector is in the plane of incidence and always pointing in the direction of the electron detector. For the thin films, a near normal emission (θ=2°) detection angle was used. This corresponds to an angle of incidence of $\alpha=\theta-90°=88°$. (Note that the angles are not that well defined for the cleaved bulk sample due to surface roughness.)

Figure 1 compares the valence band spectra from the 50 nm thick Co_2MnSi layer buried underneath MgO/AlO_x with different thickness of the MgO interlayer with spectra from bulk material. The valence band spectra of the thin films agree well with those reported from $Co_2Mn_{1-x}Fe_xSi$ bulk samples,[21,22] even though the emission is strongly suppressed in the film with the 20 nm thick MgO layer. In particular, the peak in the density of states at −1.3 eV below ϵ_F is clearly resolved (see Fig. 2). The low lying s-band below −8 eV is only seen in Figs. 1(a) and 1(c). This part, in addition to the lower parts of the p and d bands, is covered by the emission from oxygen 2p states in MgO in Fig. 1(b) where the MgO film is 20 nm thick. The similar structure of the valence band close to ϵ_F in the thin films and the bulk material is obvious from Fig. 2.

The electron mean free path (λ) in MgO is expected to be about 9 nm at 6 keV energy, as calculated from the TPP2M equation (Tanuma–Powell–Penn[23]). In Al_2O_3, one has a mean free path of 11 nm at the same kinetic energy, which should be much smaller in Co_2MnSi (7 nm). From those values, one expects that the electrons emitted from the Fermi energy to easily penetrate the thin MgO and AlO_x films but not through the 50 nm thick Co_2MnSi layer. The electron mean free path is easily extracted from the experiment by comparing the intensities for different thickness of the MgO layer. Figure 3(b) displays the relative intensities $I_{2\ nm}/I_{20\ nm}$. It is seen that the factor $I_{2\ nm}/I_{20\ nm}$ is constant for energies between −4 eV and ϵ_F. The scaling factor amounts to $I_{2\ nm}/I_{20\ nm}=2.878\pm0.016$ on average. The constant intensity ratio is expected as MgO does not contribute to the emission close to the Fermi energy due to its wide band gap. From the exponential decay of the intensity $I(z)\propto\exp\{-z/\lambda\}$ with the layer thickness z, one finds the electron

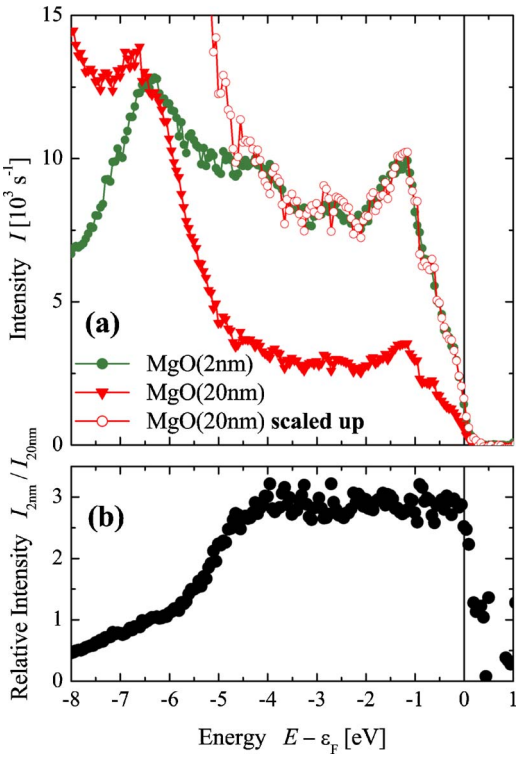

FIG. 3. (Color online) Comparison of the spectra of the buried Co_2MnSi for different MgO thicknesses. (a) compares the spectra and (b) shows the relative intensities of the spectra for different MgO thickness.

mean free path in the MgO layer from $\lambda = \Delta z / \ln(I_{2\ \mathrm{nm}}/I_{20\ \mathrm{nm}})$ to be $\lambda_{\mathrm{MgO}} = 17$ nm.

In Fig. 3(a), the valence band spectra for different MgO thicknesses are directly compared by scaling up the intensity of the 20 nm layer. The identical structure of the spectra, in particular close to the Fermi energy, is easily recognized. The high intensity with a center at about −1.3 eV is due to emission from flat *d* bands (see also Fig. 2) belonging to minority states localized in the Co planes and the highly localized Mn *d* majority states (e_g), as already described in detail for the emission from bulk samples.[21,22] The Co t_{2g} like states mainly define the upper energy of the minority valence bands, whereas the lower intensity at the Fermi energy arises from steep delocalized majority *d* bands with t_{2g} character at Γ.[2,24]

The value observed here for the electron mean free path in MgO is about twice as large compared to the one calculated from the TPP2M equation. This is explained by the high crystalline order of the MgO film and its large optical gap which prevents inelastic scattering mediated by interband transitions. The large mean free path makes it possible to look through the material of the tunnel barrier as seen in Figs. 2(b) and 3.

In summary, the present study demonstrates the feasibility of HAXPES to explore the valence band electronic structure in deeply buried metallic layers. In particular, it was shown that buried Co_2MnSi films exhibit the same valence density of stateslike bulk samples that is typical for half-metallic ferromagnets. This result confirms the promise of an epitaxial, single-crystalline Co_2-based Heusler compound film as a ferromagnetic electrode for spintronic devices.

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[1] C. Felser, G. H. Fecher, and B. Balke, Angew. Chem., Int. Ed. **46**, 668 (2007).
[2] H. C. Kandpal, G. H. Fecher, and C. Felser, J. Phys. D: Appl. Phys. **40**, 1507 (2007).
[3] J. Kübler, A. R. Williams, and C. B. Sommers, Phys. Rev. B **28**, 1745 (1983).
[4] R. A. de Groot, F. M. Müller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[5] S. Yuasa, J. Phys. Soc. Jpn. **77**, 031001 (2008).
[6] M. P. Raphael, B. Ravel, Q. Huang, M. A. Willard, S. F. Cheng, B. N. Das, R. M. Stroud, K. M. Bussmann, J. H. Claassen, and V. G. Harris, Phys. Rev. B **66**, 104429 (2002).
[7] S. Kämmerer, S. Heitmann, D. Meyners, D. Sudfeld, A. Thomas, A. Hütten, and G. Reiss, J. Appl. Phys. **93**, 7945 (2003).
[8] W. H. Wang, M. Przybylski, W. Kuch, L. I. Chelaru, J. Wang, F. Lu, J. Barthel, H. L. Meyerheim, and J. Kirschner, Phys. Rev. B **71**, 144416 (2005).
[9] K. Inomata, S. Okamura, A. Miyazaki, M. Kikuchi, N. Tezuka, M. Wojcik, and E. Jedryka, J. Phys. D: Appl. Phys. **39**, 816 (2006).
[10] M. Oogane, Y. Sakuraba, J. Nakata, H. Kubota, Y. Ando, A. Sakuma, and T. Miyazaki, J. Phys. D: Appl. Phys. **39**, 834 (2006).
[11] D. Ebke, J. Schmalhorst, N.-N. Liu, A. Thomas, G. Reiss, and A. Hütten, Appl. Phys. Lett. **89**, 162506 (2006).
[12] Y. Sakuraba, M. Hattori, M. Oogane, Y. Ando, H. Kato, A. Sakuma, T. Miyazaki, and H. Kubota, Appl. Phys. Lett. **88**, 192508 (2006).
[13] T. Ishikawa, T. Marukame, H. Kijima, K.-I. Matsuda, T. Uemura, and M. Yamamoto, Appl. Phys. Lett. **89**, 192505 (2006).
[14] T. Marukame, T. Ishikawa, S. Hakamata, K.-I. Matsuda, T. Uemura, and M. Yamamoto, Appl. Phys. Lett. **90**, 012508 (2007).
[15] T. Marukame, T. Ishikawa, K.-I. Matsuda, T. Uemura, and M. Yamamoto, Appl. Phys. Lett. **88**, 262503 (2006).
[16] T. Ishikawa, S. Hakamata, K.-I. Matsuda, T. Uemura, and M. Yamamoto, J. Appl. Phys. **103**, 07A919 (2008).
[17] T. Saito, T. Katayama, T. Ishikawa, M. Yamamoto, D. Asakura, and T. Koide, Appl. Phys. Lett. **91**, 262502 (2007).
[18] H. Kijima, T. Ishikawa, T. Marukame, H. Koyama, K. Matsuda, T. Uemura, and M. Yamamoto, IEEE Trans. Magn. **42**, 2688 (2006).
[19] H. Kijima, T. Ishikawa, T. Marukame, K.-I. Matsuda, T. Uemura, and M. Yamamoto, J. Magn. Magn. Mater. **310**, 2006 (2007).
[20] T. Marukame, H. Kijima, T. Ishikawa, K.-I. Matsuda, T. Uemura, and M. Yamamoto, J. Magn. Magn. Mater. **310**, 1946 (2007).
[21] B. Balke, G. H. Fecher, H. C. Kandpal, C. Felser, K. Kobayashi, E. Ikenaga, J.-J. Kim, and S. Ueda, Phys. Rev. B **74**, 104405 (2006).
[22] G. H. Fecher, B. Balke, S. Ouardi, C. Felser, G. Schönhense, E. Ikenaga, J.-J. Kim, S. Ueda, and K. Kobayashi, J. Phys. D: Appl. Phys. **40**, 1576 (2007).
[23] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. **21**, 165 (1993).
[24] H. C. Kandpal, G. H. Fecher, C. Felser, and G. Schönhense, Phys. Rev. B **73**, 094422 (2006).