Transition-metal silicides as materials for magnet-semiconductor heterostructures*

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The injection of a spin-polarized current into a semiconductor, one of the key requirements for spintronics, poses the challenge for computational materials science to possibly screen suitable materials. In a number of theoretical investigations, we have put forward magnetic intermetallic compounds grown epitaxially on Si as promising candidates. We employed density functional theory calculations with the GGA-PBE exchange-correlation functional and the full-potential augmented plane wave plus local orbital (FP-APW+lo) method, as implemented in the WIEN2k package. In the spirit of computational materials science, we investigated the stability and magnetic properties of thin films of the Heusler alloy Co_2MnSi, as well as of binary late transition metal monosilicides, in contact with the Si surface. For the Heusler alloy Co_2MnSi, we could show that the (001) surface retains the half-metallic character of the bulk if a fully Mn-terminated surface is prepared. At interfaces with Si, a finite density of states at the Fermi energy was found for both spin channels, but the half-metallic behavior recovers only a few layers away from the interface. For the monosilicides of the late 3*d*-transition metals (Mn, Fe, Co, Ni), we predict a CsCl-like structure that has not yet been observed as bulk compound but may be stabilized epitaxially on Si(001). For very thin films of CoSi and MnSi grown in this structure, our calculations find a ferromagnetic ground state. Recently, we identified the atomic structure of MnSi films on Si(111) which is close to the natural crystal structure of bulk MnSi (B20), and also shows large magnetic moments of the Mn atoms at the surface and interface. All MnSi films have a high degree of spin polarization (between 30% and 50%, depending on film thickness) at the Fermi level, and are thus promising materials for fabricating electrical contacts for spin injection into Si. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723182]

I. INTRODUCTION

In recent years, a field of research has emerged in solid state physics under the title spintronics. It aims at making use of the spin degree of freedom of electrons, in addition to the charge degree of freedom, for the purpose of storage and processing of information. It is one objective of this field to combine semiconductor technology with magnetic materials, with the particular application of injecting a spin-polarized current from a ferromagnet into a semiconductor. Despite some progress with dilute magnetic semiconductors, the most mature magnetic materials are late 3*d* transition metals and their compounds, because these materials are structurally well characterized and often have Curie temperatures well above room temperature, an advantage over presently available dilute magnetic semiconductors. For these reasons, it is very attractive to study the properties of thin films of transition metals and their compounds on semiconductor substrates, in particular on the technologically most widely used substrate, silicon. To identify candidates that are promising to be employed for spin injection, the material should fulfill the following criteria:

- Structural stability as an epitaxial film on Si;
- sharp and structurally well-defined interface with Si;
- high magnetic ordering temperature—high degree of spin polarization at the Fermi level.

Presently, half-metallic Heusler alloys[1] are under investigation as candidates to be used for spin injection. Here, we

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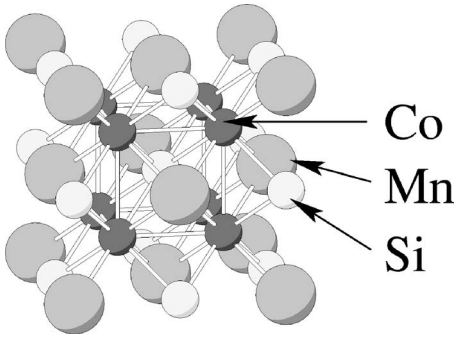

FIG. 1. Ball-and-stick model of the Co_2MnSi Heusler alloy in the $L2_1$ crystal structure. Large balls represent Mn, small light balls Si, and small dark balls Co atoms. The topmost layer is the MnSi-terminated (001) surface.

present a theoretical study of the Heusler alloy Co_2MnSi, a material with $L2_1$ crystal structure (see Fig. 1) and a high Curie temperature of 985 K.[2] Moreover, the fact that this material has been predicted to be a half-metal[3–5] makes it very attractive. This means that a spin polarization of electrons of up to 100% at the Fermi level is achievable in principle, because magnetic half-metals have a finite density of states at the Fermi level in one spin channel *only*, whereas in the other spin channel the Fermi energy lies in a gap of the density of states. Experimental values of the spin polarization have so far remained clearly below 100%, but show considerable scatter depending on the sample preparation. In bulk Co_2MnSi samples, a spin polarization of 56% has been measured,[6] while for samples grown on sapphire a spin polarization of about 60%[7] has been inferred from Andreev reflection. As one possible explanation, it has been argued that imperfections of the crystal structure and chemical disorder in the alloy[8] could substantially reduce the degree of spin polarization. Indeed, neutron diffraction measurements have found an antisite concentration as high as 10%–14% in arc-melted samples.[9] Moreover, for a possible future integration of Heusler alloys into conventional electronics, one has to keep in mind that the lattice constant of Co_2MnSi is about 4% larger than that of Si, while it matches closely with the lattice constants of Ge or GaAs. Due to the closer lattice match, epitaxial growth of Co_2MnSi on Ge or GaAs substrates is probably easier than on silicon. While there are no reports in the literature of Co_2MnSi growth on Si or Ge up to now, epitaxial growth of thin films on GaAs(001) has been achieved recently. In these samples, spin polarization at the Fermi energy of 55% has been inferred from Andreev reflection measurements,[10] while spin-resolved photo-emission on another sample indicated a spin polarization of only 11%.[11] However, the experimental data for thin films could be affected by the unknown atomic structure of the interface or possibly by a different intermetallic phase that could be formed, e.g., by a chemical reaction at the interface between the Heusler alloy and the substrate. From the limited experimental data available so far, information about the interface properties of Co_2MnSi with semiconductors is still lacking. It is also unclear which factors, in terms of the atomic and electronic structure, eventually govern these properties. In order to learn more about the determining factors, we have performed a theoretical study of the (001) surface[12] of Co_2MnSi. Subsequently, we present calculations for Co_2MnSi on Si(001), assuming an atomically sharp interface. To obtain a better understanding of realistic interfaces, we have studied diffusion and incorporation of single Mn atoms on the Si(001) surface, and low-coverage structures of Mn and Mn-silicides on Si.[13] Moreover, we have investigated the properties of pure silicide films, both MnSi,[14] as well as other late-transition-metal silicides,[15] on Si(001). While these materials are more closely lattice-matched to Si than Co_2MnSi, we infer from the calculated magnetic moments and exchange coupling strengths that they are expected to have a lower Curie temperature than Co_2MnSi films, or will even be nonmagnetic, as we find to be the case for FeSi and NiSi.

II. CALCULATIONAL DETAILS

We perform density functional theory calculations, using the full-potential linearized augmented-plane-wave plus local-orbital method, as implemented in the Wien2k code.[16] For electronic exchange and correlation, the generalized gradient functional PBE96 is employed. The surfaces and interfaces are described in the periodic slab geometry, using slabs of up to 15 layers for Co_2MnSi, or eight Si layers plus six Co_2MnSi layers for substrate-plus-film geometries, in all cases exploiting inversion symmetry of the slabs. Muffin-tin radii of 1.06 Å for Co and Si and 1.11 Å for Mn together with a cut-off energy for the interstitial plane-wave basis of 15.2 Ryd were used. Integration over the surface Brillouin was performed using the tetrahedron method on a regular mesh of (10×10) or (12×12) **k**-points, for supported Co_2MnSi films and pure Co_2MnSi surfaces, respectively. Convergence of the results was checked by comparing to single runs with a (16×16) **k**-point mesh.

III. THE (001) SURFACE OF Co_2MnSi

The $L2_1$ crystal structure of Co_2MnSi (space group $Fm3m$) can be described as consisting of (001) planes fully occupied by Co atoms, alternating with Mn+Si planes (see Fig. 1). Hence, the bulk-truncated (001) surface can be Co-terminated or MnSi-terminated. However, for an alloy surface, there is no need for conservation of the bulk stoichiometry; rather, one has to account for the possibility of surface segregation or capping layers. In order to identify the most stable surface termination under given experimental conditions, the framework of *ab initio* thermodynamics[17] is the appropriate choice. Here, the total energy for a multitude of surface atomic structures is calculated using density functional theory. The surface free energy in thermodynamic equilibrium with a given environment is obtained by subtracting the free energy of the constituent elements Co, Mn, and Si in phases acting as reservoirs, described by chemical potentials. The fact that the surface is required to be in equilibrium with the Co_2MnSi bulk yields one equation of constraint, resulting in two variable chemical potentials, which we chose to be μ_{Co} and μ_{Mn}. The surface free energy depends linearly on these variables. To identify the most stable surface for a pair of values (μ_{Co},μ_{Mn}), we screened a large

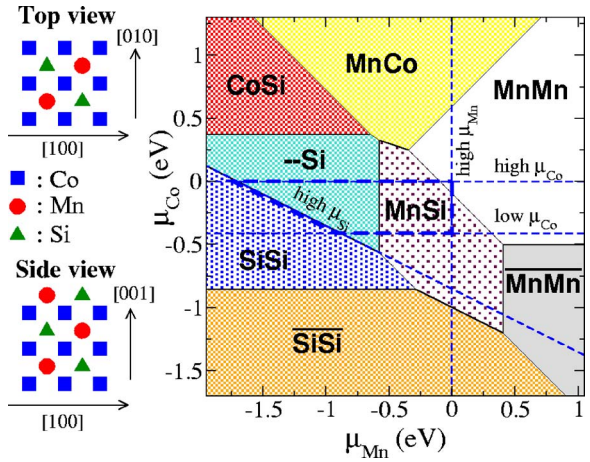

FIG. 2. Calculated phase diagram of $Co_2MnSi(001)$ films (reprinted figure with permission from Ref. 12, ©2005 by the American Physical Society). The shadings indicate the regions of stability of different surface terminations, dashed lines mark the stability limits with respect to bulk materials. The labels with over lines refer to a MnSi subsurface layer, while the others refer to a Co subsurface layer.

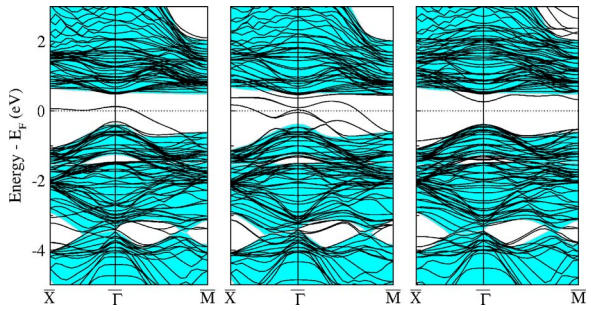

FIG. 3. Surface band structure the minority-spin bands at the $Co_2MnSi(001)$ surface for MnSi termination (left), pure Si (middle), and pure Mn termination (right). In the first two cases, surface band(s) cross the Fermi level, associated with the loss of half-metallicity. Shaded areas indicate the projected bulk band structure.

number of possible surface structures for the one yielding the lowest surface free energy. The results are represented as a phase diagram in the (μ_{Co}, μ_{Mn}) plane (Fig. 2).

We have performed DFT calculations for a total of 15 tentative structures that could be realized with the (1×1) lateral unit cell of $Co_2MnSi(001)$, among them the full Co subsurface layer capped either by a complete Mn surface layer, a mixed MnSi surface layer, or a Si surface layer, with half or full coverage. Alternatively, structures with a MnSi subsurface layer, with a complete Co surface layer, or one of the above mentioned surface layers, were investigated, in all cases involving full structural relaxation of the atomic coordinates compatible with the symmetry operations of the (1×1) unit cell.

As a result, we find that only the structures with a surface layer of Mn, mixed Mn-Si or pure Si, each on a subsurface layer of Co, are thermodynamically stable, for Mn-rich, stoichiometric, or Si-rich conditions of the environment, respectively.[12] We note that the assumption of a full thermal equilibrium, which is a pre-requisite for the formally elegant discussion of surface properties within *ab initio* thermodynamics, is not always experimentally realizable, in particular for material systems with a high melting point and/or low vacuum pressure. Hence, it is conceivable that the range of conditions under which these surface structures can be stabilized experimentally is actually somewhat wider than predicted by this theory.

For the envisaged applications of Co_2MnSi films, it is important to know if and under which conditions the half-metallic gap persists at a surface or interface. We first discuss the origin of the half-metallic properties of bulk Co_2MnSi, following Ref. 18: This material displays an overall spin magnetic moment of 5 μ_B per bulk unit cell, with the main contribution coming from the magnetic moment of the Mn atoms. Correspondingly, there are five more electronic bands occupied in the majority compared to the minority spin channel: While all bands with a major 3*d* character are occupied in the majority spin channel, the Fermi level in the minority spin channel is located in a gap which opens up between 3*d* bands of different point group symmetry. A group-theoretical analysis shows that the gap lies between electronic states of t_{1u} and e_{1u} symmetry, consisting mainly of 3*d* orbitals of pairs of Co atoms.[18] In the following, we study first the (001) surface and then the interface with Si(001), with particular emphasis on the electronic states near or appearing in the gap.

Since the local symmetry is disturbed near the surface or interface (e.g., Mn atoms have only four Co neighbors rather than eight), the group-theoretical arguments given in favor of the existence of a gap need to be modified. Indeed, our calculations predict that, for all three $Co_2MnSi(001)$ surfaces found to be stable, surface states appear in the gap of the minority spin channel (see Fig. 3). In the cases of MnSi or full Si termination, the surface bands cross the Fermi level, and thus the half-metallicity is lost. An orbital analysis shows that the surface states originate from 3*d* orbitals at the subsurface Co atoms pointing along the surface normal. While in the bulk structure the gap appears due to hybridization between the 3*d* orbitals of Co atoms in the Co-Mn-Co groups, this hybridization is reduced in the truncated Co-Mn groups at the surface, and gap states appear. However, on the fully Mn-terminated surface, the surface states appear only above or below the Fermi level. The hybridization of Co with both surface Mn atoms seems to compensate for the symmetry break at the surface.

IV. Co_2MnSi FILMS ON Si(001)

For the envisaged application of Heusler alloy thin films for spin injection, it is important to recognize how quickly the bulk half-metallic property recovers away from a surface or interface that could possibly introduce perturbations due to additional electronic states, as we saw above. To this end, we have performed calculations for films consisting of three double-layers (=Co layer plus MnSi layer) on Si(001). We chose both the surface and the interface to be a MnSi layer, because this structure is stable as a surface structure over a wide range of chemical environments, as we found above. It could possibly be prepared either by depositing Co_2MnSi crystallites using the method of sputtering of bulk samples and annealing, or by an initial reactive epitaxy of an ultrathin Mn layer on Si(001) (see below), followed by a molecular

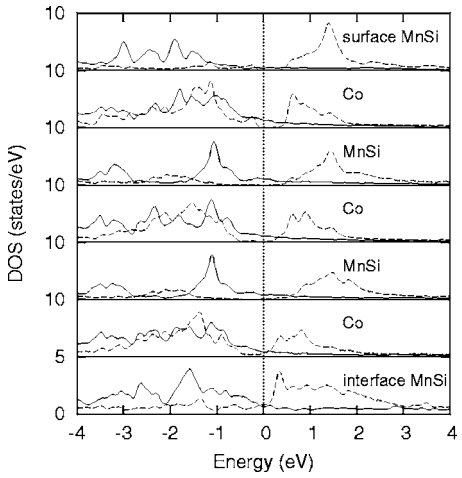

FIG. 4. Electronic density of states projected onto each of the different layers (top to bottom) of a three double-layer Co_2MnSi film on Si(001) (reprinted figure with permission from Ref. 15 ©2005 by the American Physical Society). The Fermi energy is set to zero. Full and dashed lines indicate the density of states in the majority and the minority spin channel, respectively.

beam epitaxy of Co_2MnSi using sources of elemental Co, Mn, and Si. The calculated density of states for the structurally relaxed film (Fig. 4) shows a fast recovery of the half-metallic properties in the interior of the film, i.e., the density of states around the Fermi level in the minority spin channel drops quickly when going from the Co layer next to the MnSi interface layer to a Co layer further away. A systematic study of Heusler alloy films, taking different surface and interface atomic structures into consideration, can be found in Ref. 15.

V. EPITAXY OF Mn ON Si(001)

Next we briefly discuss the possibilities for epitaxial growth of MnSi and Co_2MnSi films on Si(001) in the light of our computational results. It is often argued that the efficiency of the achievable spin injection depends on the abruptness of the interface between the magnetic layer and silicon. (This is because magnetic atoms diffused into the substrate might act as the source of spin-flip scattering, with possibly a detrimental effect on the spin polarization of the injected current.) To clarify the issue of interdiffusion, we have investigated the binding energy of Mn atoms at various sites both at and below the Si(001) surface. Our calculations show that a Mn atom is most strongly bound at interstitial subsurface sites of the Si(001) surface directly below the Si surface dimers characteristic of the Si(001) reconstructed surface.[13,14] These binding sites are energetically more favorable than either sites on the surface (between two Si dimers) or as sites in the third layer, by 0.9 and 0.8 eV, respectively. Similar results have been reported in the literature from density functional theory calculations using large supercells in conjunction with the pseudopotential approximation.[19,20] By depositing less than half of a monolayer of Mn at suitable temperatures, it should be possible to occupy selectively the subsurface interstitial sites *only*. This structure could be frozen in by overgrowing it at lower temperatures. Overgrowth with Si would result in a δ doping layer of Mn, that is predicted to have interesting half-metallic properties.[21] Low-temperature overgrowth by a Co_2MnSi layer could result in a sharp interface between Co_2MnSi and the Si substrate, a feature that is very desirable for spintronic applications.

VI. EPITAXY OF Mn ON Si(111)

MnSi in its thermodynamic ground state crystallizes in a cubic structure with eight atoms per unit cell, the B20 crystal structure. Its crystal symmetry, described by the point group $P2_13$, is incompatible with the Si(001) surface. Therefore, we assumed epitaxial growth of MnSi on Si(001) to lead to films with a hypothetical CsCl-like structure.[14] According to our calculations, this predicted crystal structure of MnSi has an equilibrium lattice constant only 2% larger than that of Si, and is energetically higher than the B20 structure by only 0.25 eV per formula unit of MnSi. However, for the Si(111) substrate it is conceivable that MnSi films with the B20 structure could be grown epitaxially, too. The surface lattice constants for MnSi(111) in the B20 structure and for Si(111) differ by less than 3%, and both the substrate and the MnSi film have a threefold rotational symmetry axis perpendicular to the surface. We have explored possible epitaxial film structures by means of DFT calculations, comparing them to MnSi films with a hypothetical CsCl-like structure. Our calculations show that the films derived from the B20 structure, inducing a $\sqrt{3}\times\sqrt{3}$ reconstruction on Si(111), are in general lower in energy than the films with the CsCl-like structure.[22] These findings are in agreement with scanning-tunneling microscopy studies following Mn deposition on Si(111), where flat islands with local $\sqrt{3}\times\sqrt{3}$ surface reconstruction have been observed.[23,24] For this reason, we conclude that the Si(111) substrate is better suited to prepare MnSi thin films by epitaxy.

To assess the magnetic properties of the films, we calculate atomically resolved spin magnetic moments by integrating the spin-resolved charge density within the muffin-tin sphere of each atom. For all MnSi films investigated, we find that the spin magnetic moments of the Mn atoms near the surfaces and interfaces are strongly enhanced $(2-3\mu_B)$ compared to those in bulk MnSi $(<0.5\mu_B)$. The calculations of layer-projected densities of states show that the degree of spin polarization at the Fermi level in the MnSi films is generally high, between 30% and 50%. Moreover, films with a Mn content corresponding to two monolayers of Mn or less show an energetic preference for parallel alignment of the spin magnetic moments as compared to an antiparallel alignment. So far, the magnetic Curie temperature T_C of the films is not known experimentally, but calculations based on the electronic structure as obtained from density functional theory are in progress.[25] If T_C turns out to be sufficiently high, the binary silicide MnSi, in addition to the Heusler alloys, could also be of relevance for spintronic applications, e.g., for spin valves.

VII. CONCLUSION

The structural, electronic, and magnetic properties of metallic thin films of late transition metal silicides on silicon have been investigated by means of density functional theory

calculations. The main focus has been on the half-metallic Heusler compound Co_2MnSi, but growth of thin films of binary silicides, in particular MnSi, has been discussed as well. While for the free $Co_2MnSi(001)$ surface, a specific surface termination (a full Mn layer) could be identified that preserves the half-metallicity, the interfaces of Co_2MnSi with Si(001) investigated here did not retain this property. However, the energy gap in the minority spin channel characteristic of half-metallic Co_2MnSi was found to recover only a few layers away from the interface. Moreover, our calculations demonstrate that very thin films of MnSi also display sizeable magnetic moments at the surface and interface Mn atoms, as well as a considerable spin polarization of electrons at the Fermi level. Thus they may also be relevant as future spintronic materials.

ACKNOWLEDGMENT

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[1] *Half-metallic Alloys—Fundamentals and Applications, Lecture Notes in Physics*, edited by P. H. Dederichs and I. Galanakis (Springer Verlag, Berlin, 2005).
[2] P. J. Brown, K. U. Neumann, P. J. Webster, and K. R. A. Ziebeck, J. Phys. Condens. Matter **12**, 1827 (2000).
[3] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[4] S. Ishida, S. Fujii, S. Kashiwagi, and S. Asano, J. Phys. Soc. Jpn. **64**, 2152 (1995).
[5] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **66**, 094421 (2002).
[6] L. Ritchie *et al.*, Phys. Rev. B **68**, 104430 (2003).
[7] L. J. Singh *et al.*, J. Appl. Phys. **95**, 7231 (2004).
[8] S. Picozzi, A. Continenza, and A. J. Freeman, Phys. Rev. B **69**, 094423 (2004).
[9] M. P. Raphael *et al.*, Phys. Rev. B **66**, 104429 (2002).
[10] L. J. Singh *et al.*, J. Appl. Phys. **99**, 013904 (2006).
[11] W. H. Wang *et al.*, Phys. Rev. B **71**, 144416 (2005).
[12] S. J. Hashemifar, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **94**, 096402 (2005).
[13] M. Hortamani, H. Wu, P. Kratzer, and M. Scheffler, Phys. Rev. B **74**, 205305 (2005).
[14] H. Wu, M. Hortamani, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **92**, 237202 (2004).
[15] H. Wu, P. Kratzer, and M. Scheffler, Phys. Rev. B **72**, 144425 (2005).
[16] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, an Augmented Plane Wave and Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (Techn. Univ. Wien, Austria, 2001).
[17] K. Reuter, C. Stampfl, and M. Scheffler, in *Handbook of Materials Modeling*, edited by S. Yip (Kluwer, Dordrecht, 2004), and references therein.
[18] I. Galanakis, J. Phys. Condens. Matter **14**, 6329 (2002).
[19] G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, Phys. Rev. B **68**, 113310 (2003).
[20] G. M. Dalpian, A. J. R. da Silva, and A. Fazzio, Surf. Sci. **566–568**, 688 (2004).
[21] H. Wu, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **98**, 117202 (2007).
[22] M. Hortamani, P. Kratzer, and M. Scheffler (unpublished).
[23] K. Schwinge, C. Müller, A. Mogilatenko, J. Paggel, and P. Fumagalli, J. Appl. Phys. **97**, 103913 (1999).
[24] A. Kumar, M. Tallarida, M. Hansmann, U. Starke, and K. Horn, J. Phys. D **37**, 1083 (2004).
[25] M. Hortamani, L. Sandratskii, I. Mertig, P. Kratzer, and M. Scheffler (unpublished).