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Thermodynamic stability, magnetism and half-metallicity of various (100) surfaces of Heusler alloy Ti_2FeSn

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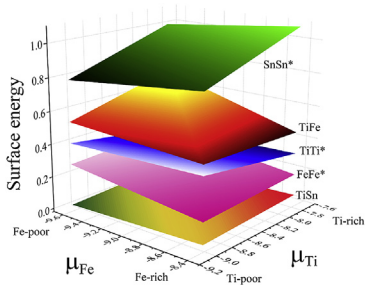
HIGHLIGHTS

- The TiSn termination is the most stable while the SnSn* termination is the most unstable.
- The TiSn and TiFe terminations exhibit the half-metallic character.
- The FeFe*, TiTi* and SnSn* terminations lose the half-metallicity.
- Atomic magnetic moments at the (100) surfaces are greatly different from the bulk values.

GRAPHICAL ABSTRACT



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ABSTRACT

For the Ti_2FeSn Heusler alloy, the thermodynamic stability, electronic and magnetic properties of the five different terminations FeFe*, TiFe, TiTi*, TiSn and SnSn* of the (100) surface have been studied by using first-principles calculations. The results show that, the TiSn termination is the most stable one while the SnSn* termination is the most unstable one. Both the density of states (DOS) and atomic magnetic moments (AMMs) of the central layers are similar to those of the bulk Ti_2FeSn case due to no influence of surface effect as we expected. The TiSn and TiFe terminations exhibit half-metallic character with 100% spin-polarizations at the Fermi level and with the spin-down band gaps of 0.36eV and 0.08eV, respectively. The TiSn termination with the lowest surface energy is the most suitable one in the spin-transfer torque magnetic random access memories (STT-MRAM) devices. The spin polarizations of the FeFe*, TiTi* and SnSn* terminations are 74.9%, 72.8% and 72.1%, respectively.

1. Introduction

Half-metallic (HM) materials, that exhibit a metallic character in one spin channel and a semiconductor character in the other spin channel, have attracted more and more attentions in the field of spintronic devices since the prediction of HM ferromagnet of the half-Heusler alloy NiMnSb by first-principle calculations in 1983 [1]. To date, the magnetic tunnel junctions (MTJs) are one of the most significant spin electronic devices [2], with two HM layers used as electrodes, sandwiching a semiconductor, insulator or nonmagnetic metal spacer layer [3], and have been widely used for sensing applications, magnetic random access memories (MRAM), the read-heads of modern hard disk drives, and so forth [4]. The spin-transfer torque magnetic random access memories (STT-MRAM), which spin-polarized current flowing between two HM layers can change the relative alignment of their magnetization

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orientations, are favorable in two aspects over their traditional counterparts: more precise addressing and lower energy consumption [5–7]. Recently, considerable interests about STT-MRAM extremely prompt the progress of the spintronic devices. For instance, the $Mn_{3-x}Ga$ ($0 \leq x \leq 1$) alloys with DO_2 tetragonally distorted Heusler-like phase are less vulnerable to the thermal fluctuation at moderate coercitive fields [5,8–10], combined with the high spin-polarization, high Curie temperature, low magnetization, have attracted many experimental efforts. Moreover, the Mn_2YZ Heusler alloys, also attract considerable attention due to their potential applications in STT devices [11].

Ti_2FeSn Heusler alloy, a kind of full-Heusler alloy with the Hg_2CuTi structure, was observed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) [12]. According to the first-principles calculations, the Ti_2FeSn alloy also has the completely spin-polarization (100%), high Curie temperature (475 K) and low magnetization ($2\mu_B$) [13,14]. The completely spin-polarization 100% and high Curie temperature are very crucial for the efficient spin injection in the MTJs from a HM ferromagnet layer to a semiconductor, insulator or nonmagnetic metal spacer layer. The low magnetization can easily change the relative alignment of spin-polarized current flowing between two HM layers in STT-MRAM devices. Moreover, the positive values of the cohesive energy, the low formation energy, and mechanical stableness indicate the Ti_2FeSn can be considered in realistic application [14]. However, as mentioned above, in both MTJs and STT-MRAM devices, the Ti_2FeSn thin films should be used. So in this paper we investigate the thermodynamic stability, magnetism and half-metallicity of five different terminations of the (100)-oriented thin films of the Ti_2FeSn.

We cleave the bulk Ti_2FeSn Heusler alloy with Hg_2CuTi structure along the [100] direction. Firstly, we create two standard epitaxial terminated surfaces: TiFe and TiSn terminations. Second, the artificial terminations are also interesting, for examples, Kratzer et al. found that the bulk half-metallicity was maintained by replacing the Si atom with Mn atom at the (001) MnSi-terminated surface of the Co_2MnSi Heusler alloy [15], Han et al. also found the pure V termination recovered the bulk HM character by replacing the Ga atom with V atom at VGa-terminated surface [16]. So we also create three artificial terminations: FeFe*, TiTi* and SnSn* terminations by substituting Ti with Fe on the TiFe surface, Fe with Ti on the TiFe surface and Ti with Sn on the TiSn surface in order to check whether these terminations preserve the bulk HM character.

Thus in this paper, we present a comprehensive first-principles study of the surface effect on the thermodynamic stability, electronic and magnetic properties of the five different terminations FeFe*, TiFe, TiTi*, TiSn and SnSn* of the (100) surface. For comparison, we also investigate the structural and electronic properties of the bulk Ti_2FeSn. The paper is organized as follows. Section 2 gives the detail of the calculation methods. Then, we concentrate on the bulk properties in Section 3.1, the surface structures in Section 3.2, the surface stability in Section 3.3, the surface density of states in Section 3.4 and the surface magnetic moments in Section 3.5. Finally, we draw conclusions in Section 4.

2. Calculation methods

The calculations were performed by using the Vienna *ab-initio* simulation package (VASP) based on the density function theory (DFT) [17–20]. The electron-ionic core interaction is represented by the projector augmented wave (PAW) potentials [21] which are more accurate than the ultra-soft pseudopotentials (USPP). To treat electron exchange and correlation, we chose the Perdew-Burke-Ernzerhof (PBE) [22] formulation of the generalized gradient approximation (GGA), which yields the correct ground-state of the alloys. All of the self-consistent loops are iterated until the total energy difference of the systems between the adjacent iterating steps is less than 1×10^{-4} eV. And the constituent atoms are fully relaxed until the maximum Hellmann–Feynman forces are less than 0.02 eV/Å. The cutoff energy for the plane wave sets is chosen to be 320eV. The Brillouin zone is sampled with Monkhorst-Pack scheme using $(3 \times 3 \times 3)$ and $(9 \times 9 \times 1)$ k-meshes for bulk and surface structures of the alloy. The Ti $3d^2 4s^2$, Fe $3d^6 4s^2$, and Sn $5s^2 5p^2$ electrons are treated as valence electrons.

3. Results and discussions

3.1. Bulk properties

Heusler alloys can be classified into two main groups: half-Heusler alloys with the chemical formula XYZ and full-Heusler alloys with the chemical formula X_2YZ, the X and Y atoms are transition metal (TM) atoms and Z is a sp atom. Heusler alloys usually have the structure of four interpenetrating face-centered-cubic (fcc) lattices and four unique crystal sites, namely A (0,0,0), B (0.25,0.25,0.25), C (0.5,0.5,0.5) and D (0.75,0.75,0.75) in Wyckoff coordinates along the diagonal of the unit cell [23–25]. The sp atom Z always occupies the D site, moreover, extensive researches have revealed that the atomic site occupation in the crystal structure obeys an empirical rule that the TM atoms with more valence electrons preferentially occupy atomic sites near the main-group atoms Z [26–28], in this case, for Ti_2FeSn Heusler alloy, the Fe atom has more valance electrons than Ti atom, thus two Ti atoms occupy A and B sites, namely Ti^A and Ti^B atoms, while the Fe atom and Sn atom occupy C and D sites, respectively, as shown in Fig. 1. The calculated equilibrium lattice constant a is 6.326 Å for the bulk Ti_2FeSn and the atomic magnetic moments are $1.507\mu_B$, $0.889\mu_B$, $-0.432\mu_B$ and $0.018\mu_B$ for Ti^A, Ti^B, Fe and Sn atoms, respectively.

In order to understand the bulk electronic structure, Fig. 2 shows the total density of states (DOS) (black) and partial density of states (PDOS) projected onto Ti^A-3d (red), Ti^B-3d (green), Fe-3d (blue) and Sn-5p (brown) for full-Heusler alloy Ti_2FeSn. The PDOS of the Sn-5s are not presented here because they are located in deep energy region. From the total DOS, we can see that the spin-down channel has a semiconductor character with a band gap of 0.68eV, while the spin-up channel is metallic, thus the bulk Ti_2FeSn has a HM character. The lower and wider PDOS of the p charges indicate these electrons are delocalized, localized d charges contribute most to the total DOS. The spin-down band gap comes from the d-d hybridization between the Fe-3d state below the

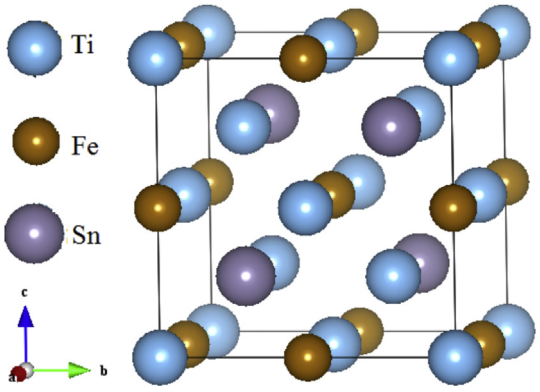

Fig. 1. Crystal structure of the full-Heusler alloy Ti_2FeSn. The blue, yellow and purple balls are Ti, Fe and Sn atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)