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**Surface half metallicity and thermodynamic stability of 001-plane Ti2XSi (X=Mn, Co) Heusler alloys (HAs): A DFT approach**

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**Abstract**

We report the surface stability and surface half-metallicity of Ti2XSi (X=Mn/Co) [001] slab with natural TiSi and TiX(X=Mn/Co) terminals from the [first principles calculation](https://www.sciencedirect.com/topics/physics-and-astronomy/first-principle). We started our calculation from the bulk optimization followed by the electronic and [magnetic properties](https://www.sciencedirect.com/topics/materials-science/magnetic-property) by adopting [GGA](https://www.sciencedirect.com/topics/physics-and-astronomy/generalized-gradient-approximation) exchange correlation for treating all [electrons interaction](https://www.sciencedirect.com/topics/physics-and-astronomy/electron-scattering). We have also analyzed the surface stability by calculating the surface energies as a function of constituents chemical potentials within the framework of *ab-initio* thermodynamics. Within the allowed chemical potentials range, TiSi(Ti2MnSi) terminated surface found to be the most energetically favorable [thin film](https://www.sciencedirect.com/topics/materials-science/thin-films) while the TiX terminated surfaces show strong molecular attraction. The bulk half [metallicity](https://www.sciencedirect.com/topics/physics-and-astronomy/metallicity) is preserved in TiSi(Ti2MnSi) terminated surface with 100% [spin polarization](https://www.sciencedirect.com/topics/materials-science/spin-polarization) while the other terminal surfaces are metallic. The results of atomic site partial magnetic moments in the surface states along with their corresponding values in the bulk structure are also presented.

**Introduction**

The extensive theoretical and experimental studies on novel Heusler compounds [1] have been pursued after the discovery of peculiar half metal ferromagnetic (HMF) property by de Groot *et al.,* [2] from the band structure calculation in NiMnSb, where one of the spin channels is semiconducting and the other is metallic resulting 100% spin polarization at the Fermi level. The diverse functional properties of Heusler compounds includes HMF, high Curie temperature, large perpendicular magneto-anisotropy, low magnetic dumping, low saturation magnetization, tunneling magneto-resistance effect, Current-perpendicular-to-plane giant magneto-resistance etc., are crucial for the development of spin wave based spintronic device which explicitly rely on the degree of spin polarization at the Fermi level [3], [4], [5]. The components of spintronic application includes giant magneto-resistance (GMR) and magnetic random access memory(MRAM), spin injectors, spin computer applications and spin-transfer torque device [6], [7], [8], [9], [10], [11], [12], [13]. In order to integrate the HMF property for the device application, it is very essential to fabricate the sample in nano-scale thin film. Epitaxial thin films growth technique is the prior pavement for device fabrications [14], [15], [16], [17], [18]. Regrettably, cleaving of surfaces or nano-structured Heusler alloys usually destroyed the bulk HMF property due to the breaking of bonds along the translation direction and release free conducting electrons on the surfaces [19]. As a result of which the preservation of the bulk half metallic nature in low dimensional thin film is highly challenging for its application in spintronic technology. It has been identified from the theoretical and the experimental work that Zincblende magnetic semiconductors also exhibit half-metallicity but they have low Curie Temperature (below room temperature) [20]. The thin film of rutile CrO2 and perovskite La0.7Sr0.3MnO3 shows half metallic nature with almost 100% spin polarization at low temperature as obtained from Andreev reflection measurement [21]. So, in this regard Heusler alloys (HAs) have comparatively high Curie temperature well above the room temperature for practical applications. However, there are no experimental report on the half metallicity (100% spin polarization) of Heusler alloys at the room temperature so far [22]. Interestingly, for the first time Jourdan *et al.* confirmed the direct half metallicity with 93% spin polarization in Co2MnSi *in-situ* epitaxial thin film at room temperature using ultraviolet photoemission spectroscopy [23]. Nevertheless, the surface half metallicity for 001-surface of Co2MnSi was predicted before the experiment from *ab-initio* density functional theory(DFT) investigation [24]. Therefore, predicting the nature of materials from first principles calculation is somewhat reliable to realise thin film growth in device application. The nature of low magnetic moment, high Curie temperature, low formation energy and mechanical stability make Ti-based Heusler hetero-junction a potential candidate for current-perpendicular- to-plane (cpp) GMR devices and spin transfer torque MRAM applications [25], [26], [27], [28].To the best of our knowledge, we have not come across any experimental study on the surface half metallicity of Ti-based Heusler alloys. Moreover, the surface half metallicity was predicted on *XA*-type Ti2FeGe[001] [28] and Co-doped Ti2Fe1−�Co�Sn [001] [29] from the first principles approach. We are also aware of the fact that no rigorous study (experiment and theory) have been performed on the surface states of Ti2MnSi and Ti2CoSi. Moreover, theoretical prediction of surface electronic structure of the analogous compounds of transition metal based Heusler alloys (HAs) with *XA*(Hg2CuTi-type) structure have already been reported; Ti2MnAl [001] where all the two natural Ti-Al, Ti-Mn terminals and three artificial modelled Ti-Ti, Mn-Mn and Al-Al terminations shown metallic character [30]. Ti2CoSn [001] where TiSn terminal nearly gives the half metallicity with 94.2% spin polarization [31]. In this work, we have presented the surface electronic structure and thermodynamic stability of inverse *XA*(Hg2CuTi-type) full Heusler alloy Ti2(X)Si[001] slab. Motivated, with the aim of devices fabrication with HMF|semiconductor hetero-structures, the range of equilibrium lattice constant of Ti2XSi ≊ 6.00 Å is well matched with the varieties of semiconductors such as CdSe (6.05 Å), InAs (6.05 Å), ZnTe (6.10 Å) and GaSb (6.10 Å) without hard in-plane lattice perturbation at the interfaces, thus can enhance the interfacial spin polarisation and stability. By comparing the existing literature of the bulk structure, we briefly discuss about the bulk electronic structure calculated by using the equilibrium lattice constant. Further, we have presented the surface electronic structure and thermodynamic stability, also analyzed the effect of *sp*-elements in Ti-based Ti2XSi [001] surfaces with their corresponding terminations.

**Section snippets**

**Computational method**

The first principles calculation were performed using DFT [32] based on the projector augmented wave (PAW) method which constitute the core ionic interaction as implemented and programmed in Vienna *ab-initio* Simulation Package (VASP) [33]. All electron interactions were treated using the electron correlation exchange energy within the generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof(PBE) formalism [34]. A plane wave cut off energy of 300 eV and 460 eV for the bulk and

**Bulk Ti2(X)Si (X=Mn, Co)**

The equilibrium lattice parameter, total magnetic moment and atomic resolved magnetic moment of bulk structure of Ti-based inverse full Heusler Ti2XSi (X= Mn, Co) calculated from GGA are presented in Table 1. Our calculated equilibrium lattice constants are in well-agreement with the previous reports with relatively negligible deviation.

In order to analyse the electronic properties of their bulk systems, we have presented the total and atomic resolved density of states (DOS) in Fig. 2. For both

**Conclusion**

The first principles calculation based on density functional theory (DFT) have been performed to study the structural stability, electronic and magnetic properties of (001) surfaces of inverse Ti2(X)Si (X=Mn,Co) full Heusler alloy having XA-phase. The 001 surface with four terminated faces have been exfoliated theoretically. Out of the four explored terminal surfaces, TiSi(TMS) is the most stable with lowest surface energy which agrees well with its smallest surface relaxation. However, the

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**CRediT authorship contribution statement**

**:** Writing – original draft, Writing – review & editing. **Lalthakimi Zadeng:** Conceptualization, Data curation, Formal analysis, Validation, Writing – original draft, Visualization. **Lalmuan Chhana:** Formal analysis, Data curation, Investigation, Methodology. **Lalhriat Zuala:** Formal analysis, Data curation, Investigation. **D.P. Rai:** Writing – original draft, Methodology, Resources, Validation, Formal analysis, Visualization, Validation, Writing – review & editing.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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