Spin gapless semiconductor like Ti$_2$MnAl film as a new candidate for spintronics application

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A novel Heusler ferrimagnet Ti$_2$MnAl film has been grown on Si(001) substrate using magnetron sputtering. Characteristics of its magnetic and transport properties reveal the spin-gapless-semiconductor (SGS) nature of the stoichiometric Ti$_2$MnAl, in agreement with theoretical prediction. The as-grown SGS-like Ti$_2$MnAl film demonstrated high Curie temperature, nearly compensated ferrimagnetic properties with small coercivity and low magnetization. It also showed semiconductor-like behavior at room temperature allowing good compatibility with commercial Si-based semiconductor. In this regards, Ti$_2$MnAl film is a potential candidate material for spintronics application, especially for the minimization of energy consumption of device.

1 Introduction Spin gapless semiconductors (SGSs) are recently proposed spintronics materials with superior performance compared with half metals and diluted magnetic semiconductors [1–4]. According to first-principles electronic structure calculations, there is a large gap in the spin down band structure and the Fermi level falls within this gap. The valence and conduction bands touch each other in the spin-up channel and the Fermi level falls within a zero-width gap. Therefore, it indicates that SGS has 100% spin polarized carriers with tunable capabilities and the speed of the fully polarized spin electrons in the SGS could be much faster than in diluted magnetic semiconductors (DMSs). Due to its unique half-metallic high spin polarization and semiconductor-like conductivity, using SGS as electrode materials in the spintronics devices is expected to be a potential way to improve the spin injection efficiency into semiconductor substrate, such as Si and GaAs. After the proposal of concept of SGS, PbPdO$_2$ was first experimentally demonstrated to show SGS-like behavior [2]. More recently, six inverse Heusler structured compounds, such as Ti$_3$MnAl, Mn$_2$CoAl, are predicted to show SGS properties, which were expected to exhibit high Curie temperatures and thus were suitable for spintronics applications [4]. Quaternary Heusler compounds, such as CoFeMnSi, CoFeCrAl, were also predicted to be new families of SGS [5]. After the experimental realization of SGS in the first inverse Heusler compound of bulk Mn$_2$CoAl sample [3], thin films of Mn$_2$CoAl were also investigated [6, 7]. The SGS nature of Mn$_2$CoAl was confirmed by both theoretical calculations and experiments. In addition, the inverse Heusler compound Fe$_2$CoSi was found to be a zero-gap half-metallic alloy which demonstrates a crossover of magnetoresistance against temperature due to the dominant spin carriers changing from the gapless minority spin channel to the majority spin channel at the Fermi level [8]. So far few materials have been synthesized for the purpose of investigating SGS related properties.

The SGS Ti$_2$MnAl actually exhibits a zero total spin magnetic moment [4] and thus can be classified as half-metallic antiferromagnet, also known as half-metallic ful...
ly-compensated ferrimagnet (HF-FCF) [9]. The advantage of HF-FCFs is that they create no external fields and thus lead to minimal energy losses. In this regard, HF-FCF Ti$_2$MnAl is very promising for the spintronics application in order to minimize energy consumption. In this Letter, we report the magnetic properties of Ti$_2$MnAl films grown on Si(001) substrate using magnetron sputtering. Characteristics of magnetic and transport properties supported the SGS nature of the stoichiometric Ti$_2$MnAl. The obtained Ti$_2$MnAl sample exhibited small coercivity and low magnetization at room temperature (RT) allowing the easy switch of spin moment and the minimization of energy consumption in the device applications.

2 Experimental details Thin films of Ti$_2$MnAl were deposited on Si(001) substrates by magnetron sputtering system with a base pressure of $1 \times 10^{-7}$ Torr. A composite target including Ti target and several Mn and Al flakes was used as source materials. The stoichiometric composition of Ti$_2$MnAl was obtained by varying the proportion of Ti, Mn, and Al in the composite target. The purity of raw elements is 99.99%. The as-studied samples were deposited at different temperatures under a working pressure of $1 \times 10^{-2}$ Torr (Ar gas) with dc power of 30 W. The crystal structure was determined by X-ray diffraction (XRD) using the Cu K$_\alpha$ radiation. The morphology of the sample and the element mapping were measured by scanning electron microscope (SEM). Electron probe microanalysis (EPMA) was used for the accurate characterization of the elements and composition. The magnetic and transport properties were measured using a superconducting quantum interference device magnetometer (MPMS, Quantum Design), physics property measurement system (PPMS, Quantum Design) and vibrating sample magnetometer (VSM).

3 Results and discussion Figure 1 shows the logarithmically scaled XRD patterns for 600-nm-thick Ti$_2$MnAl films grown on Si(001) substrates at temperatures from RT to 400 °C. In this figure, besides peaks from Si substrate, only one small bump located at around 41° is observed, which can be indexed to the (220) diffraction of the Hg$_2$CuTi-type inverse Heusler structure according to theoretical calculation [4]. It was clear that the obtained Ti$_2$MnAl samples are of poor crystallinity which was almost unaffected by the growth temperature (Fig. 1). In this work, we focused on the 30 °C -grown samples. The average grain size of the film was estimated to be around 1 nm using Scherrer’s formula. The SEM image shown in Fig. 2(a) indicates that the sample is homogeneous and consists of fine crystallites. Figure 2(b)–(d) showed elements mapping of Ti, Mn, and Al, respectively, demonstrating clearly the even distribution of constituent elements. Both XRD and SEM results indicated that the as-grown Ti$_2$MnAl sample is free of secondary phases. The accurate composition of the Ti$_2$MnAl sample is 1.96:1.09:1 for Ti:Mn:Al determined by EPMA measurement.

Figure 3 shows magnetization vs. applied field ($M$–$H$) curves at different temperatures for the Ti$_2$MnAl sample. The $M$–$H$ curves exhibit distinct hysteresis loops with a low saturation magnetization of 35 emu/cm$^3$, a small coercivity of 23 Oe at RT and a saturation magnetization of 48 emu/cm$^3$ (equal to 0.21 $\mu_B$/formula), a coercivity of 200 Oe at 10 K, which demonstrated clearly ferro(ferri)-magnetic ordering of the Ti$_2$MnAl sample. Usually some second phases of tiny magnetic clusters cannot be detected by traditional methods, such as XRD, SEM, and TEM. For example, some so called ideal DMS are actually a mixture of DMS and magnetic clusters [10, 11]. Here all possible unitary or binary phases are antiferromagnetic or nonmagnetic except the ferromagnetic $\tau$-phase of MnAl [12, 13]. The ferromagnetic $\tau$-MnAl is a metastable phase the bulk form of which can be obtained either by quenching the high-temperature phase followed by isothermal annealing at temperatures between 400 °C and 700 °C or by a controlled cooling process from high-temperature nonmagnetic hcp-structured $\varepsilon$-phase. The $\tau$-phase of MnAl could only be obtained when the temperature above 100 °C.

![Figure 1](image1.png) XRD pattern of Ti$_2$MnAl thin films grown on Si(001) substrate at different temperatures.

![Figure 2](image2.png) (a) SEM image of the Ti$_2$MnAl sample and (b), (c), (d) the elements mapping of Ti, Mn, Al, respectively. The inset in Fig. 2(a) shows the elemental contents by EDS.
Figure 3 (a) The magnetic field-dependent magnetization curves for Ti$_2$MnAl/Si(001) film measured at room temperature. The inset shows the magnified $M$–$H$ curve at low field region. (b) Magnetization vs. applied field curves at the temperature of 10 K and 600 K (inset) for Ti$_2$MnAl film.

Figure 4 Variation of resistance as a function of temperature under zero magnetic field for the Ti$_2$MnAl sample. The inset 1 (left side) shows the fitting of conductance referring to the equation of $\sigma(T) = \sigma_o + \sigma_a \exp(-E_g/k_B T)$. The inset 2 (right side) shows the fitting of resistance referring to the equation of $\rho = a + bT + cT^2$.

peculiar band structure. The slight change of $\rho(T)$ slope was observed in the MBE-grown Mn$_2$CoAl film with SGS properties, where a similar metallic-like behavior is seen at lower temperatures, followed by a maximum of resistance at $T = 200$ K and a negative slope above RT [6]. Therefore, the observed $\rho(T)$ behavior here indicated the SGS-like nature of Ti$_2$MnAl sample.

According to Jamer [6], the total conductivity arises from two contributions, i.e., carrier–phonon scattering and thermally activated carriers. At low temperatures $\rho(T)$ is governed by the phonon dominated mobility demonstrating metallic behavior, at high temperatures $\rho(T)$ is governed by the thermally-released carriers, leading to semiconducting behavior. This mechanism probably also applied to our case. At low temperatures our $\rho(T)$ curve cannot fit to $T^2$ [18], therefore electron–hole scattering can be excluded. We applied a thermal activation model with a narrow energy gap [19] to the semiconductor-like region at high temperatures for Ti$_2$MnAl. As shown in the inset 1 of Fig. 4, the conductivity above 125 K is well approximated by a simple model, $\sigma(T) = \sigma_o + \sigma_a \exp(-E_g/k_B T)$. The best fit yields an energy barrier ($E_g$) of 43 meV, which approximates to the 62 meV in the Mn$_2$CoAl film [6].

Figure 5(a) shows the zero field cooling (ZFC) and field cooling (FC) magnetization vs. temperature ($M$–$T$) curves measured under applied fields of 100 Oe and 500 Oe, respectively. By applying 500 Oe, for both ZFC and FC processes, magnetization increases with the decrease of temperature down to 15 K, being metallic-like. Usually the sigh change of $\rho(T)$ slope is often observed in semimetals or semiconductors with narrow gap where atomic disorder, defects or non-stoichiometry gives rise to impurity levels governing low temperature conduction [16, 17]. SGS-like material will also demonstrate the slight change of $\rho(T)$ slope due to its
Figure 5 (a) Temperature-dependent magnetization curves under zero field cooling (ZFC) and field cooling (FC) conditions for Ti$_2$MnAl film. Note that the displayed value of magnetization measured at 100 Oe is the triple of the real measured value. (b) Temperature-dependent magnetization curves measured at temperatures from 300 K to 650 K for Ti$_2$MnAl film.

netic configuration and electric properties resulting from a change of band structure below a certain low temperature (a characteristic of SGS). Another important characteristic is the linear temperature dependence of resistance and magnetization in the region of above 100 K, as seen in Figs. 4 and 5(a). This behavior is remarkable and is not normal if Ti$_2$MnAl is considered to be a regular metal or semiconductor which usually exhibit exponential increase or decrease in conductivity. Such a linear behavior was also reported for Mn$_2$CoAl which was theoretically and experimentally confirmed as a SGS [3]. Therefore, the as-studied Ti$_2$MnAl might have similar properties with the SGS of Mn$_2$CoAl.

ZFC and FC $M$–$T$ curves merge at RT, as shown in Fig. 5(a), where distinct magnetic signals of the sample are still present (see Fig. 3(a)). The dropping down of magnetization to zero seems to happen at much high temperature above 300 K. In order to determine the Curie temperature ($T_C$) of the sample, high temperature $M$–$T$ measurement by VSM was carried out as shown in Fig. 5(b). When measured at the applied field of 100 Oe the magnetization increases monotonically upon an increase of temperature to 600 K. By applying 500 Oe the magnetization increases at first and then decreases monotonically at the temperature above 500 K, from which the $T_C$ could be estimated between 650 K and 700 K. A distinct magnetic hysteresis signal is still observed at the temperature of 600 K, as shown in the inset of Fig. 3(b). Therefore, it is sure that Ti$_2$MnAl has a very high $T_C$, which is in agreement with the theoretical prediction that Ti$_2$MnAl combines a zero total spin moment with a very high $T_C$ as expected from the very large sum of the absolute values of the spin moments (5.49 $μ_B$) being identical to that of Mn$_2$CoAl with the $T_C$ of 720 K [4].

The results of the magnetoresistance (MR) measurements at different temperatures are displayed in Fig. 6. MR exhibits a negative dependence on the applied field at RT; upon decreasing temperature, it turns to be positive dependence. The negative MR was due to the decreased scattering centers caused by an increase in the magnetic domain with increasing magnetic field, which is also evidence for the ferrimagnetic ordering in the Ti$_2$MnAl film [21]. While the positive MR observed at low temperature might be due to the spin fluctuations/flip induced by the field on the canted spin structure that causes an increase in the resistivity. The observed MR behavior here is similar to that observed for Mn$_2$CoAl [3], again confirming the similar properties of Ti$_2$MnAl compared with Mn$_2$CoAl. The change of sign of MR at low fields was also observed at 15 K, as seen from Fig. 6, in agreement with the more complicated behavior of spin gapless materials in low fields resulting from the influence of the ferrimagnetic order and the nonsatureted magnetization.

4 Conclusion In summary, we have prepared off-stoichiometric Ti$_2$MnAl films with Hg$_2$CuTi type-like inverse Heusler structure. The characteristics of magnetic and transport properties reveal SGS-like behavior of the sample, therefore, we can expect the SGS nature of stoichiometric Ti$_2$MnAl, in agreement with theoretical predic-
tion. HF-FCF nature of Ti$_2$MnAl leads to the observation of small saturation magnetization, which is superior to Mn$_2$CoAl with high saturation magnetization from the point of view of spintronics application. The as-studied SGS-like Ti$_2$MnAl film is probably a high $T_C$ semiconducting material which allowed high spin injection ratio into Si-based semiconductors. The very small coercivity and low magnetization at RT allow the easy switch of magnetization and the minimization of energy consumption. The method of sample preparation used here is also compatible with commercial production process. In this regards, Ti$_2$MnAl film is a nice potential candidate material for spintronics application.

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References