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## Realization of Efficient Tuning of the Fermi Level in Ironbased Ferrimagnetic Alloys

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#### Abstract

The Stoner criterion allows only three single elements possessing room temperature (RT) ferromagnetism: cobalt (Co), nickel (Ni), and iron (Fe). Although these three elements have played central roles in magnetism-based materials, their large work function (4.5 ~ 5.2 eV) are becoming a non-negligible obstacle for realization of spin devices using non-metallic materials with finite energy gaps, because injection of electron spins into these non-metallic materials is strongly hampered due to the large Schottky barrier height. Hence, a novel ferromagnetic or ferrimagnetic material simultaneously possessing RT ferromagnetism or ferrimagnetism and high Fermi energy is strongly required. Here, we show that an Fe-based alloy, FeGd, allows circumventing the obstacle. Surprisingly, only 20% of Gd incorporation in Fe dramatically modulates the Fermi energy from -4.8 to - 3.0 eV, which is the largest modulation in all metallic alloys, reported thus far. The coexistence of ferrimagnetism and nonzero spin polarization at RT of FeGd supports its abundant potential for future applications in low-carrier-density materials such as monolayer, organic, and non-degenerate inorganic semiconductors.

#### **I. INTRODUCTION**

The number of elements exhibiting room temperature (RT) ferromagnetism is strongly restricted by the Stoner criterion [1]. Only iron (Fe), cobalt (Co), and nickel (Ni) exhibit Curie temperatures ( $T_c$ ) much higher than RT and sizable spin polarization at the Fermi level  $(E_{\rm F})$  among single elements. This restriction has encouraged scientists to synthesize a wide variety of compound ferromagnets and ferrimagnets by using any of them as a host material. The other restriction for single-element ferromagnets is that the  $E_{\rm F}$  of these three ferromagnetic elements is far below the vacuum level (-4.5 to -5.2 eV) [2], mainly because 3d electrons are responsible for ferromagnetism. This strong restriction invokes difficulty in selecting suitable ferromagnetic and ferrimagnetic materials, especially for the formation of heterojunctions without unwanted barriers and depletion regions for non-metallic materials, because the majority of ferromagnetic and ferrimagnetic materials are Fe/Co/Ni-based specimens and their  $E_F$  is far below the vacuum level. Indeed, the difficulty becomes quite salient in spin-polarized-carrier injection (extraction) into (from) low-carrier-density materials such as organic semiconductors, atomically flat semiconductors such as transition metal dichalcogenides (TMDs) [3], Weyl semimetals, and so forth, although they are now playing central roles in modern condensed matter physics. One good example of the difficulty is a ferromagnetic material/semiconductor (inorganics, organics, and TMDs) interface [4]. Since most ferromagnetic materials possess a low  $E_{\rm F}$ , i.e., high work function (WF), the injection of negatively charged spin carriers (electrons) into materials with a low carrier density is difficult. Although a limited approach to circumvent this obstacle is to dope electrons to the host semiconducting materials, this approach does not allow versatile control of the polarity of spin carriers, and the dense dopant strongly suppresses the

lifetime of injected spins into semiconducting materials in principle by the Elliott-Yafet mechanism [5]. Thus, carrier doping makes the whole device system more intricate and/or hampers the creation of ambipolar magnetic/spintronic devices and logic systems, such as spin lasers [6], spin light-emitting diodes [7], spin transistors [8], and spin logics [9]. Notably, this problem has not manifested itself in ferromagnetic/nonmagnetic-metal heterojunctions because no Schottky barrier or depletion region forms at the heterointerface, and thus, this difficulty arises in the modern condensed matter physics era. Given the current status of materials science, a material possessing simultaneous ferromagnetism or ferrimagnetism and high  $E_{\rm F}$  (low WF) is urgently needed to circumvent these obstacles. Here, we report drastic WF modulation of iron (Fe)gadolinium (Gd) binary alloys, Fe100-xGdx, since pure Gd has a low WF. Fe78Gd22 possesses an extraordinarily low WF and exhibits the coexistence of RT ferrimagnetism and nonzero spin polarization at  $E_{\rm F}$ , which fulfils the conditions for bypassing the abovementioned obstacles to accelerate physical and materials science. Surprisingly, only 20% Gd incorporation in Fe enables the dramatic modulation of WF from 4.9 to 3.0 eV-the most efficient modulation among all metallic alloys, while the  $T_c$  is still higher than RT.

#### **II. SAMPLE FABRICATION AND EXPERIMENTAL PROCEDURE**

Fe<sub>100-x</sub>Gd<sub>x</sub> thin films were deposited in an ultra-high vacuum chamber (base pressure  $< 1 \times 10^{-7}$  Pa). Fe was evaporated by resistive heating, and Gd was evaporated by electronbeam heating. To control the composition of *x*, the deposition rate of each metal was monitored by a quartz crystal thickness monitor. A thermally oxidized Si substrate was employed for the measurements of the magnetization curves and the anomalous Hall

effect (AHE) signals. Hall-bar-shaped  $Fe_{100-x}Gd_x$  channels for measurement of the AHE were fabricated by electron beam lithography and a lift-off process. For fabrication of the devices for *I-V* measurements, *n*-type Si with moderate doping  $(10^{15} \text{ cm}^{-3} \text{ of phosphorous})$ was doped) was employed. The 1 cm×1 cm Si substrates were cleaned using SEMICO-CLEAN23, ultrasonicated and then dipped into 2% aq. HF solution. On the back of the substrate, an ohmic Au<sub>98</sub>Sb<sub>2</sub>/n-Si contact was formed using thermal evaporation in an ultra-high vacuum chamber followed by thermal annealing at 350°C. After forming the back-side ohmic contact, the top  $Fe_{100-x}Gd_x$  electrodes were fabricated by a lift-off process. Before deposition of the  $Fe_{100-x}Gd_x$  layer, the naturally oxidized layer was removed by dipping the substrates for 30 seconds into 2% HF solution less than 5 min before being put into the vacuum chamber. Two different  $Fe_{100-x}Gd_x$  layers were fabricated to measure the WF. One has a uniform Gd composition (single-composition sample), and the other has an intentionally modulated Gd composition along the surface normal (gradatedcomposition sample). For the fabrication of the gradated-composition sample, Gd was first deposited. After the deposition of a 10 nm-thick Gd layer, the shutter for Fe deposition was opened, and then the deposition rate of Gd was gradually decreased from 2.0 nm/min down to 0 nm/min. The deposition rate of Fe was kept at 1.0 nm/min. Finally, a 20 nm-in thick Fe layer was formed. The crystal structure of the  $Fe_{100-x}Gd_x$  layer was amorphous except for the pure Fe (x = 0) or Gd (x = 100) layers, which were polycrystalline (see Supplemental Material (SM) 1 [10]).

Ultraviolet photoelectron spectroscopy (UPS) equipped with X-ray photoelectron spectroscopy (XPS) (Versa Probe, ULVAC-PHI) was used for the measurements of the WF. The surface of the measured samples was milled by  $Ar^+$  ion milling, and the WF and *x* were measured by UPS and XPS, respectively. To measure the UPS spectra, the samples

were irradiated with ultraviolet light with a photon energy of 21.22 eV, and a bias voltage of -10 V was applied. For the XPS measurements, the samples were irradiated with X-rays with a photon energy of 1486.6 eV.

The magnetization curves were measured by using a vibrating sample magnetometer with a temperature controlling system (VSM-5, Toei Industry). The AHE measurements were carried out using a physical property measurement system (PPMS, Quantum Design). A constant charge current of 0.1 mA was applied, and the DC voltage was monitored under the application of a perpendicular magnetic field.

#### III. WF of Fe100-xGdx alloys

The WF of Fe<sub>100-x</sub>Gd<sub>x</sub> alloys with various values of *x* was measured using UPS equipped with XPS. The atomic composition was simultaneously measured by XPS, which enables a direct comparison of *x* and WF at the same surface. The UPS spectra at various values of *x*, are summarized in Fig. 1(a). The secondary edge of the UPS spectrum corresponding to the photo electrons with the lowest energy, was adjusted to -21.22 eV (see SM-2 [10,11]). The positions of the  $E_F$  were determined by fitting the convolution of the Fermi-Dirac function to a Gaussian function [11], as indicated by the red dashed lines. The WF of pure Fe (*x*=0) and Gd (*x*=100) was  $4.9\pm0.1$  and  $2.9\pm0.1$  eV, respectively, comparable to a previous study [2]. The peaks in the UPS spectra of pure Fe (*x*=0) and pure Gd (*x*=100) located at approximately 0.8 (indicated by the blue arrow) and 5.0 eV (indicated by the red arrow) below  $E_F$  correspond to the high density of state of the majority spins of the 3*d* electron in bcc-Fe and those of the 4*f* electrons of hcp-Gd, respectively, which is supported by first-principles calculations carried out using the Vienna Ab initio Simulation Package (VASP) (see SM-3 [10,12–14]). The central result

of this study is that WF shifts drastically towards lower value from  $4.9\pm0.1 \text{ eV}$  to  $3.1\pm0.1 \text{ eV}$  when *x* changes from 0 to 20. The WF at x = 20 is comparable to that of pure Gd, even though the composition of Gd is just 20%. Surprisingly, the peak of the 3d electron for the Fe<sub>100-x</sub>Gd<sub>x</sub> alloy (indicated by the blue arrow) shifts towards higher energy when *x* increases from 0 to 20, indicating that the 3d electrons, main contributors of ferromagnetism and spin polarization, still contribute to the conductance even for the noticeable change in *E*<sub>F</sub>. It is noted that because crystal structure of Fe<sub>100-x</sub>Gd<sub>x</sub> alloys are amorphous except for the pure Fe (x = 0) and Gd (x = 100) samples, a calculated band structure of a crystalline Fe<sub>100-x</sub>Gd<sub>x</sub> by using VASP is not comparable to the experimental results. A simple superposition of the band structures of Fe and Gd is also incorrect. However, since the peak feature indicated by blue arrow is gradually shifted from 3d electrons of Fe with increasing *x* as shown in Fig. 1(a), we concluded that these peaks are related to 3d electrons of Fe.

The *x*-dependence of the WF is summarized in Fig. 1(b). WF was drastically reduced down to  $3.1\pm0.1$  eV when *x* was increased from 0 to 20 and showed almost constant value for *x* > 20. Similar results were also obtained for the single-composition samples as shown in Fig. 1(b). The notable change in WF has not been observed in other ferromagnetic alloys, such as Co<sub>100-x</sub>Fe<sub>x</sub> [15] and Ni<sub>100-x</sub>Fe<sub>x</sub> [16]. We stress that the large modulation of the WF is also notable among nonmagnetic alloys. Figure 1(c) shows a summary of the modulation efficiency of the WF,  $\eta$ , for a variety of binary alloys.  $\eta$  was obtained from the change in the WF achieved by adding a low WF element of 1% (in the case of Fe<sub>100-x</sub>Gd<sub>x</sub> alloys, Gd corresponds to the "low WF element"). Because the data (except for those of the Fe<sub>100-x</sub>Gd<sub>x</sub> alloys) were quoted from previous works [17–22], the number of points varies among the works. Therefore, the averaged  $\eta$  was calculated by

using at least 3 points whose *x*-range was approximately 20% to avoid overestimation or underestimation. For Fe<sub>100-x</sub>Gd<sub>x</sub>,  $\eta$  is 88.4 meV/% — more than tenfold that in ferromagnetic metals consisting of 3*d*-transition elements (Co<sub>100-x</sub>Fe<sub>x</sub> and Ni<sub>100-x</sub>Fe<sub>x</sub>) and the highest value among binary alloys that include nonmagnetic materials.

#### VI. Magnetization curves and anomalous Hall measurements

Materials involving finite magnetization at RT and such a large  $E_{\rm F}$  variation are useful for spintronic and spin-orbitronic applications that require a specific  $E_{\rm F}$ . Therefore, we carried out magnetization measurements by using a vibrating sample magnetometer at 300 K. The atomic composition was measured by XPS. The measured magnetization curves (*M*- $B_x$  curves) of the single-composition Fe<sub>100-x</sub>Gd<sub>x</sub> samples are shown in Figs. 2(a)-2(d). An external magnetic field with a magnetic flux density of  $B_x$  was applied along the in-plane direction of the film plane. The  $Fe_{100-x}Gd_x$  samples with x = 21, 14, and 0exhibited saturation of the magnetization M, indicating ferromagnetism or ferrimagnetism at 300 K [Figs. 2(b), (c), and (d), respectively]. The similar saturation in M was also obtained for the Fe<sub>100-x</sub>Gd<sub>x</sub> samples with x = 23. In contrast, the Gd sample (x = 100) exhibited no saturation or hysteresis, indicating paramagnetic features due to its  $T_{\rm c}$  being lower than 300 K [Fig. 2(a)]. The saturation magnetization  $M_s$  as a function of x is shown in Fig. 2(e). The reduction in  $M_s$  with increasing x for x < 21 is not due to a weakened exchange coupling between spins but due to the ferrimagnetic character, i.e., magnetic compensation between the Fe and Gd atoms [23]. Temperature dependence of Mnormalized by magnetization at 300 K,  $M_{300K}$ , under application of  $B_x = 1$  T were summarized in Fig. 2(f).  $T_c$  as a function of x is summarized in the inset of Fig. 2(f).  $T_c$  of Fe sample is roughly estimated to 1060 K, consistent with the literature [24]. For,

Fe<sub>86</sub>Gd<sub>14</sub>, surprisingly, comparable  $T_c$  with that of Fe was obtained. Whereas  $T_c$  was steeply decreased for x > 14,  $T_c$  of Fe<sub>79</sub>Gd<sub>21</sub> and Fe<sub>77</sub>Gd<sub>23</sub> is sufficiently higher than 300K, indicating ferrimagnetism is sufficiently maintained even at 300 K.

The AHE was measured at various temperatures to confirm finite spin polarization at  $E_F$ . We fabricated Hall bars, as schematically shown in the inset of Fig. 3(a). We firstly measured temperature dependence of resistivity  $\rho_{xx}$  of Fe<sub>100-x</sub>Gd<sub>x</sub> layers with Hall bar structure. The results are summarized in Figs. 3(b) and 3(c). For Fe and Gd samples,  $\rho_{xx}$ was decreased with decreasing temperature and slightly saturated at low temperature, which is a typical feature of pure metals. Slightly high  $\rho_{xx}$  of Gd than that of Fe is also consistent with previous researches. In contrast, for the other Fe<sub>100-x</sub>Gd<sub>x</sub> samples,  $\rho_{xx}$  was increased with decreasing temperature, a typical feature of highly disordered metals [25].

For the AHE measurements, a charge current *I* was applied in the *x*-direction, and the voltage difference along the *y*-direction ( $V_{xy}$ ) was measured by sweeping the magnetic field along the *z*-direction ( $B_z$ ). The typical AHE signals i.e., Hall resistivity,  $\rho_{xy}$ , as a function of  $B_z$ , for Fe<sub>100-x</sub>Gd<sub>x</sub> samples measured at various temperatures are plotted in Figs. 4(a)-4(d). For Fe sample positive  $\rho_{xy}$  was obtained for  $B_z > 0$  and saturated around 2 T. Clear AHE signals were obtained at wide range of temperature from 4 to 300 K. Whereas clear AHE signals with opposite polarity to that of Fe sample were obtained below 250 K for the Gd sample, the AHE signal almost disappeared at 300 K, indicating that spin polarization and ferromagnetism almost disappeared at 300 K, consistent with the magnetization curve shown in Fig.2(a). It is noted that clear AHE signals were obtained even at 300 K for Fe<sub>77</sub>Gd<sub>23</sub> and Fe<sub>79</sub>Gd<sub>21</sub>, which manifests a finite spin polarization at 300 K. The amorphous structure in the Fe<sub>100-x</sub>Gd<sub>x</sub> (0< x<100) alloys excludes the intrinsic AHE induced by the Berry curvature; the possible origin of the AHE is the extrinsic effects, including skew scattering and side jump – spin-dependent scattering [26], and thus, we attributed the AHE to finite spin polarization at 300 K.

#### V. Electrical characteristics of Fe100-xGdx/n-Si interface

To confirm the highly effective modulation of the  $E_{\rm F}$  at the metal/semiconductor interfaces, Schottky barrier diodes made of Fe<sub>100-x</sub>Gd<sub>x</sub>/n-type Si were investigated at 300 K. Vertical Schottky barrier diodes of  $Fe_{100-x}Gd_x$  on the *n*-Si substrate were fabricated as shown in the inset of Fig. 5(a). Capacitance-voltage measurements of the Fe/Si Schottky barrier diodes reveal a Schottky barrier height of 0.61 eV, consistent with the value in the literature [27] (see SM-4 [4,10,28,29]). The current-voltage characteristics of the Schottky barrier diodes measured at RT are shown in Figs. 5(a)-5(d). A current-rectifying characteristic was obtained in Fe/Si [Fig. 5(d)), where the ratio of on current to off current (On/Off ratio) at  $\pm 1.0$  V is 890. In contrast, On/Off ratio of 1 was realized for  $x \ge 21$ , indicating ohmic contacts to n-Si. Since Si is a typical semiconductor of the Bardeen limit with a considerably low S factor (S $\approx$ 0.1) [30], where S is defined as  $S = \partial \Phi_{\rm B} / \partial X_m$ , and  $\Phi_{\rm B}$  and  $X_m$  are the Schottky barrier height and the metal electronegativity, respectively, the  $E_{\rm F}$  of the metal hardly controls the Schottky barrier height due to Fermi level pinning. The ohmic behavior of  $Fe_{100-x}Gd_x/Si(x>21)$  indicates that the WF of  $Fe_{100-x}Gd_x/Si(x>21)$  $_x$ Gd<sub>x</sub> (x>21) is sufficiently lower than the electron affinity of Si (4.0 eV), which is consistent with the results of the UPS measurements shown in Fig. 1(a). For semiconductors with a Schottky limit ( $S \simeq 1$ ), such as few-layer graphene and SnSe<sub>2</sub> [31], a sufficient modulation of the Schottky barrier height is expected by adding only a few percent Gd. For the Si-based spintronic devices, realization of a spin injector and detector with significantly low interfacial resistance is expected by using  $Fe_{100-x}Gd_x$  alloys, which

is a great advantage compared to other ferromagnetic or ferrimagnetic contacts with appreciable interfacial resistance due to the existence of the Schottky barrier or oxide tunneling barrier [32,33] (see SM-6 [10,34–37]).

#### Conclusions

Prior to this study, it was thought that ferromagnetic and ferrimagnetic materials restricted by the Stoner criterion have low E<sub>F</sub> and that Schottky barriers inevitably arise at the interfaces with materials with finite energy gaps, including monolayer, organic, and non-degenerate inorganic semiconductors. We found significant modulation of the  $E_{\rm F}$  in ferrimagnetic metals with a finite spin polarization at RT, which overcomes the issue of the Schottky barrier for materials with finite energy gaps. Thus, this study pioneers an approach to creating ambipolar spin devices based on these gapped materials, such as a spin laser [6], a spin light-emitting diode [38], and a spin logic gate [9], by simultaneously achieving considerably low interfacial resistance and finite spin polarization at the  $E_{\rm F}$ . One of the remained challenges is clarifying a relationship between the crystal structure and the spin related properties. It is well known that the atomic arrangement between ferromagnetic material (FM) and nonmagnetic material (NM) is a major factor of the spin polarization of injected electrons. Considering that WF strongly depends on the atomic arrangement, the interfacial resistance of FM/NM interface is also expected to be dependent on the atomic arrangement. Therefore, more efficient modulation of the interfacial resistance with a sizeable spin polarization might be possible by controlling the crystal structures of  $Fe_{100-x}Gd_x$ . Whereas growth techniques for epitaxial growth of  $Fe_{100-x}Gd_x$  on Si with different crystal orientation have not been established so far, a systematic research focusing of the atomic arrangement would be important for the

innovation of next-generation spintronic devices.

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#### Author contributions

NY carried out the experiments and analyzed the data. SH carried out the first-principles

calculation. NY, ES, and YA conceived the experiments. NY, MS, and YA wrote the manuscript. All the authors discussed the results.

#### **Competing interests**

The authors declare no competing interests.

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#### **Figure legends**

Figure 1 (a) Results of the UPS measurements. The x-axis represents the energy of the electron on the basis of the vacuum level, and the y-axis shows the intensity in units of counts per second (cps). The UPS spectra of Fe<sub>100</sub>Gd<sub>0</sub>, Fe<sub>83</sub>Gd<sub>17</sub>, Fe<sub>80</sub>Gd<sub>20</sub>, Fe<sub>0</sub>Gd<sub>100</sub> samples were obtained from the single-composition samples, whereas the other spectra were obtained sequentially from the gradated-composition sample. The red dashed lines represent the Fermi energy estimated by fitting using convolution of the Fermi-Dirac function and Gaussian function. The blue arrows indicate the UPS peaks that are identical to the energy of the Fe 3d band. The green and red arrows indicate the UPS peaks that are identical to the energy of the Gd 4*f* band. (b) Comparison of the composition dependence of the work function, WF among ferromagnetic/ferrimagnetic alloys. The x-axis shows the surface composition, and the y-axis shows the measured WFs. The green and blue plots represent the WF values of Ni<sub>100-x</sub>Fe<sub>x</sub> and Co<sub>100-x</sub>Fe<sub>x</sub>. The pink plots represent the WF values of Fe<sub>100-x</sub>Gd<sub>x</sub>. The filled (open) circles represent the results of the gradated (single)-composition sample. (c) Comparison of the WF modulation efficiency  $\eta$  based on the composition of binary alloys for a variety of alloys.  $\eta$  is the change in the WF due to adding a low WF element of 1%.

**Figure 2** Magnetization curves of  $Fe_{100-x}Gd_x$  films measured at RT by using a vibrating sample magnetometer for (a) Gd, (b)Fe<sub>79</sub>Gd<sub>21</sub>, (c)Fe<sub>86</sub>Gd<sub>14</sub> and (d) Fe single-composition samples. An in-plane magnetic field was applied to the sample. (e) Saturation magnetization  $M_s$  obtained by magnetization curves as a function of *x*. The pink area is magnetic compensation area reported in Ref [27, 28](f) Temperature evolution of

magnetization, *M* at  $B_x = 1$  T normalized by *M* at 300 K for Fe<sub>100-x</sub>Gd<sub>x</sub> single-composition samples. The inset shows Curie temperature  $T_c$  as a function of *x*.

**Figure 3** (a) A schematic of device structure for the measurements of resistivity and anomalous Hall effect. (b) Temperature dependences of resistivity  $\rho_{xx}$ , for Fe<sub>100-x</sub>Gd<sub>x</sub> single-composition samples with various *x*. (c) Temperature dependences of  $\rho_{xx}$  normalized by  $\rho_{xx}$  at 300 K.

**Figure 4** (a)-(d) Results of anomalous Hall measurements of the Hall bar-shaped  $Fe_{100-x}Gd_x$  single-composition samples at various temperatures. Hall voltage was measured under application of an out-of-plane magnetic field. A dc charge current of 0.1 mA was applied. The device geometry and current-voltage configuration are shown in Fig. 3(a).

**Figure 5:** (a)-(d) Semi-log plots of the current-rectifying characteristics for the  $Fe_{100-x}Gd_x$  single-composition samples measured at 300 K. A gold (Au) antimony (Sb) ohmic contact was fabricated at the back side of *n*-Si substrate. Device structure was shown in the inset of Fig. 5(a). The size of  $Fe_{100-x}Gd_x$  electrodes was 0.29 mm<sup>2</sup>.



Fig. 1, N. Yamashita et al.



Fig. 2, N. Yamashita et al.



Fig. 3, N. Yamashita et al.



Fig. 4, N. Yamashita et al.



Fig. 5, N. Yamashita et al.