Tunneling magneto resistance in trilayer structures composed of group-IV-based ferromagnetic semiconductor \( \text{Ge}_{1-x}\text{Fe}_x \), MgO, and Fe

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The group-IV-based ferromagnetic semiconductor \( \text{Ge}_{1-x}\text{Fe}_x \) (GeFe) is one of the most promising materials for efficient spin injectors and detectors for Si and Ge without the conductivity mismatch problem, because it can be epitaxially grown on Si and Ge substrates with flat and smooth interfaces, and because its conductivity can be widely controlled by B doping. The Curie temperature \( T_C \) of GeFe can be increased to 210 K, which is higher than the highest \( T_C \) value reported for (Ga,Mn)As (200 K). Furthermore, X-ray magnetic circular dichroism measurements have revealed that nanoscale local ferromagnetic regions, which are formed in the local high-Fe-content regions, exist even at room temperature well above \( T_C \). Thus, GeFe has a potential for device applications operating at room temperature. Recently, first-principles calculations have suggested that the Fermi level \( E_F \) is located in two overlapping highly spin-polarized bands formed in the band gap of GeFe: spin-down d(e) band and spin-up p–d(t2) band. Thus, it is important to clarify how these bands contribute to spin injection and detection. Thus far, there has been no report of the successful detection of spin-dependent tunneling in magnetic tunnel junctions (MTJs) using group-IV FMSs. In this study, we have observed tunneling magnetoresistance (TMR) in epitaxially grown Fe/MgO/Ge0.935Fe0.065. This is the first observation of TMR in MTJs with a group-IV FMS. We found that spin-polarized carriers in the p–d(t2) band of GeFe are mainly responsible for the tunneling transport.

We fabricated MTJs composed of Fe (14 nm)/MgO (d nm)/Ge0.935Fe0.065 (50 nm)/Ge:B (B: \( 4 \times 10^{19} \text{cm}^{-3} \), 70 nm) grown on a p+-Ge(001) substrate by low-temperature molecular-beam epitaxy (LT-MBE) [Fig. 1(a)]. The growth process is described as follows. After the Ge substrate was chemically cleaned with ultrapure water, ammonia water, and acetone, followed by cleaning and etching with ultrapure water and buffered HF in a cyclic manner for 1 h, it was introduced into the ultrahigh-vacuum MBE growth chamber through an oil-free load-lock system. After degassing the substrate at 300 °C for 30 min and successive thermal cleaning at 740 °C for 15 min, we grew the Ge:B buffer layer at 300 °C, which was followed by the growth of the 50-nm-thick Ge0.935Fe0.065 layer at 240 °C. The MgO barrier layer was grown by electron beam deposition in our MBE growth chamber at 80 °C with a growth rate of 0.02 Å/s. The thickness \( d \) of the MgO barrier was changed from 3 to 9 nm in

Fig. 1. (a, b) Schematic structures of (a) the Fe/MgO/GeFe trilayer sample fabricated in our study and (b) its epitaxial relationship. In (b), the black and gray lines represent the unit cells and covalent bonds, respectively. (c)–(j) RHEED patterns of the (c, d) annealed Fe layer, (e, f) as-grown Fe layer, (g, h) MgO layer, and (i, j) Ge0.935Fe0.065 layer with the electron-beam azimuth along the (c), (e), (g) (110) direction and (d), (f), (h), (j) (100) direction of the Ge(001) substrate.
Fe layer, the sample was annealed at 250 °C for 30 min after the growth. We used in-situ reflection high-energy electron diffraction (RHEED) to monitor the crystallinity and surface morphology during the growth [Figs. 1(c)–1(j)]. The diffraction patterns indicate that the MgO and Fe layers are epitaxially grown on Ge0.935Fe0.065 with the epitaxial relationship of Fe[100](001)∥MgO[110](001)∥Ge0.935-Fe0.065[100](001) shown in Fig. 1(b), which is the same as that of Fe/MgO/Ge.14,15) The diffraction patterns of the top Fe layer change from spotty [Figs. 1(e) and 1(f)] to streaky [Figs. 1(c) and 1(d)] with annealing, reflecting the improvement of the surface flatness. The root mean square of the surface roughness of the top Fe layer measured by atomic force microscopy (AFM) was about 0.24 nm, which means that an atomically flat surface was obtained. The $T_C$ value of the Ge$_{0.935}$Fe$_{0.065}$ layer was 100 K.4) Figures 2(a) and 2(b) show the cross-sectional high-resolution transmission electron microscopy (HRTEM) images of the sample. One can see that almost the entire region of the trilayer has an epitaxially grown single-crystal structure with smooth and flat interfaces. There are some amorphous-like crystal domains, which are indicated by the yellow arrows in Figs. 2(a) and 2(b), between the regions that have slightly different tilts of the crystal orientation indicated by the white dashed lines in Fig. 2(b).

For tunneling transport measurements, square mesas of 700 x 700 µm$^2$ size were fabricated on the sample using photolithography and Ar-ion etching. As shown in Fig. 3(a), the resistance–area product $RA$ is symmetric about $V = 0$ for all the MTJs with $d$ from 3 to 9 nm at 3.5 K, where $V$ is the bias voltage applied to the top electrode with respect to the substrate. This suggests that the Schottky barrier is not formed at the MgO/GeFe interface. This result can be understood by considering the $E_F$ position; it was reported that $E_F$ is pinned at about 0.12 eV above the valence band maximum (VBM) at the MgO/p-Ge interface, and recent angle-resolved photoemission spectroscopy (ARPES) measurements for GeFe showed that $E_F$ is located at 0.35 eV above the VBM in impurity bands, which are indicated by the pink area in the inset of Fig. 3(a). RA increases exponentially as $d$ increases [Fig. 3(b)]. This is a typical feature of tunnel junctions. In the Wentzel–Kramers–Brillouin (WKB) approximation, the slope of the ln $RA$–$d$ characteristics is given by $2\sqrt{2m^*V_b/h}$. From our results, $m^*V_b$ (kg·eV) is estimated to be 0.035$m_0$ for Fe/MgO/GeFe. Here, $m_0$ is the free-electron mass, $m^*$ is the effective mass of holes, and $V_b$ is the barrier height. This value is significantly lower than the reported values for the MgO barrier in the literature [1.1$m_0$ and 3.6$m_0$ for the epitaxial MgO(001) barrier in Fe/MgO/Fe and FeCo/MgO/Fe structures, respectively].17,18) In Fe/MgO/Fe MTJs, it is known that the barrier height is decreased by oxygen-vacancy defects in the MgO barrier.19) The low barrier height of our junctions is probably due to the presence of the amorphous-like crystal domains in the MgO layer, which are seen in the TEM lattice images [see Figs. 2(a) and 2(b)], in addition to the oxygen-vacancy defects. These domains may have a role of leak paths and decrease the tunnel resistance, lowering the barrier height.

Figure 4(a) shows the magnetic field dependence of $RA$ measured with $V = 40$ mV at 3.5 K when $d$ is 3 nm. The magnetic field $H$ was applied along the [110] axis in the plane of the Ge substrate. Note that the $RA$–$H$ data showed no notable dependence on the in-plane direction of $H$, reflecting the weak magnetic anisotropy of GeFe. The red and blue curves (major loop curves) were obtained by sweeping $H$ from positive to negative and negative to positive, respectively. The jumps of $RA$ at $\mu_0H = \pm 2$ mT in the major loop.
correspond to the magnetization reversal of the top Fe layer.\(^{12}\) The RA values measured with the opposite magnetic field sweep directions gradually become closer with increasing \(|\mu_0 H|\), reflecting the gradual saturation of the magnetization in the \(\text{Ge}_{0.935}\text{Fe}_{0.065}\) layer.\(^{8}\) As can be seen in the minor loop [green curve in the inset of Fig. 4(a)], the antiparallel magnetization configuration is stable at \(\mu_0 H = 0\) T. This is a typical feature of TMR. Note that the measurements of RA–H performed on a reference \(\text{Al}/\text{Ge}_{0.935}\text{Fe}_{0.065}/\text{Ge:B}\) sample, which does not have a MgO barrier layer, did not show a clear magnetoresistance, indicating that the observed magnetoresistance in Fe/MgO/GeFe originates from the tunneling transport through the MgO barrier.

We can calculate the TMR curves using the magnetization curves of Fe and GeFe. From Julliere’s model,\(^{20}\) the TMR ratio defined as \([\text{RA}(\mu_0 H) − \text{RA}(200 \text{ mT})]/\text{RA}(200 \text{ mT})\) is given by

\[
\text{TMR ratio} = \frac{P_{\text{Fe}}P_{\text{GeFe}}[1 - \cos(\theta_{\text{Fe}} - \theta_{\text{GeFe}})]}{1 + P_{\text{Fe}}P_{\text{GeFe}} \cos(\theta_{\text{Fe}} - \theta_{\text{GeFe}})}.
\]

Here, \(\text{RA}(\mu_0 H)\) represents the RA value obtained under \(\mu_0 H\) (mT), \(P_{\text{Fe}}\) (\(P_{\text{GeFe}}\)) and \(\theta_{\text{Fe}}\) (\(\theta_{\text{GeFe}}\)) are the spin polarization \(P\) and the direction of the magnetization relative to the [110] axis (\(\parallel H\)) in the Fe (GeFe) layer, respectively. When \(P_{\text{Fe}}P_{\text{GeFe}} \ll 1\), the denominator in Eq. (1) becomes \(1\). Because the magnetization of the Fe layer is sharply reversed (i.e., \(\theta_{\text{Fe}} = 0^\circ\) or \(180^\circ\)), \(\cos(\theta_{\text{Fe}} - \theta_{\text{GeFe}})\) is expressed by \(M_{\text{Fe}}^sM_{\text{GeFe}}^s\), where \(M_{\text{Fe}}\) (\(M_{\text{GeFe}}\)) is the \(H\) direction component of the magnetization of Fe (GeFe) and \(M_{\text{Fe}}^s\) (\(M_{\text{GeFe}}^s\)) is the saturation magnetization of Fe (GeFe). Thus, the TMR ratio of our MTJs should be approximately proportional to \(1 - M_{\text{Fe}}^sM_{\text{GeFe}}^s/M_{\text{Fe}}^sM_{\text{GeFe}}^s\). Figure 4(b) shows the calculated TMR ratio obtained using \(M_{\text{Fe}}\) and \(M_{\text{GeFe}}\). Here, the magnetization curve of the \(\text{Ge}_{0.935}\text{Fe}_{0.065}\) layer was estimated by magnetic circular dichroism (MCD) at 5 K with a photon energy of 2.3 eV corresponding to the L-point energy gap of bulk Ge measured for a \(\text{Ge}_{0.935}\text{Fe}_{0.065}\) film, which was grown under the same conditions as our MTJ sample.\(^{8}\) We assumed that the magnetization curve of the top Fe layer has a rectangular shape with the coercive fields of \(\pm 2\) mT. We can see that the calculated TMR curves qualitatively reproduce the experimental TMR curves [Fig. 4(b)]. The slight difference between the experimental and calculated TMR curves may originate from the presence of the small tunneling anisotropic magnetoresistance of GeFe, or from the difference between the magnetization near the MgO/GeFe interface and that of the entire GeFe film.

Figure 5(a) shows the TMR ratio as a function of \(\mu_0 H\) at various temperatures measured with \(V = 40\) mV when \(d = 3\) nm. The TMR ratio (at \(\mu_0 H = 2\) mT) decreases [Fig. 5(b)] and the hysteresis becomes smaller [Fig. 5(a)] with increasing temperature, reflecting a decrease in the magnetization of the \(\text{Ge}_{0.935}\text{Fe}_{0.065}\) layer.\(^{8}\) These results also support our conclusion that the measured magnetoresistance is due to the TMR effect.

First-principles supercell calculations performed on GeFe suggested that the Fermi level is located in two overlapping impurity bands that have opposite spin directions formed in the band gap; one is a narrow spin-down d(\(e\)) band, in which \(P\) is almost 100%, and the other is a spin-up p–d(\(t_2\)) band, in

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"Fig. 4. (a) Magnetic field (\(\mu_0 H\)) dependence of RA of the MTJ with \(d = 3\) nm measured with a bias voltage \(V = 40\) mV at 3.5 K. The magnetic field \(H\) was applied along the [110] axis in the plane of the Ge substrate. The red and blue curves (major loop curves) were obtained by sweeping \(H\) from positive to negative and negative to positive, respectively. The black arrows indicate the magnetization configurations of the top Fe and bottom \(\text{Ge}_{0.935}\text{Fe}_{0.065}\) layers. The inset shows the magnified plot of the TMR curves. The green curve is the minor loop. (b) Calculated TMR curves at 5 K.

Fig. 5. (a) TMR ratio, which is defined as \([\text{RA}(\mu_0 H) − \text{RA}(200 \text{ mT})]/\text{RA}(200 \text{ mT})\), as a function of \(\mu_0 H\) at various temperatures. (b) TMR ratio at \(\mu_0 H = 2\) mT as a function of temperature when \(d = 3\) nm and the bias voltage \(V = 40\) mV."
which \( P \) is about 70\%.\(^9\) In recent ARPES measurements for Ge\(_{0.935}\)Fe\(_{0.065}\), it was confirmed that the Fe 3d impurity states actually have a finite contribution to the density of states at \( E_F \).\(^9\) Because the observed sign of the TMR ratio is positive in Fe/MgO/GeFe and the \( P \) value of Fe is also positive, our result means that the spin-up \( p\)-\( d(t_2) \) band is responsible for the tunneling properties.\(^9\) From the TMR ratio of about 0.27\% observed at 3.5 K [Fig. 4(a)], the \( P \) value of the Ge\(_{0.935}\)Fe\(_{0.065}\) layer is estimated to be 0.17\% using Julliere’s model,\(^20\) when we use the effective \( P \) value of the top Fe layer estimated from TMR observed for Fe/MgO/Fe (\( P = 75\% \)).\(^9\) This value obtained for GeFe is much smaller than that predicted by the first-principles supercell calculations (70\%).\(^9\) This is probably due to the leak current, which does not contribute to TMR, through the amorphous crystal domains. Thus, the TMR ratio is expected to be enhanced in the Fe/MgO/GeFe MTJs by improving the crystallinity of the MgO tunnel barrier and decreasing the leak current through the amorphous crystal domains in MgO.

In summary, we have grown MTJs composed of epitaxial Fe/MgO/Ge\(_{0.935}\)Fe\(_{0.065}\) and demonstrated the first successful observation of TMR in the MTJs containing a group-IV ferromagnetic semiconductor. This result confirms the presence of spin-polarized carriers at \( E_F \) in GeFe. The observed sign of the TMR was positive, which revealed that the largely spin-polarized carriers in the \( p\)-\( d(t_2) \) band are dominant for the tunneling. The TMR ratio will be increased in the Fe/MgO/GeFe MTJs by improving the crystallinity of the MgO tunnel barrier and decreasing the leak current through the amorphous crystal domains in MgO. Our results show that GeFe is promising for spin injectors and detectors of future Si- and Ge-based spintronic devices.

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