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Abstract

In 2007, a Nobel Prize is awarded to Dr. Albert Fert and Peter Grünberg for their contribution in giant magnetoresistance (GMR) effect. The magnetic head based on GMR effect has significantly increased the storage density in the hard disk drive (HDD) and brought the coming of the digital age. Besides, the rapid development of GMR sensor has opened a wide and promising range of applications, including the aspects in automobile, traffic monitor, biomedicine, and space, etc. As continuously extending the market, it needs GMR sensor with much lower cost, smaller size, higher sensitivity, and compatibility with the CMOS technology. In light of that, we give a review about the recent progress of the MR effect in Mn$_x$Ge$_{1-x}$ system, which refers to the material growth and magnetic and MR property. Through engineering the Mn$_x$Ge$_{1-x}$ structure, it could realize the transition from negative to positive MR, geometric-enhanced giant MR, and electric-field controlled MR. The fact of well-designed MR effect and high compatibility with Si technology brings a high potential and advantage for fabricating Mn$_x$Ge$_{1-x}$-based MR sensors, which could be widely used in magnetic head and biomedical sensors, among others, with the superiority of much lower manufacturing cost, lower power dissipation, higher integration density, and higher sensitivity.

Keywords: magnetoresistance, geometric-enhanced MR, electric-field controlled MR, Mn$_x$Ge$_{1-x}$ system, MR sensor

1. Introduction

Magnetic sensors have been widely used in analyzing and controlling thousands of functions by human beings for many decades [1–3]. A digital world has arrived and been driven by the tremendous increase of storage density in the hard disk drive (HDD) using the state-of-the-art
magnetic sensor [4]. The convenient transportation has been promised in a safe manner because of the high reliability of the noncontact switching and monitor with magnetic sensor [5–7]. The portable medical system relies on the magnetic sensor for nondestructive diagnostic applications [8–10]. Factories have high productivity due to the high stability and precision as well as low cost of magnetic sensors [3, 11].

There are numerous types of magnetic sensors [6], such as search-coil sensors, fluxgate sensors, magneto-optical sensors, optically pumped magnetometer, magnetoresistance (MR) sensors, Hall effect sensors, and superconducting quantum interference device (SQUID) magnetometer, among others. Most of them are based on the direct magnetic and electric response. A magnetic sensor can directly convert the magnetic signal into an inductive voltage signal [12] or resistance variation [5], and its sensitivity determines its operating regime and potential applications. For example, SQUID magnetometer with a high sensitivity of $10^{-10}$–$10^{-4}$ gauss has been used for measuring magnetic field gradients or differences due to permanent dipole magnets in major applications of brain function mapping. The fluxgate and MR sensor can provide the medium field sensitivity of $10^{-6}$–$10^{-2}$ gauss, which has been used for the magnetic compass and magnetic anomaly detection. Hall effect sensors with a low sensitivity of $1$–$10^6$ gauss have been exploited for applications in noncontact switching and current meters. In consideration of the operating regime, the MR sensor is one of the most commonly used sensors in everyday life [4, 5, 11, 13, 14]. Additionally, it demonstrates some specific advantages [4, 5] comparing to others, including high compatibility with the CMOS process technology, high scalability, low power dissipation, and low manufacture cost.

MR sensors using the resistance as the detectable signal involve the contributions from different mechanisms, such as anisotropic magnetoresistance (AMR) [5], giant magnetoresistance (GMR) [5, 15, 16], and tunnel magnetoresistance (TMR) [17, 18]. AMR sensor could exhibit large field sensitivity and more significantly could detect the field direction, which has been widely used as the magnetic head in HDD and automotive sensors to determine many quantities, like throttle valve position, chassis height, and pedal position [5]. However, since the discovery of GMR effect in 1988 [15], it has gradually replaced the role of the AMR effect for the sensor application, which provided more advantages, such as larger output signal, miniaturization opportunity, and the possibility to make a 360° angle sensor. As a derivative of GMR effect, TMR effect could have much higher sensitivity and integration density [18]. A successful paradigm for sensor evolution is the magnetic read head. A dramatic shift to storing data from the analog to current digital world started in the 2000s and was dominantly driven by the emergence of spintronics exemplified by the introduction of the AMR read head in 1991 by IBM [19], the GMR read head in 1997 [20, 21], and the TMR read head in 2006 [21]. Prior to the introduction of the MR read head, the storage densities of HDD had increased at a growth rate of 25% per year. With the introductions of the AMR head in 1991, the growth rate of storage density increased to 60% per year, while the introduction of GMR read head made the growth rate further to 100% per year. Due to such dramatic impact, the 2007 Nobel Prize in Physics was awarded to Albert Fert and Peter Grünberg for the discovery of GMR effect. The recent areal density growth has slowed resulting mainly from the thermal instabilities, known as the superparamagnetic effect [22, 23]. While the continual effort attempts to address the fundamental limitation of GMR sensor for much higher sensitivity and thermal instability, searching for other high-efficient MR sensors has never been stopped.
As a potential candidate, the geometric-enhanced MR could demonstrate a large MR value as a function of magnetic field, and the underlying mechanism arises from the dependence of the current path on the sample shape and electrode configuration [24]. GMR effect can give rise to a negative MR, whereas the geometric-enhanced MR usually is positive. The current deflected from the electric-field direction by Lorentz force, and the inhomogeneity in current path determined the MR sensitivity. Previously, Thio et al. reported a large MR up to 28% at 500 gauss in the inhomogeneous Hg$_{1-x}$Cd$_x$Te thin film associated with the composition fluctuation [24, 25]. Furthermore, Solin et al. configured an inhomogeneous structure by embedding concentric gold in nonmagnetic indium antimonide matrix and showed a MR value as high as 100% at 500 gauss [24]. All of these results point to a new way for designing new type of MR sensors, and the related research is still in progress.

As the demand for the sensors with higher integration density and lower manufacturing cost is continuously growing, it calls for not only innovative sensor configuration but also novel material candidate with much higher sensitivity to magnetic field, higher compatibility with CMOS technology, and lower power consumption. Mn$_x$Ge$_{1-x}$ [26] as the silicon-compatible material appears to be an appealing candidate for application in MR sensors through the combined use of GMR [27] and geometric-enhanced MR [28]. In light of that, we give a review of the current research progress in Mn$_x$Ge$_{1-x}$ thin film and nanostructures, as well as their possible application in MR sensors. The fundamental aspects of the MR mechanisms are listed in the first section. The following section gives a systematic and comprehensive review about the Mn$_x$Ge$_{1-x}$ material growth, structure characterization, and MR measurement. MR phenomena based on different mechanisms including GMR, geometric-enhanced MR, and even electric-field controlled MR have been well discussed, and the correlation between the structures and MR properties is established. The final section gives an outlook of the potential application of the Mn$_x$Ge$_{1-x}$-based MR sensors and estimates their implicit impact. Exploiting Mn$_x$Ge$_{1-x}$-based MR sensors may set a new stage for the next-generation sensors with improved sensitivity, higher scalability, and higher compatibility with current CMOS technology.

2. The fundamental principles in MR sensors

2.1. The definition of MR effect

The definition of the MR comes from the resistance variation of a material as a function of magnetic field, which can be described by the following equation:

$$MR = \frac{R(B) - R(0)}{R(0)} = f(B)$$

where the R(B) and R(0) are the resistance at the magnetic field of B and zero, respectively. The MR value follows different functions with the magnetic field based on the mechanism differences. In a traditional semiconductor, the MR abides by the orbital MR effect with the origin from Lorentz force. The deflection of the current due to the magnetic field produces an increase of the current path length and thus an increase of resistance. The relation between them can be described as:
\[ MR = \frac{\rho_B}{\rho_0}(1 + C_1(\mu B)^2) \]  

(2)

where \(\rho_B/\rho_0\) is the specific relative resistance, \(C_1\) is a geometrical parameter, and \(\mu\) is the carrier mobility. However, the MR response in such principle is very weak and thus limiting their broad application.

### 2.2. AMR effect

The AMR effect was initially discovered in 1857 by William Thomson [5]. It happened in the ferromagnetic materials, which arose from the spin-orbit interaction and the resistance depended on the orientation of the current relative to magnetization direction [29]. Usually, the resistance is higher for the current direction parallel to the magnetization and lower for the current perpendicular to the current. Such angle dependence could be described by the following equation:

\[ R = R_0 + \Delta R \cos^2 \theta \]  

(3)

Apparently, the signal extrema are achieved at angles of 0° and 90°, and the steepest response slope is at an angle of 45°. Thus, to achieve the highest sensitivity, the sensor was normally designed with the initial magnetization direction to the current direction at an angle of 45°. Typical AMR response is about 1–4% [5, 29], which is good enough for allowing the use of AMR sensors in practical application.

### 2.3. GMR effect

GMR was discovered independently by Albert Fert and Peter Grünberg in 1988 [15, 16]. Since then, great progress in improving the GMR value has been achieved, and the use of GMR effect in practical applications has significantly changed the world. The most important application is the use of GMR read head, which has dramatically increased the areal density in HDD and brought the advent of the digital world. The significance of the GMR discovery was recognized by the Nobel Prize in Physics awarded to Fert and Grünberg in 2007. In the GMR effect, the resistance relies on the angle between magnetization directions at different locations in the materials, which could happen in granular systems [30–32] or ferro-/non-ferro-multilayer materials [33, 34]. For real application, the multilayer structure is mainly considered rather than the granular system which is normally in an uncontrollable growth condition. The basic principle of GMR effect is the spin-dependent scattering, in which a parallel direction between the current spin and magnetization can generate a low scattering, while its antiparallel direction is in a high scattering. The resistance as a function of the angle between magnetization directions is described by:

\[ R(\theta) = R(0) + \Delta R[1 - \cos \theta]/2 \]  

(4)

where \(\Delta R\) is the value of \(R(180°)-R(0°)\). This equation can show that the angle dependence of the GMR effect has a period of 360°, which forms an obvious contrast to the AMR effect with a period of 180°.
2.4. TMR effect

As one specific case of GMR, the TMR [35–37] happened as the nonmagnetic conductive layer was substituted by an insulating layer in the multilayer structure, named as magnetic tunnel junction (MTJ). In this structure, electrons can pass through this insulator by means of the quantum tunnel effect. In early reports, the insulating layer in MTJ was constituted by Al$_2$O$_3$, which demonstrated a MR level of MTJ about 40% [36]. Recently, this level has been significantly improved to 200% by using MgO as the insulating layer [17, 18]. The improvement of TMR level has significantly increased the areal density of HDD; meanwhile, it has boosted the development of spin-transfer torque-based magnetoresistive random access memory (STT-MRAM) for the next-generation memory application [38].

2.5. Geometric-enhanced MR effect

Geometric-enhanced MR is another specific case of the orbital MR associated with the material shape [24, 28]. A typical structure is consisted of a composite including conductive metal and less conductive semiconductor. The electric field, $E$, is normal to the equipotential surface of the highly conductive metal. The current density is written as $J = \sigma(H)E$, where $\sigma(H)$ is the conductivity tensor. At $H = 0$, the tensor of $\sigma(H)$ is diagonal, so $J = \sigma E$ and the current flows into the conductive metal, which acts as a short circuit. At high $H$, the off-diagonal component of $\sigma(H)$ gives rise to a deflection of $J$ from $E$, and the deflection angle is called as Hall angle [39], which is dependent on the Hall mobility $\mu$ and $H$. In a sufficiently large $H$, the current may deflect around the conductive metal and flow in the less conductive semiconductor, which acts as an open circuit. The transition from short circuit at low $H$ to open circuit at high $H$ results in a geometric enhancement of the MR.

3. The research progress of MR effect in Mn$_x$Ge$_{1-x}$ system

3.1. MR effect in the Mn$_x$Ge$_{1-x}$ thin film

Mn$_x$Ge$_{1-x}$ could go through different MR effects through engineering Mn-doping concentration, Mn$_x$Ge$_{1-x}$ phase, and geometric structure. At the beginning, we pay our attention to the MR effect that happens in Mn$_x$Ge$_{1-x}$ thin film. The Mn$_x$Ge$_{1-x}$ thin film was grown on Ge substrate by a Perkin-Elmer solid-source molecular beam epitaxy (MBE) with Ge and Mn Knudsen cells. Ge substrate was cleaned by immersing in acetone and isopropyl alcohol with ultrasonic agitation, followed by dipping in 1% hydrofluoric (HF) acid. Then, the substrate was directly transferred into the MBE chamber for thin-film growth at around 200°C. After growth, its microstructure and composition were comprehensively characterized by transmission electron microscopy (TEM) equipped with energy-dispersive spectroscopy (EDS). Its magnetic property and magnetoresistance were revealed by SQUID and physical property measurement system (PPMS).

Figure 1(a) is a typical cross-sectional TEM image of the grown thin film, which shows some dark parts embedded in the Ge matrix. To understand the detailed structure, high-resolution TEM (HRTEM) was employed, and typical [110] zone axis TEM results are shown in Figure 1(b)–(d).
In Figure 1(b), stacking faults (SFs) could be clearly observed in the Ge matrix and feature a triplet periodicity of Ge (111) lattice spacing [40]. The formation of SFs might come from the strain accumulation of Mn doping and lattice-mismatched precipitates. Figure 1(c) was collected from the relatively-uniform doped region and clearly displays a very good crystallinity. Meanwhile, some precipitates could be noticeably observed in the thin-film sample, as shown in Figure 1(d). It clearly shows another set of lattice structure that is different from the Ge matrix. Using the lattice spacing of the Ge as the reference, we calculated the observed lattice spaces of the cluster, which matched well with the (002) and (010) atomic planes of the hexagonal Mn$_5$Ge$_3$ phase [41, 42]. Furthermore, it can be confirmed that the Mn$_5$Ge$_3$ (002) plane was parallel to the Ge (111) plane. To determine the Mn-doping concentration, EDS was carried out, and the result reveals that the average Mn concentration is ~4%, as shown in Figure 1(e). The magnetic property of the grown Mn$_x$Ge$_{1-x}$ film was measured by SQUID, and the result is shown in Figure 1(f). Magnetic hysteresis can be observed between 10 and 250 K, and it disappears around 300 K. To further determine the $T_c$ and detect any magnetic precipitates, zero-field-cooled (ZFC) and field-cooled (FC) magnetic measurements were performed under a small magnetic field of 200 Oe. As shown in Figure 1(g), the magnetization vanishes near 300 K, indicating a $T_c$ = 300 K, which further confirms the formation of Mn$_5$Ge$_3$ ($T_c$ = 296 K) [43]. Two blocking temperatures coexist in the ZFC curve, with the lower one at 20 K and the higher one at 200 K, which are attributed to Mn-rich coherent Mn$_5$Ge$_3$ nanostructures [44] and Mn$_5$Ge$_3$ precipitates [27], respectively. Both of them could be well resolved in the TEM characterization in Figure 1(a), as indicated by white arrows and red-dotted squares, respectively.

For sensor application, it should explore the MR effect of the Mn$_x$Ge$_{1-x}$ thin film to reveal its control parameters. To this end, the current sample accompanied by a more Mn-doped sample (6%) was fabricated into micrometer Hall bar structures by photolithography for the
magnetotransport measurement. Figure 2 shows the temperature-dependent MR curves of the two samples with an out-of-plane magnetic field. Figure 2(a) is the MR curves of the 4% Mn-doped sample, and it shows only positive MR in the whole temperature range. Careful examination could find that the MR curve follows a parabolic shape in the whole temperature range except for a small deviation happening at low magnetic field at 1.9 K. The parabolic dependence exclusively indicates that the orbital MR is dominant in this sample [45], while the small deviation should come from the magnetization-enhanced orbital MR [46]. As the Mn dopants increase to 6%, however, the orbital MR is suppressed, and a negative MR is demonstrated at low temperatures, as shown in Figure 2(b). It implies that the enhanced magnetization in more Mn-doped sample significantly boosts the spin-dependent scattering and thus generating the negative MR [45]. However, as the magnetization becomes weak at high temperatures, the positive MR shows up and the orbital MR is dominant again. Through tuning the Mn-doping concentration in Mn$_x$Ge$_{1-x}$ thin film, the engineering of negative and positive MR is conveniently realized, although it still needs to enlarge the MR value for the potential application in MR sensors.

3.2. MR effect in Mn-rich Mn$_x$Ge$_{1-x}$ coherent nanostructures

To precisely control the MR and seek for a large value in Mn$_x$Ge$_{1-x}$ system, Mn-rich Mn$_x$Ge$_{1-x}$ coherent nanostructures are well designed based on its growth thermal dynamics and kinetics characteristics. As already well documented, Mn atoms preferred to form intermetallic compounds [47, 48] with Ge at high growth temperatures, while they tended to form Mn-rich Mn$_x$Ge$_{1-x}$ coherent nanostructures [27, 44, 49, 50] at low growth temperature. By choosing proper growth conditions, Mn-rich Mn$_x$Ge$_{1-x}$ coherent nanostructures with different morphologies were formed by MBE, and their effect to MR properties are well discussed. Following the same cleaning procedure as described above, Ge substrate was loaded into the MBE chamber for superlattice growth. A high-quality Ge buffer layer was first deposited at 250°C, and then the growth temperature was cooled down to 70°C for the subsequent superlattice growth. Ten periods of Mn$_x$Ge$_{1-x}$ and Ge layers were alternatively deposited on the substrate. By adjusting the nominal thickness of Ge space layer from 6 to 25 nm while keeping the Mn$_x$Ge$_{1-x}$ layer at
about 4 nm, Mn$_x$Ge$_{1-x}$ nanocolumns, nanodots, and nanowells were obtained, respectively. Figure 3(a) shows a typical cross-sectional TEM image of the Mn$_x$Ge$_{1-x}$ nanocolumns with a nominal Ge space layer of 6 nm, in which well-aligned nanocolumns with dark contrast can be clearly observed. To reveal the detailed lattice structure, HRTEM experiments were carried out, and the result is shown in Figure 3(b). Careful examination of the HRTEM image verifies that the Mn$_x$Ge$_{1-x}$ nanocolumns have the same diamond lattice structure as the Ge matrix, showing a coherent growth. The formation of nanocolumns rather than layer structure indicates that Mn atoms not only agglomerate laterally but also migrate vertically into the adjacent Ge space layers [51]. After increasing the Ge space layer thickness to 11 nm, the superlattice evolves from a nanocolumn structure to a nanodot structure. From the cross-sectional TEM image shown in Figure 3(c), 10 periods of nanodots with Ge space layers are clearly observed, in which the nanodots are well aligned along the vertical direction. The alignment may follow the fact that the buried MnGe nanodots induce an elastic strain in the thin Ge space layer, which provides a preferential nucleation site for the formation of new MnGe nanodots. Through further HRTEM characterizations, these nanodots show relatively uniform size distribution with an elliptical shape (dimension of 5.5 ± 0.5 and 8 ± 0.3 nm in the
horizontal and vertical directions, respectively), as demonstrated in Figure 3(d). The fact that the vertical diameter of the nanodot is much larger than the thickness of the MnGe layer again suggests that Mn atoms migrate vertically into the adjacent Ge space layer. Figure 3(e) clearly shows the coherent growth of MnGe nanodot in the Ge matrix. After further increasing the Ge space layer thickness to 25 nm, MnGe nanowells with 10 periods were obtained, and a typical TEM image is shown in Figure 3(f). Noticeably, the nanowells are also composed of dense MnGe nanodots, whereas the nanodots are not aligned in the vertical direction. It may be due to the strain release on the top surface of the thick Ge space layer, and hence there are no energy-preferable positions for subsequent nucleation of the MnGe nanodots [52]. Similar to the previous two cases, the MnGe nanodots inside the nanowells are also coherent with the surrounding Ge matrix with a diameter range of 4–10 nm, as shown in Figure 3(g).

The magnetic properties of the formed nanostructures are disclosed by SQUID. Due to the similarity, we took the case of the Mn$_x$Ge$_{1-x}$ nanocolumn as an example, and the result is shown in Figure 4. Figure 4(a) shows the temperature-dependent M-H curves, which clearly demonstrate the ferromagnetism from 10 to 175 K and the paramagnetism at 300 K. At 10 K, the film exhibits a saturation magnetic moment of 104 kA·m$^{-1}$ that is estimated to be 0.24 μ$_B$ per Mn atom. This gives a fraction of 8% of Mn activated in Mn$_x$Ge$_{1-x}$ when considering the value of 3 μ$_B$ in each fully active Mn atom [53]. To further understand its magnetic property, the ZFC and FC curves were performed with a magnetic field of 200 Oe in SQUID, and a typical result is shown in Figure 4(b). The differences between them give an insight into the anisotropic barrier distribution, blocking temperature, and Curie temperature [54]. Two blocking temperatures could be well resolved with one at 25 K and the other at 250 K. As discussed above, the two blocking temperatures indicate the coexistence of Mn-rich Mn$_x$Ge$_{1-x}$ nanostructures and Mn$_5$Ge$_3$ nanoparticles in the film. The former has been well recognized in Figure 3, whereas the latter could be occasionally observed by comprehensive TEM characterization. Such fact proves that the ZFC and FC measurement in SQUID is more sensitive to detect magnetic particles than TEM [44, 54]. The Curie temperature of the nanocolumns is around 300 K proven from the almost zero magnetic moment at this temperature, which further confirms the existence of Mn$_5$Ge$_3$ ($T_c$ ~ 296 K).

Figure 4. (a) Temperature-dependent hysteresis loops of Mn$_x$Ge$_{1-x}$ nanocolumns with out-of-plane external magnetic field. (b) ZFC and FC curves. Inset is a schematic drawing of the sample setup during the SQUID measurements.
Since the Mn-rich Mn$_x$Ge$_{1-x}$ coherent nanostructures demonstrate different morphologies, it is of great interest to reveal their MR properties and explore the potential application for MR sensors. The samples were fabricated into micrometer-size Hall bar structures, and the measurements were performed in PPMS. The temperature range is from 2 to 300 K with an external magnetic field up to 10 T in an out-of-plane direction. For Mn$_x$Ge$_{1-x}$ nanocolumns, negative MR is observed below 50 K, and a transition to positive MR happens at high temperatures, as shown in Figure 5(a). The origin of the negative MR should come from the spin-dependent scattering mechanism. In the absence of magnetic field, the carrier transport between the nanocolumns with relatively random spin alignment is believed to result in a strong spin-dependent scattering and thus in a high resistance. The high magnetic field would align the spin of the nanocolumns preferentially in one direction. The reduction of spin scattering leads to a low resistance, hence generating a negative MR. The positive MR at high temperatures follows a parabolic shape, which indicates that an orbital MR effect is dominant.

However, the negative MR disappears in Mn$_x$Ge$_{1-x}$ nanowells and nanodot structures, respectively, shown in Figure 5(b) and (c), and instead only positive MR presents in the entire temperature range. Careful examination can find that the positive MR in both of the samples does not follow a perfectly parabolic shape and shows very large values at low temperatures. Especially, the MR value in Mn$_x$Ge$_{1-x}$ nanodot structure is as high as 1000% at 2 K, which is hard to be simply explained by orbital MR. Instead, the geometric-enhanced MR due to the existence of conductive Mn$_x$Ge$_{1-x}$ dots is likely to respond to the large MR [24, 43]. To elucidate the underlying physics of the geometric effect, we consider the current density and the total electric field in semiconductors, which can be described by \( J = \sigma(H)E \), where the \( \sigma(H) \) is described as follows:

\[
\sigma(H) = \begin{pmatrix}
\frac{\alpha}{1 + \beta^2} & \frac{\alpha \beta}{1 + \beta^2} & 0 \\
\frac{\alpha \beta}{1 + \beta^2} & \frac{\alpha}{1 + \beta^2} & 0 \\
0 & 0 & \sigma
\end{pmatrix}
\]  

(5)

Here, \( \beta = \mu H \). In the absence of magnetic field, the tensor \( \sigma(H) \) is diagonal, and the current density can be simply described by \( J = \sigma E \). In this scenario, the current flowing is parallel to the electric field and concentrated into the conductive Mn$_x$Ge$_{1-x}$ nanodots in the Mn$_x$Ge$_{1-x}$ nanowell or nanodot structures, acted as a “short circuit.” However, at a high magnetic field, the off-diagonal term of \( \sigma(H) \) indicates that the current is deflected from conductive Mn$_x$Ge$_{1-x}$ nanodots to the Mn-dilute Ge matrix with low conductivity, resembling an “open circuit.” The transition from the “short circuit” at zero fields to the “open circuit” at high fields produces an increase in resistance. The increased amplitude is significantly dependent on the resistance ratio of Mn$_x$Ge$_{1-x}$ nanodots to the Mn-dilute Ge matrix, and the deflection angle is defined by magnetic field and carrier mobility [24]. Through this mechanism, it is also very simple to explain why the Mn$_x$Ge$_{1-x}$ nanodot structure shows much larger MR compared to Mn$_x$Ge$_{1-x}$ nanowell structure. Compared to Mn$_x$Ge$_{1-x}$ nanodot structure, the disordered conductive nanodots in Mn$_x$Ge$_{1-x}$ nanowell structure make it hard to bypass the conductive nanodots even after deflection around one dot, thus generating lower MR ratio.
The above results clearly demonstrate that the negative-to-positive MR and even large MR can be well engineered through well designing the Mn-rich \( \text{Mn}_x\text{Ge}_{1-x} \) coherent nanostructures. Therefore, it points out a new direction to easily engineer \( \text{Mn}_x\text{Ge}_{1-x} \) nanostructures through strain approach, which may provide a great advantage in designing MR sensors for more functionality.

3.3. Geometric-enhanced and electric-field controlled MR in \( \text{Mn}_x\text{Ge}_{1-x} \) nanomesh

The strain engineering of \( \text{Mn}_x\text{Ge}_{1-x} \) nanostructures provides a potential approach for satisfying the demand of MR sensors with multifunctionality; however, the self-assembly formation of \( \text{Mn}_x\text{Ge}_{1-x} \) nanodots increases the difficulty in accurate control of MR. Therefore, we pay our attention to the pattern-assistant growth of \( \text{Mn}_x\text{Ge}_{1-x} \) nanostructures and disclose their MR property. In this section, \( \text{Mn}_x\text{Ge}_{1-x} \) nanomesh is demonstrated, which could simultaneously provide the nanostructure benefit [55] and large-scale uniform fabrication [28]. The growth of \( \text{Mn}_x\text{Ge}_{1-x} \) nanomesh is also proceeded in the MBE chamber. Before that, great effort has been devoted to fabricate the pattern structure. A 100-nm-thick SiO\(_2\) thin film was firstly deposited on a Ge (111) wafer by PECVD, followed by the formation of a large-scale and close-packed hexagonal single layer of nanospheres on the SiO\(_2\) substrate, as shown in Figure 6(a). By adjusting O\(_2\)-plasma etching time, the nanospheres were successfully shrunk to 160 nm with a 60 nm gap between them as shown in Figure 6(b). Using the nanosphere as the mask, the pattern was transferred to the bottom SiO\(_2\) layer by a two-step etching. Dry etching was firstly employed to etch SiO\(_2\) layer till a 10 nm SiO\(_2\) left. Then, wet etching was hired to remove the left SiO\(_2\) layer. After dissolving the nanospheres, periodic SiO\(_2\) nanopillars were obtained on the substrate, and a typical scanning electron microscopy (SEM) image is shown in Figure 6(c). After carefully cleaning, the substrate was loaded into the MBE chamber for the \( \text{Mn}_x\text{Ge}_{1-x} \) growth. After degassing at 600°C for 30 min, the patterned substrate was in situ cooled down to 160°C for the \( \text{Mn}_x\text{Ge}_{1-x} \) nanomesh growth with a Ge growth rate of 0.2 Å/s and a controlled Mn flux as the dopant source.

The SiO\(_2\) mask was subsequently removed after MBE growth by selective etching, and only \( \text{Mn}_x\text{Ge}_{1-x} \) nanomesh was remained. A typical morphology of the sample was captured by SEM.

Figure 5. (a)–(c) Temperature-dependent MR curves of the \( \text{Mn}_x\text{Ge}_{1-x} \) nanocolumns, nanodots, and nanowells, respectively. The \( \text{Mn}_x\text{Ge}_{1-x} \) nanocolumns show negative MR below 50 K, while a positive value dominates at high temperature. For \( \text{Mn}_x\text{Ge}_{1-x} \) nanodots and nanowells, however, only positive MR is observed in the whole temperature range from 2 to 300 K.
as shown in Figure 6(d). A periodic nanomesh structure exhibits a nanomesh width of 60 nm and a hole diameter of 160 nm; a magnified SEM image is also shown in the inset. To further characterize the microstructure of the formed nanomesh, cross-sectional TEM was employed, and the results are shown in Figure 6(e)–(h). The focused ion beam was employed to cut the sample along the diameter of the hole. Before that, a Cr/Au layer was deposited to protect the sample from damage of the ion beam. Figure 6(e) is a low-resolution cross-sectional TEM image of the Mn$_x$Ge$_{1-x}$ nanomesh, which clearly shows that the nanomesh is grown on the Ge substrate as defined by the SiO$_2$ pattern. The zoom-in image shows that the Mn$_x$Ge$_{1-x}$ nanomesh has a height of 25 nm and a width of 60 nm, consistent with the SEM result. HRTEM
image clearly demonstrates the coherent growth of the Mn$_x$Ge$_{1-x}$ nanomesh on Ge substrate, as shown in Figure 6(f). It does not reveal any observable precipitate. The Fourier transform image as shown in Figure 6(h) gives only one set of periodic patterns, indicating a perfect epitaxial growth. This image can be indexed to the [011] zone axis of the Ge diamond lattice, and the epitaxial growth direction is along [111].

SQUID measurement was performed in the following to well understand the magnetic property of the Mn$_x$Ge$_{1-x}$ nanomesh. Figure 7(a) shows the temperature-dependent hysteresis loops of the sample, when an external field is applied parallel to the sample surface. The S-shaped hysteresis loops indicate the ferromagnetism above 350 K. Figure 7(b) is the magnified hysteresis loop obtained at 10 K, clearly showing a small coercivity of 100 Oe with a saturation magnetization of 0.87 $\mu_B$ per Mn. At 350 K, the magnified hysteresis loop demonstrates that the coercivity still remains a value of 40 Oe, as shown in Figure 7(c). Furthermore, Arrott plots [55] were also used to evaluate the $T_c$ as shown in Figure 7(d). We observe that even at 350 K, the intercept, namely, reciprocal of the susceptibility, does not vanish, indicating that the $T_c$ has not been reached yet. The extrapolated dashed line indicates that the $T_c$ is beyond 350 K, which agrees well with the hysteresis loops. Figure 7(e) shows the temperature-dependent $M_s$ ranging from 10 to 400 K, and it clearly shows a weak temperature dependence and a large magnetization remaining at 400 K. All of the data support that the $T_c$ is over 400 K. The temperature-dependent coercivity is shown in Figure 7(f), demonstrating a coercivity decrease from 100 to 35 Oe in the temperature range from 10 to 400 K. The small coercivity indicates the soft ferromagnetism of our sample, which may come from the Mn-dilute nature.

Figure 7. (a) Magnetic hysteresis loops of the Mn$_x$Ge$_{1-x}$ nanomeshes measured at different temperatures from 10 to 350 K. (b)-(c) The magnified hysteresis loop obtained at 10 and 350 K, respectively. (d) Arrott’s plots showing that the $T_c$ is above 350 K. (e)-(f) The temperature-dependent saturation moment and coercivity, respectively.
In this unique nanostructure, it is of great interest to investigate its MR property. The sample is fabricated into a micrometer-size Hall bar structure, and the measurement is performed in PPMS, as shown in Figure 8. Figure 8(a) shows the temperature-dependent resistivity of the Mn Ge$_{1-x}$ nanomesh under the magnetic field of 0 T (blue square) and 4 T (red circle), respectively, demonstrating a huge difference. A clear metal-to-insulator transition without applying magnetic field (0 T) can be observed with a low-temperature ($T < 30$ K) activation region and a high-temperature ($T > 30$ K) saturation region. From the Arrhenius relation [56], the activation energy of the nanomesh is estimated to be about 11 meV, which is lower than the substitutional Mn acceptor energy level (160 meV). The underlying mechanism comes from the high-doping level and the presence of exchange interaction, inducing the boarding and possible splitting of the impurity band. Above 30 K, the R-T curve could be well fitted by a power-law relation ($T^\alpha$) with $\alpha \approx 1.6$, close to the value 1.5 predicted for hole scattering by phonons in Ge. The fitting was plotted in red over the blue data in the R-T curve. An intriguing phenomenon is the observation of a giant positive MR in the nanomesh with an out-of-plane magnetic field, as shown in Figure 8(b)–(d). At a magnetic field of 4 T,

![Figure 8](image-url)

Figure 8. (a) Temperature-dependent resistivity of the Mn Ge$_{1-x}$ nanomeshes measured without an applied magnetic field (square symbol) and with a magnetic field of 4 T (circle symbol), clearly showing a metal-to-insulator transition. The solid line is the fitting curve. (b) The schematic illustration of scattering mechanism. (c)–(d) Temperature-dependent MR measured at low-temperature and high-temperature regions, respectively.
the MR as high as 2000% at 10 K with the maximum of 8000% at 30 K is observed and still remains 75% at 300 K. Analogously, the giant MR could not be simply attributed to the orbital MR effect, which only contributes a small value. Instead, the geometric-enhanced MR is very plausible to explain the result. To understand this phenomenon, the nanomesh structure could be considered as a highly conductive percolation network with periodic nanoholes. Without applying the magnetic field, the current flows through the Mn\textsubscript{\textit{x}}Ge\textsubscript{\textit{1-x}} nanomesh with the current directions parallel to the local electric field. As the magnetic field is applied, the current is deflected due to the Lorentz force; the current and local electric fields are no longer collinear. The angle between them is determined by the Hall angle \( \theta = \arctan \left( \mu_{\text{H}} \right) \), where the \( \mu_{\text{H}} \) is the Hall mobility. For a sufficiently high magnetic field, the current is obviously deflected from the highly conductive nanomesh to the insulated nanoholes, resulting in a high resistance. The transition from the extremely low resistance at zero magnetic field to the extremely high resistance at a large magnetic field gives rise to the giant MR, as illustrated in Figure 8(b). Thus, it may be concluded that the lower the initial resistance of the nanomesh is, the larger the MR became at a given magnetic field. It can be verified from the deviation of the R-T curves of 4 T and 0 T, as already shown in Figure 8(a).

The Mn\textsubscript{\textit{x}}Ge\textsubscript{\textit{1-x}} nanomesh is a type of diluted magnetic semiconductor [53, 57] that could provide the ability of electric-field control of ferromagnetism. Therefore, the electric-field controlled MR could be possibly realized to develop new MR sensors with more functionalities. To demonstrate the spin-related MR effect, it is in need of weakening the geometric-enhanced MR effect. One effective approach is to increase the initial resistance of the nanomesh while reducing the carrier mobility. To this end, more Mn-doped Mn\textsubscript{\textit{x}}Ge\textsubscript{\textit{1-x}} nanomesh was grown, and the transport property is shown in Figure 9. Figure 9(a) shows the R-T curve of the nanomesh, in which a metal-to-insulator transition is observed; however, the resistivity was found to be more than one order of magnitude larger than the above sample. The increased resistivity may come from the increased scattering center [58]. Figure 9(b) and (c) shows the temperature-dependent MR curves of the sample. Intriguingly, the geometric-enhanced MR becomes less pronounced, which may be due to the dramatically increased resistivity and the decreased Hall angle from the lower mobility. Instead, a negative MR for temperature below 40 K and a positive MR above 160 K are observed. In the intermediate temperature region (40–160 K), the MR contains two contributions: a positive MR appears at a low magnetic field and a negative slope at high field. Such negative-to-positive MR transition could be attributed to two competitive effects: the spin-dependent scattering by magnetic polarons gave rise to a negative MR [59, 60], and their spatial fluctuations led to the positive MR [59, 60]. As a magnetic field is applied, the carrier mobility increases due to the suppression of the spin-dependent scattering by the magnetic polarons, giving rise to the negative MR, which is proportional to the susceptibility \( \chi(H) \) of the sample. However, the spin-dependent scattering effect by the magnetic polarons decreases with increasing temperature, which makes the positive MR from the spatial fluctuations of magnetic polarons gradually to show up. Due to the strong \textit{p-d} exchange coupling in Mn\textsubscript{\textit{x}}Ge\textsubscript{\textit{1-x}}, the magnetic polarons will cause a strongly localized valence band splitting into two spin subbands \( \epsilon = \pm 1/2SJ\mathbf{M}(\mathbf{r}) \), where J is the
exchange coupling energy, $S$ is the spin of electron, and $M(r)$ is the local magnetic moment of the magnetic polaron. This could form a complicated landscape for the valence band with hills and valleys, serving as hole traps. With increasing magnetic field, the hole traps become deeper, the number of itinerant holes decreases, and thus the MR increases. This positive MR is proportional to the square of the magnetization ($M^2(H)$) [59], which can be reflected from the steep slope of the positive MR. As the temperature further increases, the contribution from the spin-dependent scattering becomes weaker, and finally only positive MR dominates the transport.

Furthermore, electric-field control of MR was measured under different gate biases. For that, a 25-nm-thick $\text{Al}_2\text{O}_3$ layer was deposited by atomic layer deposition (ALD) on the nanomesh surface as the gate dielectric, followed by the e-beam evaporation of Cr/Au as the gate metal contact. Due to the unique nanomesh structure, the almost-wrap-around gate can be realized to provide a 3D electric-field control of the conduction channel, thus giving a highly efficient and robust carrier modulation. Figure 9(d)–(f) shows the gate bias-dependent MR of the Mn$_x$Ge$_{1-x}$ nanomesh sample measured at 40, 60, and 100 K, respectively. When the gate bias changes from $-8$ to $8$ V, a clear negative-to-positive MR transition is observed at 40 K. As described above, this phenomenon should also stem from the competitive effect between the spin-dependent scattering-induced negative MR and the spatial fluctuation-induced positive MR. As already reported [53], the hole-mediated ferromagnetism in Mn-doped Ge enables the electric-field control of magnetic phase transition from a strong ferromagnetism to a soft ferromagnetism, when changing the gate bias from negative to positive. Therefore, as a negative

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**Figure 9.** (a) R-T curve of the Mn$_x$Ge$_{1-x}$ nanomeshes with more Mn dopants. (b)–(c) Temperature-dependent MR measured at low-temperature (<80 K) and high-temperature (>100 K) regions, respectively, showing a MR transition from a negative to positive value. (d) Electric-field controlled MR at 40 K, clearly showing a transition from negative to positive when the gate was biased from negative to positive. (e)–(f) Electric-field controlled MR transition at 60 and 100 K, respectively.
gate bias is applied on our sample, the enhanced ferromagnetism with larger susceptibility ($\chi(H)$) in the $\text{Mn}_x\text{Ge}_{1-x}$ nanomesh could provide a strong spin-dependent scattering, consequently giving rise to a negative MR. When the gate bias is swept to positive value, the weakened ferromagnetism gives rise to a weaker spin-dependent scattering. From another point of view, as the gate bias goes to the positive range, the decreased density of magnetic polarons due to reduced carrier density probably transforms the system from an overlap-together state to a disconnecting state, which thus increases the polaron fluctuation, and hence the positive MR dominates. In addition, gate-dependent MR curves at 60 K and 100 K are shown in Figure 9(e) and (f), respectively. At 60 K, the MR transition from the negative to positive value can still be clearly observed when tuning the gate bias. However, the control effect is not as strong as that of 40 K in the negative bias range. This effect can be explained by the fact that even at 0 V, the hole density at 60 K is already high enough to align the magnetic moments of most Mn ions along one direction. Further increasing the negative bias does not significantly enhance the ferromagnetism. At 100 K, it shows a similar effect, i.e., an even weaker control effect in the negative bias range. This extraordinary property may offer a great advantage for designing new MR sensors with voltage-controlled, low-power, high-sensitivity, and non-volatile functionalities.

4. The potential application of $\text{Mn}_x\text{Ge}_{1-x}$ in MR sensors

The development and utilization of MR sensors have tremendously impacted human beings’ life, which refers to a broad range of aspects, including magnetic HDD [4, 23], electric compass [3], biomedical sensors [8, 9], car traffic monitoring [7], and antitheft system [5], among others. The future development in MR sensors should rely on these two perspectives: applications and physics. The discovery of new physics will lead to a new sensor technology toward much smaller size, lower power consumption, lower cost, and higher performance, thus broadening the applications. In turn, the economic benefit from the application will promote further developing high-performance sensors with new physics. In light of that, $\text{Mn}_x\text{Ge}_{1-x}$-based MR sensors with high compatibility with silicon technology should have a high potential to satisfy this demand. Here, we will give a discussion for its potential application in different functionalized MR sensors.

4.1. High-density information storage

The density of information storage in HDD has significantly increased in the past two decades, which promotes the coming of cloud computing age. The advent of MR read head technology transitioning from the AMR [19] read head to the GMR [34] and TMR [37] read head is the major drive in remarkably increasing storage density of HDD. The GMR and TMR sensors in read head usually comprise two magnetic metal layers separated by a thin nonmagnetic space layer. The basic operation of the magnetoresistance head is to convert the magnetic field that exists above the data bits recorded on the disk to a change in resistance that can be read out. Therefore, the MR sensitivity is extremely important and should be high enough to
distinguish two states (0 and 1); meanwhile, the material for MR sensor could be easily scaled down and integrated with other electric components. Compared to the metal component in current MR sensor, Mn$_x$Ge$_{1-x}$ could have high compatibility with the mature Si technology [54] and hence significantly reduces the manufacturing cost. By utilizing the well-designed giant MR in Mn$_x$Ge$_{1-x}$ system, it will be of much interest to develop Mn$_x$Ge$_{1-x}$-based MR sensor for high-density magnetic record technology.

4.2. Biomedical sensor

The medical industry has been always striving for noninvasive methods for diagnosing human illness. Due to the electric nature of brain and neuron activity, magnetic sensing is an effective way to detect the brain illness. Meanwhile, it can also be used for unraveling the mystery of the brain how to functionalize, which is of great help for building future brain computer [62] with extremely low power consumption and high performance. Besides, other parts in the body without electric activity can also be detected by magnetic sensor. One effective way is to decorate the cell with nonharmful magnetic particles as the markers. For instance, Wang et al. reported a CMOS magnetic sensor to monitor the pulsatile movements of cardiac progenitor cells tagged with magnetic particles [8]. In addition, magnet tracker can also be used to determine the position of the medical tool inside the body to observe biomechanical motions [3]. In fact, the magnetic signal in biological system normally is very small and usually needs big and heavy equipment for detecting. Therefore, highly sensitive MR sensor is necessary toward miniaturizing the equipment. Mn$_x$Ge$_{1-x}$ appears to be an ideal candidate for fabricating biomedical MR sensor with high sensitivity, high compatibility with CMOS technology, and no poison to human body.

5. Conclusion

MR sensors have dramatically changed the life of human beings in a wide range of applications, including automotive sensor, traffic monitor, mobile phone, HDD, and biomedical sensors, among others. The MR sensors are being developed toward much lower cost, lower power consumption, higher compatibility with CMOS technology, and higher sensitivity. Addressing such demand calls for new material candidate with new physics, improved sensitivity, and easy manufacturing. In this context, we give a review in the recent progress in Mn$_x$Ge$_{1-x}$ system, including material growth and magnetic and magnetotransport properties. The Mn$_x$Ge$_{1-x}$ evolved from thin-film superlattice to patterned nanostructures, and their MR behavior could be well engineered and transformed between the negative and positive. Furthermore, geometric-enhanced giant MR as high as 8000% at 30 K at 4 T is demonstrated. More intriguingly, the electric-field controlled MR emerges, which not only demonstrates great physical meaning but also significantly enhances the functionality of MR sensors with more tuning dimensions. The Mn$_x$Ge$_{1-x}$ system with the advantages of well-controlled MR, and high compatibility with Si technology may set a stage for designing a new breed of MR sensors applicable in magnetic read head and biomedical sensor with much higher performance.
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