Room-Temperature Electric-Field Controlled Ferromagnetism in Mn$_{0.05}$Ge$_{0.95}$ Quantum Dots

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ABSTRACT Room-temperature control of ferromagnetism by electric fields in magnetic semiconductors has been actively pursued as one of important approaches to realize practical spintronic and nonvolatile logic devices. While Mn-doped III–V semiconductors were considered as potential candidates for achieving this controllability, the search for an ideal material with high Curie temperature ($T_C > 300$ K) and controllable ferromagnetism at room temperature has continued for nearly a decade. Recently, Mn$_{0.05}$Ge$_{0.95}$ quantum dots (QDs) were demonstrated to have a $T_C$ above 300 K. However, the field control of ferromagnetism based on hole-mediated effect remained at low temperatures and thus prohibited spintronic devices operable at ambient environment. Here, we report a major breakthrough toward such room-temperature spin FETs and nonvolatile spin logic devices.

KEYWORDS: diluted magnetic semiconductors · spintronics · nonvolatile · Mn$_{0.05}$Ge$_{0.95}$ · quantum dots · electric-field controlled ferromagnetism · magnetic polarons

Electric field control of ferromagnetism has a potential to realize spin field-effect transistors (spin FETs) and nonvolatile spin logic devices via carrier-mediated effect. With the manipulation of carrier spins, a new generation of nonvolatile (green) computing systems could be eventually developed for many low-power-dissipation applications in all fields, including sensor network, health monitoring, information, sustainable wireless system, etc. Since Datta and Das first introduced the concept of spin FETs in 1990, enormous efforts were dedicated to creating a device wherein the carrier transport is modulated by electrostatic control of carrier spins. One of the major challenges, however, is to find an ideal material with room-temperature controllable spin states. In recent years, emerging dilute magnetic semiconductors (DMSs) became one of the promising candidates since they could possibly offer high $T_C$ in excess of 300 K. The demonstration of the carrier-mediated ferromagnetism involving correlated electron/hole systems leads to a paraferro-magnetism phase transition. In principle, the collective alignment of spin states in these DMSs can be manipulated by the modulation of carrier concentrations through gate biasing in a FET structure. For this kind of spin FETs, the “source” and “drain” may be completed through “nanomagnets”, which are in turn controlled by the gate; and no carrier transport is needed. Clearly, one may also involve the control of source–drain conductance by gate-voltage-induced precession of injected spins (from the source). Since the early 2000s, significant progress on electric-field controlled ferromagnetism was achieved in which the ferromagnetism of a (In, Mn)As channel layer could be effectively turned on and off via electric fields in a gated FET. Such extraordinary field-modulated ferromagnetism immediately rendered the development of future spintronic devices. However, the manipulation of ferromagnetism was limited because of low $T_C$ of the Mn-doped III–V materials. Therefore, a search for new DMS materials with $T_C > 300$ K and carrier-mediated ferromagnetism becomes a current global challenge.

Here we report a major breakthrough toward such room-temperature spin FETs and spin logic devices: a successful demonstration of electric-field controlled ferromagnetism up to 300 K. In our recent study, high $T_C$ Mn-doped Ge QDs were achieved. Their magnetic field-dependent magnetizations indicated a strong ferromagnetism above...
that of the Al$_2$O$_3$, giving rise to much improved age current of the MOS capacitors in comparison with MBE-grown MgO layer significantly reduces the leak-

by molecular beam epitaxy (MBE). We noted that the using high-quality MgO as the gate dielectric grown 

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netization polarity was reversed. The carrier-mediated fer-

behavior of dipole directions when the MFM tip magne-

RESULTS AND DISCUSSION 

which can be operable at room temperature. 

nologically possible to fabricate practical spin devices, 

electric-field controllability on the ferromagnetism. The 

netic domain in the Mn$_{0.05}$Ge$_{0.95}$ QDs and a switching 

magnetism; that is, the holes are sufficient to align the 

spins of a majority of the activated Mn ions in each in-

stance, however, the hysteresis loop does not show a 

noticeable change (Figure 2a). This can be explained by 

the fact that, even at zero volt, the QD device is al-

ready accumulated with enough holes to induce ferro-

magnetism; that is, the holes are sufficient to align the 

spins of a majority of the activated Mn ions in each indi-

idual dot. Further increasing negative bias does not 

change much on the hole concentration. On the con-

trary, with a positive bias, a large amount of holes are 

depleted into the p-type Si substrate, so that hole-

mediated effect is notably reduced. The saturation mo-

ment per Mn ion decreases about 2.5 times as the gate 

bias increases from 0 to +40 V (Figure 2b). Figure 2c summarizes the change of remnant moments as a func-

tion of gate voltage. The inset in Figure 2c displays an 

enlarged picture to clearly show the variation of the 

remnant moments with respect to the gate bias. When 

the temperature was increased to 300 K (Figure 2g–i), 

the saturation and the remnant moments were modu-

lated by $\sim$23% and $\sim$50% at +40 V, respectively, 

which clearly showed the room-temperature control-

able ferromagnetism, although it became less pro-

nounced compared to those at 100 and 200 K (Figures 2cf). 

Device simulations using the MEDICI package$^{17}$ 

were performed to understand the distributions of 

holes in a QD. The simulated device structure was  

400 K ($T_c > 400$ K). Magnetic force microscopy (MFM) 

measurements revealed a formation of a single mag-

netic domain in the Mn$_{0.05}$Ge$_{0.95}$ QDs and a switching 

behavior of dipole directions when the MFM tip magne-

tization polarity was reversed. The carrier-mediated fer-

romagnetism was clearly observed by depleting 

holes out of the QD channel layer. In this study, we re-

port the field-controlled ferromagnetism up to 300 K by 

using high-quality MgO as the gate dielectric grown 

by molecular beam epitaxy (MBE). We noted that the 

MBE-grown MgO layer significantly reduces the leakage 

current of the MOS capacitors in comparison with 

that of the Al$_2$O$_3$,$^{16}$ giving rise to much improved 

electric-field controllability on the ferromagnetism. The 

fact that the Mn$_{0.05}$Ge$_{0.95}$ QDs possess high Curie 

temperature$^{16}$ together with the room-temperature 

electric-field controllable ferromagnetism makes it tech-

nologically possible to fabricate practical spin devices, 

which can be operable at room temperature.

Figure 1a shows a cross-section transmission electron microscopy (TEM) image of the MOS capacitor, 

consisting of electrodes (Au), MgO, Mn$_{0.05}$Ge$_{0.95}$ QDs, and p-type Si substrate. The Mn$_{0.05}$Ge$_{0.95}$ QDs have a 

dome shape with a base diameter of about 30 nm and a height of about 8 nm. The left-bottom inset is a high 

resolution TEM reveals a polycrystalline MgO layer. (b) A schematic drawing of a MOS capacitor, consisting of 
itelectrodes (Au), MgO, Mn$_{0.05}$Ge$_{0.95}$ QDs, and p-type Si substrate. Note that there is a thin Mn$_{0.05}$Ge$_{0.95}$ wetting layer on top of Si. The wetting layer has a typical thickness of several angstroms. During SQUID measurements, the top electrode was biased 

while the bottom one was grounded.

Figure 1. Structure of Mn$_{0.05}$Ge$_{0.95}$ MOS capacitor via TEM. (a) Cross-section high resolution TEM images of the Mn$_{0.05}$Ge$_{0.95}$ QDs grown on a p-Si substrate. Insets show an enlarged TEM picture and a diffraction pattern for an individual Mn$_{0.05}$Ge$_{0.95}$ QD, in which single crystallinity can be confirmed. The thickness of the gate dielectric (MgO) was estimated to be about 20 nm. The high resolution TEM reveals a polycrystalline MgO layer. (b) A schematic drawing of a MOS capacitor, consisting of electrodes (Au), MgO, Mn$_{0.05}$Ge$_{0.95}$ QDs, and p-type Si substrate. Note that there is a thin Mn$_{0.05}$Ge$_{0.95}$ wetting layer on top of Si. The wetting layer has a typical thickness of several angstroms. During SQUID measurements, the top electrode was biased while the bottom one was grounded.
designed to fit the experimental conditions. The QDs were represented by a rectangle with a width of 50 nm, a height of 6 nm, and a spacing of 150 nm. Although Mn can have two acceptor levels in Ge, during the simulation, only one shallower level ($E_a/\hbar=0.16$ eV) was considered because another deeper acceptor level ($E_a/\hbar=0.37$ eV) could barely contribute to the hole concentration. We also assumed that 60% of Mn atoms were activated in the modeling (according to the experimental data). Since the simulations did not consider the formation of the impurity bands and the compensation effects that occur in the real experiments, the calculations may not give accurate hole concentrations. However, the fundamental physics of the field controlled ferromagnetism would not change since the capacitance–voltage measurements clearly revealed the carrier redistribution under the bias. In the simulation, several physical models were adopted for accurate calculations, including the freeze-out effect at low temperature, the Fermi–Dirac model for carrier occupations, and quantum mechanical corrections by invoking the Philip’s band gap widening effect.

Figure 3 panels a–c show the calculated hole concentrations as a function of the gate voltage at 100, 200, and 300 K, respectively. At zero bias, due to the quantum confinement between the Mn$_{0.05}$Ge$_{0.95}$ QDs and $p$-type Si, the hole concentration reaches $1.22 \times 10^{18}$ and $2.08 \times 10^{18}$ cm$^{-3}$ for the top and center of the Mn$_{0.05}$Ge$_{0.95}$ QD, respectively (Figure 3a, 100 K). By applying a negative bias, holes start to accumulate in the Mn$_{0.05}$Ge$_{0.95}$ QD, leading to an increased hole concentration. For instance, at $-10$ V, the hole concentration increases eight times ($1.65 \times 10^{19}$ cm$^{-3}$) in the center of the dot, as calculated from Figure 3a. However, by applying a positive voltage, the holes are depleted into the $p$-type Si substrate. The hole concentration changes dramatically on the top surface of the Mn$_{0.05}$Ge$_{0.95}$ QDs ($\sim 10^{10}$ cm$^{-3}$), while, at the center region, the concentration of $10^{14}$–$10^{15}$ cm$^{-3}$ remains in the voltage range of +2 to +10 V. Clearly, the top surface sensitively responds to the gate bias. Figure 3e illustrates the
redistribution of holes in the QD with gate biases at 100 K. It is noted that the hole concentration in the Mn$_{0.05}$Ge$_{0.95}$ QD decreases as the bias increases from $-10$ to $+20$ V; this result further confirms the hole accumulation, depletion, and inversion processes. Similarly, we have performed the simulations at 200 and 300 K in Figure 3 panels b and c, respectively. At $+10$ V, the top of the QD exhibits a high concentration of $10^{16}$ cm$^{-3}$ at 300 K in comparison with that of 100 K ($10^{10}$ cm$^{-3}$), possibly resulting from the greater activation of the Mn impurities and thus a higher doping level of Mn in the QD. On the basis of these simulation results, we can conclude that the depletion process at high temperatures is not as strong as those at low temperatures. This explains the reduced controllability of ferromagnetism when the temperature approaches 300 K. Since the hole concentration varies with position inside the Mn$_{0.05}$Ge$_{0.95}$ QD, it is necessary to integrate the entire area of the QD and obtain a sheet density as an “effective” hole density, as shown in Figure 3d. In the accumulation mode (under zero and negative gate biases), the hole concentration does not have a noticeable temperature dependence from 10 to 300 K. However, in the depletion mode (positive biases), the holes were significantly depleted out of the Mn$_{0.05}$Ge$_{0.95}$ QD when the temperature decreases to below 100 K, primarily due to the freeze-out effect of
Note that the electric-field controlled ferromagnetism is significantly improved compared with our earlier work, which may be due to the optimized device structure and good quality MgO layer. The controllability could be dramatically affected by both the gate leakage and the activation process of Mn at different measurement temperatures.

Energy band diagrams of MgO/Mn$_{0.05}$Ge$_{0.95}$ QD/Si and MgO/Mn$_{0.05}$Ge$_{0.95}$ wetting layer/Si are schematically shown in Figure 4 panels a and c, respectively. By solving the Schrödinger equation for a rectangular quantum well with finite barriers, we estimated that the Mn$_{0.05}$Ge$_{0.95}$ QDs have five quantized energy levels with $E_1 = 21$, $E_2 = 81$, $E_3 = 167$, $E_4 = 258$, and $E_5 = 331$ meV, as shown in Figure 4a. Among these levels, $E_1$ represents the ground state, that is, the lowest energy level. In contrast, the wetting layer exhibits a higher ground state of $E_1^*$ with a value of 142 meV. Since the energy of the ground state is much lower in the QDs, the majority of the holes would prefer to transfer into the dots, giving rise to a higher density of holes compared with that of the wetting layer. Figure 4b shows a schematic drawing of the QDs and the wetting layer in the real space. The energy band diagrams are also provided at the bottom of Figure 4b to visualize the transport of the holes. Note that due to the relatively large diameter of the Mn$_{0.05}$Ge$_{0.95}$ QDs (>30 nm), the quantum confinement in the horizontal direction is not significant compared with that in the vertical direction (perpendicular to the Si surface, or along the height of the QDs).

To explore the origin of the ferromagnetism in this material system, we plotted the measured remnant magnetizations as a function of temperature, $M(T)$ (Figure 4d), at zero bias, as the nature of $M(T)$ has been found crucial in understanding the underlying mechanism of DMS ferromagnetism. The concave upward shape of $M(T)$ shown in Figure 4d is consistent with earlier reports of MnGe DMS, which agrees well qualitatively with the percolation type of ferromagnetic transition. We also compare the dependence of calculated $M(T)$ (Figure 4e) using the percolation theory approach based on the magnetic polaron model proposed by Kaminski and Das Sarma, where $M(0)$ is the remnant moment at zero temperature; $\beta$ is the “infinite” cluster volume of overlapping spheres; $a_0$ is the calculated Bohr radius; $n_h$ is the hole concentration (4.7 $\times$ $10^{18}$ cm$^{-3}$, at zero bias, Figure 3d). It must be emphasized that given the minimal nature of the model one can only hope for a qualitative agreement and it is incorrect to try getting a quantitative agreement between theory and experiment by tuning the parameters of the above model.

On the basis of above agreement on the shape of $M(T)$, we can construct a physical model based on the concept of bound magnetic polarons (BMPs) to explain

$$M(T)/M(0) = \beta[(0.86 + (a_0^3 n_h)^{1/3} \ln(T_c/T))]$$

where $M(0)$ is the remnant moment at zero temperature; $\beta$ is the “infinite” cluster volume of overlapping spheres; $a_0$ is the calculated Bohr radius; $n_h$ is the hole concentration (4.7 $\times$ $10^{18}$ cm$^{-3}$, at zero bias, Figure 3d). It must be emphasized that given the minimal nature of the model one can only hope for a qualitative agreement and it is incorrect to try getting a quantitative agreement between theory and experiment by tuning the parameters of the above model.

On the basis of above agreement on the shape of $M(T)$, we can construct a physical model based on the concept of bound magnetic polarons (BMPs) to explain the Mn acceptors.
the observed field controlled ferromagnetism.\textsuperscript{25} BMPs are regions of large magnetization resulting from all parallel polarized Mn spins. They are formed as a consequence of exchange interactions between the spins of localized carriers and magnetic ions, as illustrated in Figure 4f. Since the Mn doping concentration in our system is much larger than the hole concentration due in part to the compensation by Mn interstitials, BMPs could be developed with localized holes and a large number of Mn impurities around the hole localization center.\textsuperscript{23} One can approximate several Mn ions to a sphere within a radius of $r_n$ and assume that the Mn impurities contained inside this sphere interact with the hole and align their spins antiparallel to the hole spin, which results in the formation of a BMP.\textsuperscript{26} The radius, $r_n$, grows with decreasing temperature given by $r_n = (\alpha/2) \ln(U/n k T)$,\textsuperscript{27} where $J_0$ characterizes the strength of the exchange between carriers and magnetic ion. It was also shown that the nearby BMPs align ferromagnetically via effective coupling mediated by Mn spins lying in between the BMPs.\textsuperscript{27,28} As a result, BMPs start to overlap and form percolated clusters aligned ferromagnetically as temperature decreases (Figure 4f).\textsuperscript{23,26,28–31} From both theoretical calculations and experimental data, the MP formation was also found to be more favorable when the system dimension was reduced, particularly in the QDs case.\textsuperscript{31–33} This phenomenon was explained by the fact that the quantum confinement could localize carriers in the proximity of magnetic ions and further strengthen the exchange interactions.\textsuperscript{31–33} More interestingly, the binding energy of the MPs was remarkably enhanced when the system dimension is shrunk, resulting in a higher $T_c$ in contrast to those of bulk materials.\textsuperscript{31,34}

The above physical picture can be applied to explain the electric-field control of ferromagnetism in the Mn$_{0.05}$Ge$_{0.95}$ DMS system. The gate-controlled hole carriers in the Mn$_{0.05}$Ge$_{0.95}$ QDs may influence the formation of MPs and their interactions. If the holes density is sufficient, they can effectively mediate interactions between nearly all MPs in a dot.\textsuperscript{35} When the hole density decreases in the depletion process, however, the amount of MPs can be reduced; and meanwhile, the overlapped MPs may start to uncouple and even disappear at low carrier densities, as illustrated in the outer MPs in Figure 4f, thus reducing the net magnetization moments. When the temperature increases toward room temperature, the MPs are subject to thermal fluctuation and become less stable compared to those at lower temperatures.\textsuperscript{31,36} This is in agreement with the fact that the saturation moment decreases with increasing the temperature (zero bias). As mentioned earlier, the hole depletion process became less pronounced at 300 K when compared with that of low temperatures, for example, with $+10$ V, the holes on top of the QD do not change as much as those at 100 and 200 K (Figures 3a–c). This indicates that the QDs contain a large density of holes and possibly a high density of MPs at high temperatures because of more activation of the Mn acceptors, leading to a weak dependence of magnetization on the bias field. This analysis qualitatively explains the weak controllability of ferromagnetism at elevated temperatures. However, a detailed and quantitative theoretical treatise is still not available at this stage.

**CONCLUSIONS**

We demonstrated the field controlled ferromagnetism in the Mn$_{0.03}$Ge$_{0.97}$ QDs up to 300 K. The underlying physics lies in the effective hole-mediated ferromagnetism and improved material quality in quantum confined Mn$_{0.03}$Ge$_{0.97}$ dots. The variation of hole concentrations may directly affect the formation of the BMPs and their interactions, in turn controlling the magnetic moments of the Mn$_{0.03}$Ge$_{0.97}$ QDs. The obtained results shed light on the development of electric-field controlled spin logics and open up a new paradigm of nonvolatile systems for applications that may eventually resolve critical challenges of power dissipation and device miniaturization of today’s microelectronics industry.

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**MATERIALS AND EXPERIMENTAL METHODS**

The Mn$_{0.05}$Ge$_{0.95}$ QDs were grown on p-type Si substrates by a Perkin-Elmer solid-source MBE system. High-purity Ge (99.99999%) and Mn (99.99%) sources were evaporated by conventional high-temperature effusion cells. Prior to the growth, Si substrates were cleaned by a standard Radio Corporation of America method and thermal cleaning in the MBE chamber. The self-assembled Mn$_{0.05}$Ge$_{0.95}$ DMS quantum dots were subsequently deposited at 450 °C with a Ge growth rate of 0.2 Å/s and an adjustable Mn flux as the dopant source. The nominal thickness was designed to be 1.2 nm. The structural characteristics of the Mn$_{0.05}$Ge$_{0.95}$ QDs were investigated by TEM (a Philips F20 and a FEI Tecnai F30). The Mn composition and distribution were analyzed with EDS and EELS. For magnetic properties, a SQUID magnetometer from Quantum Design was utilized to measure field- and temperature-dependent magnetizations. As for device fabrications, MOS capacitors were made by depositing 20 nm-thick MgO on top of the Mn$_{0.05}$Ge$_{0.95}$ QDs layer via MBE (base pressure $1 \times 10^{-10}$ Torr). The deposition of MgO layer is made by electron beam evaporation of a single crystal MgO source with a rate of $\sim 1.0$ Å/min measured by a quartz deposition monitor. Then the front and back sides were metalized with 200 nm-thick Au. After that, the MOS capacitors were loaded into the SQUID magnetometer to perform bias-dependent magnetization measurements at different temperatures.

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**Supporting Information Available:** More TEM images; Field controlled ferromagnetism at various temperatures; electrical properties of MOS devices; device simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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