Magnetic properties of nanoclusters formed by implantation of Fe into Ge using a metal-vapor vacuum arc ion source

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The magnetic properties of Fe ions implanted into a germanium crystal by metal-vapor vacuum arc ion source were investigated using a Quantum Design SQUID magnetometer. The presence of Fe nanoclusters in Ge was verified by magnetization measurements. A Langevin fit was used to obtain the size distribution of the clusters. The results demonstrated that the clusters are magnetic. The magnetic behavior of the clusters was characterized by zero-field-cooled and field-cooled measurements for temperatures 4.2 to 300 K. The implanted layer with magnetic clusters shows negative magnetoresistance with a positive magnetoresistance background due to the Ge substrate for parallel magnetic-field geometry at temperatures 180 to 300 K. The negative magnetoresistance is found to become dominant with decrease of temperature. The negative magnetoresistance is attributed to the existence of magnetic clusters in the implanted layer.

I. INTRODUCTION

Magnetic nanoclusters in metals, semiconductors, and insulators have long been of interest because of their applications in magnetoresistive random access memory, magnetoresistive read heads and magnetic-field sensors. The magnetic properties of the clusters are completely different from their bulk counterparts. Also, the matrix where the clusters are embedded contributes significantly to change the magnetic properties of the clusters. Therefore, unusual magnetic properties can be found when the proper choice of magnetic material, nonmagnetic matrix, and preparation technique are made. Recently, considerable interest has been directed toward nanomagnetic materials, because of the discovery of giant magnetoresistance (GMR) in magnetic multilayers as well as in a variety of magnetic granular systems, such as Fe, Co, Ni and their alloys in Cu, Ag, and Au matrices. Multilayers of iron with semiconductor spacers have been shown to exhibit unusual magnetic properties. This system has received much attention since the discovery of antiferromagnetism in Fe/Si/Fe trilayers by Toscano et al. This careful evaluation of interdiffusion is essential for quantitative discussion of the interlayer coupling behavior in ferromagnet/semiconductor systems. Although antiferromagnetic coupling in Fe/Si superlattices is now well established experimentally, the mechanism for the coupling is not fully understood because of the difficulties in characterization of very complex diffused spacer structures. Therefore, if one can obtain more information on systems similar to Fe/Si, such as Fe/Ge, or Co/Ge or Co/Si, it will be very helpful for understanding the origin of the coupling behavior. In this aspect, some reports have been published for Fe/Ge systems.

The study of the Fe-Ge system is not only limited to multilayers but also extended to Fe-Ge alloys. For example, amorphous metal-germanium films have been the subject of extensive study over the past decade. Amorphous Fe-Ge alloys undergo two important transitions as the composition is varied. The metallic properties start at 15–25 at. % Fe, while the ferromagnetic properties start at about 40 at. % Fe. There has been a lot of effort to understand the metal-insulator transition as well as the magnetic transition in the amorphous Fe-Ge system. The magnetic properties of nanophase materials can be tuned from soft to hard, depending on the magnetic coupling between their small crystallites. The magnetic properties of nanocrystalline Fe-Ge alloys and the change in magnetic properties upon annealing, and their correlation to changes in the structure of the materials have been studied in detail by Hamdeh et al. Most of the Fe-Ge amorphous alloys were prepared by the sputter deposition method. In this work, we report the synthesis of Fe clusters in Ge (110) by ion implantation. We report the results of magnetization and magnetoresistance measurements.

II. EXPERIMENTAL PROCEDURE

Ge(110) (p-type, resistivity: 1–10 ohm cm) surfaces were implanted with Fe ions using metal-vapor vacuum arc (MEVVA) implanter for the dose $2 \times 10^{17}$ ions/cm$^2$, accelerating voltage 60 kV and an ion-beam current density of 54 $\mu$A/cm$^2$. The fractions of the charge states of the implanted Fe ions used in MEVVA implanter are Fe$^+(25\%)$, Fe$^{2+}(68\%)$, and Fe$^{3+}(7\%)$. The change in the sample temperature due to ion-beam heating was monitored by a thermocouple attached to the sample holder. The magnetic properties were obtained by using a SQUID magnetometer in the temperature range 4.2 to 300 K and the magnetic field up to 5 T applied parallel to the plane of the sample. The magnetoresistance was measured for temperatures between 30 and 300 K in fields up to 7600 G in a four-point probe configu-
ration with aluminum contact pads forming ohmic contacts. The magnetic field was applied parallel to the current direction.

III. EXPERIMENTAL RESULTS

A. Magnetization hysteresis measurements

Figures 1(a)–(c) show the magnetization hysteresis loop at temperatures 10 K, 50 K, and 80 K, respectively, for the Fe implanted Ge sample (dose: $2 \times 10^{17}$ ions/cm$^2$, accelerating voltage: 60 kV) with magnetic field $H$ parallel to the sample plane. At these temperatures there is a small coercive field $H_c$. The ferromagnetic-like hysteresis implies that most of the Fe clusters become aligned with respect to the applied magnetic field, and the anisotropy energy barrier of Fe clusters is much greater than the thermal energy. As the temperature increases, the area of the ferromagnetic-like hysteresis loop decreases as does the coercive field, and at 300 K
no hysteresis loop is observed as shown in Fig. 2(a). The data points shown in Fig. 2(a) were measured at decreasing magnetic field. The decrease in coercive field with increase in temperature implies that Fe clusters move towards a superparamagnetic region. In the superparamagnetic state, the thermal energy is greater than the magnetic-anisotropy energy barrier, and superparamagnetic relaxation occurs.

In the superparamagnetic region, under the assumption of weak interparticle interactions, magnetization \( M(H) \) can be described by a Langevin function \( L(H, T) \) (Refs. 20–25) that can be described as

\[
M(H,T) = pM_s \left( \coth \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right) = pM_s L(H, T),
\]

where \( p \) is the volume fraction of the magnetic particles, \( \mu = M_s V \) is the magnetic moment of a single particle with volume \( V \), and \( H \) is the external magnetic field. In real granular systems, it is necessary to consider a distribution in the particle sizes. Therefore, the magnetization of the granular system with Fe particles of different sizes is described by the equation

\[
M = pM_s \int_0^\infty L \left( \frac{\mu H}{k_B T} \right) f(V) dV,
\]

where \( f(V) \) is the particle size distribution. Assuming spherical particles of diameter \( d \) for simplicity, a log-normal size distribution

\[
f(d) = \frac{1}{\sqrt{2 \pi \ln \sigma}} \exp \left\{ - \frac{(\ln d - \ln d_m)^2}{2(\ln \sigma)^2} \right\}
\]

is often used, where \( V = \pi d^3/6 \), and the parameters \( d_m \) and \( \sigma \) represent the statistical median and geometric standard deviation, respectively. For fitting magnetization data, it is more convenient to use the normalized magnetization \( M/pM_s \) that changes from 0–1. Using the 0 K, \( M_s \) value for pure Fe,1.740 \( \times 10^3 \text{ emu/cm}^3 \), we fitted the room-temperature magnetization curves to Eq. 2. The fitting results are shown in Figs. 2(a) and 2(b), respectively. The particle size distribution was found to be characterized by \( d_m = 4.0 \text{ nm} \) and \( \sigma = 0.125 \). Therefore, the average Fe particle diameter from the magnetization curve is \( D_{\text{SQUID}} = 4.0 \text{ nm} \).

**B. ZFC-FC measurements**

Field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements at 100 Oe were taken for an Fe-implanted Ge sample of the dose \( \times 10^{17} \text{ ions/cm}^2 \), accelerating voltage: 60 kV. The blocking temperature \( T_B \) of the superparamagnetic clusters is 100 K.

![FIG. 2.](image)

FIG. 2. (a) Magnetization vs magnetic field at 300 K for iron-implanted Ge sample (dose: \( \times 10^{17} \text{ ions/cm}^2 \), accelerating voltage: 60 kV). The solid line is a fit to the Langevin equation. (b) The particle size distribution obtained from the Langevin equation fit.

![FIG. 3.](image)

FIG. 3. ZFC and FC magnetization curves of the iron-implanted Ge sample for the dose: \( \times 10^{17} \text{ ions/cm}^2 \), accelerating voltage: 60 kV. The blocking temperature \( T_B \) of the superparamagnetic clusters is 100 K.
size distribution in the sample. It implies that our sample is
deviated from an ideal superparamagnetic system. By using
the blocking temperature $T_B$, the cluster size can be cal-
culated using the equation\(^1\)

$$T_B = \frac{K(V)}{\ln(\tau_{SQUID}/\tau_0)k_B} \approx \frac{k(V)}{25k_B}, \tag{4}$$

where $K$ is the total magnetic-anisotropy energy per unit vol-
ume, $\tau_{SQUID}$ is the characteristic measuring time of the in-
strument ($\sim 10^{-9}$ s) and $\tau_0$ is related to the natural fre-
quency of the gyromagnetic precession ($\sim 10^{-9} - 10^{-13}$ s). Usually,
the value of $K$ for an Fe cluster will be far in excess of the
bulk Fe value because in the clusters the contributions from
shape anisotropy, surface anisotropy, and interaction between
clusters should be taken into account in addition to the bulk
anisotropy. We have obtained the value of $K$ for another Fe
implanted Ge sample (dose: $2 \times 10^{17}$ ions/cm\(^2\) and accelerat-
ing voltage 40 kV) as $1.55 \times 10^7$ ergs/cm\(^3\) and taken this
value for our calculation. We calculated the size of the Fe
clusters in this sample by taking the peak temperature ($T_{peak}$)
of the ZFC curve as $T_B = 100$ K as shown in Fig. 3. The
value of diameter calculated by the ZFC and FC curves ($D_{ZFC-FC}$ = 3.5 nm) is close to the value obtained from the
Langlevin fit ($D_{SQUID}$).

C. Magnetoresistance measurements

1. Magnetoresistance calculation of the Fe-implanted Ge layer

Magnetoresistance (MR) is the variation of electrical resis-
tance due to an external magnetic field, this is usually
defined as

$$\text{MR} = \frac{\Delta R}{R} = \frac{R(B) - R(0)}{R(0)} \times 100 \%, \tag{5}$$

where $R(B)$ is the electrical resistance in the magnetic field
($B$) and $R(0)$ is the resistance in zero magnetic field. MR
measurements were made for temperatures from 30–300 K
at the interval of 10 K on the Ge sample implanted with 60
kV Fe ions and dose $2 \times 10^{17}$ ions/cm\(^2\). The Fe-implanted Ge
layer is in the top 250 nm of the Ge substrate as analyzed by
Rutherford backscattering (RBS) channeling and sputter-
depth profiling x-ray photoelectron spectroscopy (XPS) (to
be published elsewhere). To obtain a background response
for comparison, an unimplanted sample was prepared from
the same Ge wafer. Magnetoresistance data for parallel field
taken on this background sample and the sample containing
iron were measured separately. It is to be noted that ordinary
magnetoresistance (OMR), anisotropic magnetoresistance
(AMR), and GMR are not isolated effects. AMR and OMR
are also present in systems that exhibit GMR. In such cases,
suitable measurements must be carried out to separate out the
AMR and OMR contributions.\(^2\) Pekarek et al.\(^4\) have ob-
tained a GMR value of Fe implanted in InGaAs with a posi-
tive MR background.

The magnetoresistance of the Fe-implanted Ge layer is
calculated from the experimental data using the parallel re-
sistor model. The inset of Fig. 4 shows the schematic dia-
gram of the cross section of the ion-implanted crystal, where

FIG. 4. MR (%) vs magnetic field at 300 K for the iron-
implanted Ge sample (dose: $2 \times 10^{17}$ ions/cm\(^2\), accelerating voltage: 60 kV) and unimplanted Ge. The calculated data of the Fe-
implanted Ge layer was obtained by subtracting the diamagnetic
background of the Ge substrate from the sample with implanted Fe
ions using the parallel resistor model described in the text.

the top ion implanted layer is represented as “layer” and the
bottom unimplanted crystal is represented as “substrate.”
When current is passed through the layer and substrate, un-
der zero magnetic field, if the resistance of the film is $R_f(0)$
and the resistance of the substrate is $R_s(0)$, then, for current
parallel to the film plane, the measured resistance $R(0)$ can
be related to the film and substrate resistance for current
parallel to the film plane.

Under zero magnetic field,

$$\frac{1}{R(0)} = \frac{1}{R_f(0)} + \frac{1}{R_s(0)}, \tag{6}$$

under external magnetic field $B$,

$$\frac{1}{R(B)} = \frac{1}{R_f(B)} + \frac{1}{R_s(B)}, \tag{7}$$

where $R(0)$ and $R(B)$ are experimentally measured overall
(layer+substrate) resistance values. By using an unim-
planted Ge wafer, the substrate resistance $R_s(0)$ and $R_f(B)$
can be measured separately. The above equations can be used to
calculate the over all (film+substrate) magnetoresistance as

$$\langle \text{MR} \rangle(B) = \frac{R(B) - R(0)}{R(0)}. \tag{8}$$

But, the magnetoresistance of the film is

$$\langle \text{MR} \rangle_f(B) = \frac{R_f(B) - R_f(0)}{R_f(0)} \tag{9}$$

and the magnetoresistance of the substrate is
MAGNETIC PROPERTIES OF NANOCULERST FORMED . . .

\[ \langle \text{MR} \rangle (B) = \frac{R_s(B) - R_s(0)}{R_s(0)} \]

Substituting Eqs. (6) and (7) in Eq. (8), and using Eqs. (9) and (10), we get

\[ \langle \text{MR} \rangle (B) = \frac{\langle \text{MR} \rangle (B)R_s(B) - \langle \text{MR} \rangle (B)R(B)}{R_s(B) - R(B)} \]  

Using the experimental values of \( R(B) \), \( R_s(B) \), \( \langle \text{MR} \rangle (B) \), and \( \langle \text{MR} \rangle (B) \), the magnetoresistance of the layer \( \langle \text{MR} \rangle (B) \) can be calculated. The above expression shows the relationship between the magnetoresistance of the layer and that of the substrate. We have presented the results of magnetoresistance of the Fe-implanted Ge layer for the condition \( [R_s(0)/R_s(0)]<10 \).

2. Magnetoresistance results

Figure 4 shows the resultant MR data of the Fe-implanted Ge layer obtained by subtracting the background Ge diamagnetic data from the sample containing iron clusters at room temperature using Eq. (11). It can be seen that the calculated MR of the layer is negative and the value is found to be 8.5% at 7600 G. The values plotted in Figs. 5(a) and 5(b) are calculated MR values of the Fe-implanted Ge layer for a range of temperatures 300 to 180 K using the parallel resistor model (11). In an effort to study the magnetoresistance further, we have plotted in Fig. 6 the percentage change in the magnetoresistance in the field of 7600 G from the zero-field value for various temperatures. As can be seen from Fig. 6, as temperature decreases, the negative magnetoresistance is constant at first and then grows more negative below 220 K and reaches a negative magnetoresistance of 19% at 180 K. Here, the observed values of GMR at lower temperatures are comparable to other granular systems.

IV. DISCUSSION

In the case of \( a \)-Fe,Ge\(_{1-x} \)- alloys, the long-range magnetic transition takes place only when Fe concentration is \( \geq 40 \) at. %\(^{13-15}\). According to various models, the disappearance of an Fe magnetic moment at low concentration (\( <40 \) at. % Fe) is associated with a charge-transfer mechanism, where \( 4p \) electrons of Ge are transferred to the Fe 3\( d \) band, which leads to a more complete 3\( d \) band filling and broadening mechanism, where the Fe 3\( d \) band hybridizes with the Ge \( sp \) levels, which leads to a spin-degenerate Fe 3\( d \) band. Butler et al.\(^{27}\) calculated the electronic structure of spin-dependent tunneling structures of Fe(Ge)Fe based on the assumption that electrons move from Fe to Ge. Similarly, Eastman, Shi, and Zhu\(^{22}\) observed the magnetic moment of Fe in FeGe nanophase materials (systems in which Fe clusters are embedded in a matrix composed of Ge clusters) even when the Fe concentration is very low (1.6 at. %) and found that the magnetic Fe clusters interacted with each other even at such a low concentration.

RBS random/channeling results show that our samples retain some degree of crystallinity due to ion-beam-induced crystallization and some degree of damage produced by ion-implantation. The maximum average concentration of Fe in the implanted layer is 22.86 at. % as observed by XPS measurements. Even though the ion-implanted layer is partially amorphous and the concentration of Fe is far below the critical concentration required to observe ferromagnetic properties, we have observed the presence of a magnetic moment of the Fe atoms. Also, the majority of the implanted Fe ions are in the metallic phase as determined by XPS data. Since Fe has no solubility in crystalline (c)-Ge, this high local concentration of Fe in our samples will result in the metal atoms nucleating as precipitates. Ion implantation causes lattice damage in the c-Ge, but, simultaneously, the structural ordering of Ge also takes place because of ion-beam self-annealing. As a result of dynamic annealing of the damaged Ge layer, Fe atoms will be expelled by the structurally regrowing Ge. The growing grains could grow around the Fe atoms, thereby, encapsulating them. This causes segregation of the metal phase in the semiconductor matrix.\(^{28}\)

These results show that the magnetotransport and mag-
FIG. 6. MR (%) vs temperature taken at 7600 G for the Fe-implanted Ge sample (dose: $2 \times 10^{17}$ ions/cm$^2$, accelerating voltage: 60 kV).

Nanomagnetic properties depend strongly on the microstructure of the materials and on the preparation technique. Theoretical studies[1,2,5–8] indicate that the negative MR in granular films primarily comes from the spin-dependent scattering of the conduction electrons both within magnetic clusters and at the interfaces between magnetic grains and the nonmagnetic matrix. Our magnetization measurements confirm the presence of magnetic Fe clusters in the Ge crystal. Therefore, the negative MR of the Fe-implanted Ge sample is attributed to spin-dependent scattering of charge carriers by magnetic iron clusters.

Even though there have been efforts to explain the $T$ dependence of GMR for all temperatures using electron-phonon and magnon-phonon scattering, it is far from a complete understanding. This arises from the fact that, in the case of granular systems, the $T$ dependence of MR is complicated by the presence of a distribution of particle sizes that gives rise to blocking processes. Recently, Gerber et al.[29] argued that the temperature dependence of GMR could not be explained by scattering of phonons and magnons. Both these scattering mechanisms lead to a saturation of resistivity at low temperature in zero as well as high magnetic fields. Below the blocking temperatures, the superparamagnetic clusters that are responsible for spin-dependent scattering will be blocked by the thermal energy barrier and they are no longer superparamagnetic. Therefore, conventional models cannot explain the observed strong $T$ dependence of GMR at low temperatures in granular materials.

Recently, Milner, Korenblit, and Gerber[30] explained the strong $T$ dependence of GMR in granular materials by taking the electron scattering of paramagnetic clusters into account. According to their model, small magnetic clusters or impurities are coupled via the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction in the granular materials. At lower temperatures, the ferromagnetic ordering of the small clusters causes the macroscopic resistance of spin-up electrons to differ strongly from that of spin-down ones, the effect of such scattering is strongly enhanced. Therefore, the exchange interaction between the conduction electrons and local magnetic moments of clusters changes the MR rapidly at low temperatures. These small clusters apart from superparamagnetic clusters constitute a system called the spin-glass state.[31] In the case of spin-glass clusters, the magnetic interaction among the clusters exists and is very strong at low temperatures whereas this is not the case in superparamagnetic clusters. Since the clusters are randomly distributed within the crystal, the magnetic interactions are also randomly distributed. Thus, the term “spin glass” is used in analogy with a real glass or an amorphous solid, where the atoms are randomly distributed without any order or structure. There are reports[32,33] of the observation of both spin-glass and superparamagnetic clusters in the Fe/Ag and Fe/Cu granular materials. There are many materials with intrinsic magnetic moments that have been found to possess giant negative magnetoresistance comparable or larger than that in granular materials due to various types of interaction between the conduction electrons and magnetic moments.[34] For example, amorphous $(a)$-Gd$_x$Si$_{1-x}$ (for $x$ near the metal-insulator transition) possesses a giant (many orders of magnitude) negative MR at temperatures below 80 K due to indirect RKKY exchange interaction between the conduction electrons and the local Gd moments.[35]

In the case of amorphous semiconductor alloys, the strong structural disorder enormously increases the electron concentration at the metal-insulator transition compared to that of crystalline semiconductors. These conduction electrons are localized due to disorder and, therefore, the electron-electron and electron local magnetic-moment interaction effects are stronger, which causes a large negative MR at low temperatures. The primary concern is the magnetic moment of magnetic atoms in semiconductor crystals. Our XPS measurements on this sample show that there is no bond formation of Fe and Ge and most of the Fe atoms are in the elemental state. Since there is no bonding between Fe and Ge, we expect that the magnetic moments of the Fe atoms would not have been influenced by changes in bonding. In the case of Fe implanted Ge, strong structural disorder exists due to ion implantation damage and the observed GMR values at lower temperatures are very large. The low-temperature transport properties appear to be strongly correlated with the degree of lattice damage. Samples of higher dose and, therefore, increased lattice damage exhibit higher resistivity and magnetoresistance, suggesting increasing electron scattering due to a large number of magnetic clusters and grain boundaries introduced by lattice damage. The incompletely aligned moments of the magnetic clusters due to inhomogeneity or pinning by local defects give rise to larger scattering of conduction electrons in the absence of a magnetic field. Therefore, an applied magnetic field has a more significant effect on the alignment of the magnetic moments of the clusters, thereby, more effectively reducing the resistivity in samples with large lattice distortion. Yeh et al.[36] has observed that large substrate-induced lattice distortion gives rise to larger negative MR in La$_2$Ca$_{1-x}$MnO thin films. Therefore, the higher values of GMR at low temperature in the case of the Fe-implanted Ge layers probably comes from the interaction of conduction electrons and the spin-glass state of very small magnetic clusters. However, further experiments are neces-
sary to identify exactly what kind of magnetic interaction exists among the clusters.

V. CONCLUSIONS

The magnetic measurements of Fe-implanted Ge layers shows the absence of magnetic-coercive field in the magnetization hysteresis loop at 300 K. This implies that Fe clusters are superparamagnetic at 300 K. The size of the Fe clusters, obtained by fitting the magnetization curve at 300 K, is 4.0 nm for the Fe-implanted Ge sample with implanted dose: 2 × 10¹⁷ ions/cm² and accelerating voltage 60 kV. Field-cooled and zero-field-cooled measurements were performed to identify the superparamagnetic relaxation of the Fe clusters. The presence of a size distribution of the clusters and interaction among the clusters were evidenced from ZFC and FC curves. Using the blocking temperature, the size of the clusters was obtained as 3.5 nm for the same sample. Magnetoresistance measurements were carried out on the Fe-implanted Ge sample and the positive MR due to the unimplanted Ge wafer was subtracted using the parallel resistor model to obtain MR data for the Fe-implanted Ge layer. We have measured a large negative magnetoresistance at higher temperatures for the Fe-implanted Ge layer implanted with dose 2 × 10¹⁷ ions/cm² and accelerating voltage 60 kV. The negative MR at higher temperatures is attributed to the spin-dependent scattering of charge carriers by Fe clusters, whereas the very large negative MR at low temperatures is attributed to interactions amongst Fe clusters. The strong structural disorder caused by lattice damage during implantation enhances the interaction between Fe clusters.

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