Superlattice of Fe\textsubscript{x}Ge\textsubscript{1-x} nanodots and nanolayers for spintronics application

Tianxiao Nie\textsuperscript{1}, Xufeng Kou\textsuperscript{1}, Jianshi Tang\textsuperscript{1}, Yabin Fan\textsuperscript{1}, Murong Lang\textsuperscript{1}, Li-Te Chang\textsuperscript{1}, Chia-Pu Chu\textsuperscript{1}, Liang He\textsuperscript{1}, Sheng-Wei Lee\textsuperscript{2}, Faxian Xiu\textsuperscript{3}, Jin Zou\textsuperscript{4} and Kang L Wang\textsuperscript{1}

\textsuperscript{1}Device Research Laboratory, Department of Electrical Engineering, University of California, Los Angeles, California, USA, 90095
\textsuperscript{2}Institute of Materials Science and Engineering, National Central University, Taiwan
\textsuperscript{3}State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, People’s Republic of China
\textsuperscript{4}Materials Engineering and Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane QLD 4072, Australia

E-mail: nietianxiao@gmail.com and wang@seas.ucla.edu

Received 14 June 2014, revised 28 September 2014
Accepted for publication 27 October 2014
Published 25 November 2014

Abstract
Fe\textsubscript{x}Ge\textsubscript{1-x} superlattices with two types of nanostructures, i.e. nanodots and nanolayers, were successfully fabricated using low-temperature molecular beam epitaxy. Transmission electron microscopy (TEM) characterization clearly shows that both the Fe\textsubscript{x}Ge\textsubscript{1-x} nanodots and nanolayers exhibit a lattice-coherent structure with the surrounding Ge matrix without any metallic precipitations or secondary phases. The magnetic measurement reveals the nature of superparamagnetism in Fe\textsubscript{x}Ge\textsubscript{1-x} nanodots, while showing the absence of superparamagnetism in Fe\textsubscript{x}Ge\textsubscript{1-x} nanolayers. Magnetotransport measurements show distinct magnetoresistance (MR) behavior, i.e. a negative to positive MR transition in Fe\textsubscript{x}Ge\textsubscript{1-x} nanodots and only positive MR in nanolayers, which could be due to a competition between the orbital MR and spin-dependent scatterings. Our results open a new growth strategy for engineering Fe\textsubscript{x}Ge\textsubscript{1-x} nanostructures to facilitate the development of Ge-based spintronics and magnetoelectronics devices.

Keywords: Fe\textsubscript{x}Ge\textsubscript{1-x} superlattice, nanodot, nanolay, molecular beam epitaxy, electron microscopy, magnetoresistance

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, diluted magnetic semiconductors (DMSs) have attracted a great deal of attention, since they could greatly expand the functionalities of ordinary semiconductors by combining not only the electrical charge for information processing but also the spin of electrons for information storage [1–3]. In addition, compared with ordinary ferromagnetic metal-based spintronics devices, the advantage of electric-field controlled ferromagnetism in DMSs can be taken to produce more functional devices, and it has the potential for developing a new generation of electronic devices to resolve the power consumption and variability issues in today’s microelectronics industry [4, 5]. To date, attempts within various semiconductor materials, such as Si [6], Ge [7, 8], GaAs [9] and ZnO [10], have been widely undertaken to produce DMSs with a high Curie temperature and good crystallinity. Among them, Si-/Ge-based DMS systems are highly favored for integrated spintronics because of their high compatibility with the present and mature Si technology.

Since the first report of Mn\textsubscript{x}Ge\textsubscript{1-x} thin film with electric-field controlled ferromagnetism, great efforts have been devoted to such material systems [11]. One direct and
effective way to realize/implement a room-temperature operation on a DMS system with a higher Curie temperature is to increase the magnetic dopant concentration in the Ge matrix. Unfortunately, Mn has a strong tendency to aggregate in Ge to form metallic precipitates and secondary phases [12], which prohibited the improvement of the Curie temperature and limited its comprehensive application in spintronics. In contrast, another transition metal Fe is a much more promising dopant because of its weaker tendency to form clusters, and it has much stronger ferromagnetism compared to that of Mn [13]. Despite its pronounced advantages, the nature of low solubility of Fe in Ge still makes it challenging to form pure DMS materials without iron germanium compounds.

While continuous efforts to address the fundamental issue of the Fe incorporation limitation has been made, realizing the functionality of spin injection into traditional semiconductors also requires a lattice-coherent Fe-doping DMS for less interface scattering and for a small conductivity semiconductors also requires a lattice-coherent Fe-doping DMS for less interface scattering and for a small conductivity. The hybrid structure with a layer of a nonmagnetic semiconductor and a ferromagnetic semiconductor is needed to realize spin injection. Furthermore, the precise engineering of a lattice-coherent Fe_xGe_{1-x} structure provides a novel way to design new nanodevices such as nanodot memories and nanochannels for spin injection [15, 16]. However, it is still a great challenge to create and control such a hybrid system, particularly considering the random nucleation of the Fe_xGe_{1-x} nanostructures.

In this paper, a superlattice with alternative Fe_xGe_{1-x} and Ge layers was successfully grown by employing a low-temperature molecular beam epitaxy (MBE). A Fe_xGe_{1-x} nanodot and nanolayer structure could be deliberately designed with excellent reproducibility by tuning the Fe concentration. The magnetic measurement excluded the presence of Fe_xGe_{1-x} intermetallic compounds in the formed superlattice structure. An apparent distinction in magnetotransport properties can be obtained byengineering the nanostructures, providing an extraordinary material candidate for building future spintronics devices.

2. Experimental details

The growth of the Fe_xGe_{1-x} superlattice was carried out in an ultrahigh vacuum PerkinElmer solid-source MBE system. High-purity Ge and Fe sources were evaporated from the Knudsen effusion cells. Before loading into the growth chamber, the Ge (100) wafer was carefully cleaned by rinsing in acetone, in isopropyl alcohol with ultrasonic agitation and finally in diluted hydrofluoric acid (HF). After degassing the substrate at 600 °C for 30 min, the substrate was cooled to 250 °C for Ge buffer layer growth with a thickness of about 50 nm. Subsequently, the growth temperature was lowered to 70 °C for the superlattice growth. The first Fe_xGe_{1-x} layer was grown with a Ge growth rate of 0.2 Å s⁻¹ and an adjustable Fe flux as the dopant source. The nominal deposition thickness of this layer was ~3 nm. Subsequently, a ~10 nm thick Ge space layer was deposited. By alternating the growth of the Fe_xGe_{1-x} and Ge layer, ten periods of the Ge/Fe_xGe_{1-x} superlattice were grown on the Ge substrate. By tuning the Fe concentration, Fe_xGe_{1-x} nanodots and a Fe_xGe_{1-x} nanolayer superlattice were successfully achieved with good reproducibility.

The microstructure and composition of the grown Fe_xGe_{1-x}/Ge superlattice were investigated by TEM (Philips Tecnai F20) equipped with energy-dispersive spectroscopy (EDS). Their magnetic property was measured by the superconducting quantum interference device (SQUID). Furthermore, the temperature-dependent magnetotransport properties were studied by the physical property measurement system (PPMS).

3. Results and discussions

Figure 1(a) is a schematic illustration of the designed Fe_xGe_{1-x} superlattice structure in which ten periods of Fe_xGe_{1-x} layers are embedded in the Ge matrix. Figures 1(b) and (c) are typical cross-section TEM images with low (∼1%) and high (∼3%) Fe doping, respectively, in which ten periods of dark layers can be seen. From their insets, the Fe_xGe_{1-x} layers can be found in the form of nanodots (for the case of low Fe doping) and in the form of nanolayers (for the case of high Fe doping). To confirm their composition, EDS was employed, and an example is shown in figure 1(d) in which the Fe and Ge peaks are clearly seen. To reveal the detailed lattice structure of the nanodots and nanolayers, high-resolution TEM (HRTEM) was employed. Figures 1(e) and (f) are typical HRTEM images taken from both samples from which a coherent lattice of the Fe_xGe_{1-x} nanodots and nanolayers with their Ge matrix can be seen. In the case of low Fe doping, the size of the nanodots shows a certain diameter distribution in the range of 2.5–4 nm with the dominant size of ~3 nm, according to our extensive investigation. When the Fe doping concentration is higher, the nanodots are changed to nanolayers with a thickness of ~3 nm, as marked by the dotted red lines in figure 1(f). To understand the Fe concentration-dependent structure evolution, we note that Fe in Ge has a certain tendency to agglomerate to form nanoparticles [17]. In our sample with a low Fe doping concentration, Fe and Ge co-evaporated on the Ge surface at the initial stage. The incoming Fe atoms preferred to nucleate on the Ge surface, and they acted as the energy-preferred sites to attract the new coming Fe atoms. Consequently, a structure of Fe-rich nanodots with a Fe-poor adjacent Ge matrix would be formed. As to the sample with the higher Fe doping concentration, the density of the nucleation would become larger, and Fe-rich nanodots would become bigger and bigger because much more Fe dopants were supplied. Considering the distance between the Fe nanodots from the TEM characterization, ~3 times the Fe doping concentration should be large enough to connect all of the Fe nanodots together, which consequently leads to a relatively uniform Fe doping concentration.

Magnetic properties of the two types of Fe_xGe_{1-x} nanostructures were measured by a SQUID magnetometer. Temperature-dependent M-H hysteresis loops of the Fe_xGe_{1-x}
nanodots sample are shown in figure 2(a), where the in-plane magnetic field is applied parallel to the superlattice film. At 10 K, it shows a very small coercivity field of 10 Oe, as displayed in the inset of figure 2(a). As the temperature increases, the coercivity field decreases. The linear M-H curve at 200 K implies that the Fe$_x$Ge$_{1-x}$ nanodots have become paramagnetic [18], indicating a Curie temperature (T$_c$) below 200 K. Meanwhile, it could be estimated that the saturated magnetic moment per Fe atom was 0.35 $\mu_B$ at 10 K. At 200 K, the near-zero magnetic moment indicates that the paramagnetic Fe$_x$Ge$_{1-x}$ nanodots have a small susceptibility. In comparison, Fe$_x$Ge$_{1-x}$ nanolayers show a similar magnetic behavior as that of the Fe$_x$Ge$_{1-x}$ nanodots, but the saturated magnetic moment per atom is a little larger, which suggests that the exchange coupling between the Fe ions is enhanced. It is well known that Fe in Ge can generate deep impurity acceptor levels, which will increase the hole density [19]. Meanwhile, the increased Fe doping concentration will decrease the distance between the Fe ions. Following the Ruderman–Kittel–Kasuya–Yoshida (RKKY) mechanism [20], the increased Fe doping concentration induced the increase of the hole density, and the decreasing Fe ion distance should be responsible for the magnetic moment enhancement.

To quantitatively understand the prevailing magnetism of the Fe$_x$Ge$_{1-x}$ superlattice samples, detailed zero-field-cooled (ZFC) and field-cooled (FC) magnetization measurements were performed. The ZFC curve was obtained by cooling the sample under a zero magnetic field and subsequently measuring the magnetic moment while warming up the sample.
under a field of 50 Oe. For the FC curve, however, the sample was cooled in the presence of a magnetic field (50 Oe). The difference between the two processes gives insight into detecting superparamagnetic nanostructures, estimating the blocking temperature \( T_b \) and probing the anisotropy barrier distribution \[21\]. As shown in figure 2(c), the Fe\(_x\)Ge\(_{1-x}\) nanodots display a bifurcation between the ZFC and FC curves with a \( T_b \) at \( \sim 12 \) K, which means that there exists one type of superparamagnetic nanostructure attributed exclusively to Fe\(_x\)Ge\(_{1-x}\) nanodots. Below 12 K, the anisotropy energy barrier would prefer the magnetic moments to be aligned along the easy axis. The relatively sharp peak of the \( T_b \) indicates that the Fe\(_x\)Ge\(_{1-x}\) nanodots have a narrow size distribution, which agrees well with our TEM observation showing a narrow size distribution of 2.5–4 nm. Above 12 K, Fe\(_x\)Ge\(_{1-x}\) nanodots became superparamagnetic. When we conducted the experiment, the thermal energy became larger than the anisotropy energy barrier of the Fe\(_x\)Ge\(_{1-x}\) nanodots, of which the magnetization direction can randomly flip during the measurement time. In comparison, the ZFC and FC curves in Fe\(_x\)Ge\(_{1-x}\) nanolayers are well superimposed in the absence of \( T_b \), as shown in figure 2(d). To understand the substantial differences in the ZFC and FC curves of these two nanostructures, the equation to describe the \( T_b \) as a function of the particle volume is given by \[22\]

\[
T_b = \frac{KV}{\ln \left( \frac{\tau_{SQUID}/\tau_0}{k_B} \right)} = \frac{KV}{25k_B},
\]

where \( K \) is the total magnetic-anisotropy energy per unit volume, \( \tau_{SQUID} \) is the characteristic measure time of the SQUID (\( \sim 10 \) s) and \( \tau_0 \) is the natural period of the gyromagnetic precession (\( \sim 10^{-9} \)–\( 10^{-13} \) s) \[18\]. Obviously, the \( T_b \) is proportional to the particle volume. In our Fe\(_x\)Ge\(_{1-x}\) nanodots sample, only one \( T_b \) exists in the ZFC and FC curve, indicating no other metallic precipitants or secondary phases are formed except the TEM-observed Fe\(_x\)Ge\(_{1-x}\) coherent nanodots. In comparison, the superimposed ZFC and FC curve rules out the presence of superparamagnetic nanostructures in the Fe\(_x\)Ge\(_{1-x}\) nanolayer sample, which further confirms that Fe ions uniformly distribute in the Fe\(_x\)Ge\(_{1-x}\) layer without the formation of any FeGe alloy precipitates.

Since two types of Fe\(_x\)Ge\(_{1-x}\) nanostructures with distinct magnetic properties are formed by simply engineering the Fe concentrations, it is of great interest to investigate their...
magnetotransport properties. The samples were fabricated into standard Hall bars with a typical channel width of 500 μm. For transport measurements, the magnetic field was applied perpendicular to the surface of the samples with current flowing in the plane. The measurement was performed at temperatures from 2 K to 300 K with an external magnetic field of up to 5 T. Figure 3(a) shows the temperature-dependent magnetoresistance (MR) of the Fe_{x}Ge_{1-x} nanodots, where an obvious transition from negative to positive MR could be observed when the temperature increases from 10 K to 15 K. Taking the ZFC and FC curve into account, the MR transition in the Fe_{x}Ge_{1-x} nanodots is very plausibly related to the T_{B}. Previous theoretical studies [23–25] have indicated that the negative MR in granular films comes from the spin-dependent scattering of the conduction electrons transported in magnetic clusters and at the interfaces between the magnetic grains and the nonmagnetic matrix. Below 12 K, because of the weakly localized magnetic interaction between the nanodots, all of these Fe_{x}Ge_{1-x} nanodots will reach a state called the spin-glass state [18]. In this state, the magnetic moments between different nanodots are analogous with a real glass or amorphous solid, where atoms are randomly distributed without any ordering. Both the spin-up and spin-down electrons will suffer from the spin-dependent scattering from the randomly distributed magnetic moments between different nanodots and thus give rise to a much larger scattering to the conduction electrons in the absence of a magnetic field. Therefore, an applied magnetic field will well align the magnetic moments of Fe_{x}Ge_{1-x} nanodots to reduce the spin-dependent scattering of the electrons, resulting in a negative MR. Meanwhile, it is of great interest to point out that the negative MR will change to a positive value at a high magnetic field. To understand this phenomenon, we should mention that another competitive mechanism, namely orbital MR, always coexists in the magnetotransport process; such a type of MR is approximately proportional to (μB)^2, hence inducing a positive MR in which μ is the carrier mobility [26]. At such a high magnetic field, Fe_{x}Ge_{1-x} nanodots are already magnetically polarized and therefore reduce the sensitivity of the spin-dependent scattering. Under such a circumstance, the orbital MR component is expected to dominate the conduction behavior, and MR curves display the nearly parabolic behavior, as highlighted in the inset of figure 3(a).

As the temperature increases above 12 K, the magnetic moments in each ferromagnetic Fe_{x}Ge_{1-x} nanodot will overcome the anisotropy energy barrier and flip randomly in two energy-favored directions as a result of thermal fluctuations. Correspondingly, the Fe_{x}Ge_{1-x} nanodots will change from ferromagnetic to superparamagnetic. The effect of the magnetic field on the ordering of Fe_{x}Ge_{1-x} nanodots in superparamagnetism is not as strong as that in ferromagnetism [27]. The weakened negative MR will lose the dominant role in the magnetotransport property. Therefore, only a positive MR behavior is observed, and the carriers mainly undergo a scattering characteristic of orbital MR.

In contrast, the Fe_{x}Ge_{1-x} nanolayer only shows a positive MR in the whole temperature range, suggesting that orbital MR is the dominant mechanism in this sample, as shown in figure 3(b). We should point out that the different magnetotransport behaviors unveiled in figures 3(a) and (b) mainly reflect their nanostructures deviation. Fe dopants distributed uniformly in the Fe_{x}Ge_{1-x} nanolayer and the relatively well-aligned moments of the Fe atoms due to hole-mediated RKKY interaction give rise to the smaller spin-dependent scattering of the carrier in the absence of a magnetic field. A weaker effect could be expected on the spin-dependent scattering after the magnetic field applied, therefore generating negligible negative MR. Only the MR contribution from the orbital MR is dominant, and a positive MR is demonstrated. Additionally, we noticed that at a low temperature, the MR deviated from the simple parabolic dependence on the applied magnetic field. The MR response shows a marked decrease in field sensitivity at a field comparable to the saturation magnetization of the sample. This effect might be attributed to ferromagnetic ordering of Fe ions in the Ge matrix, where the effect on the orbital MR comes from not only the external magnetic field but also from Fe ion magnetic moments, which have a strong response to the external magnetic field until

---

**Figure 3.** (a) Magnetotransport measurement of the Fe_{x}Ge_{1-x} nanodot sample at different temperatures from 2−300 K, showing a transition from negative MR to positive MR. (b) Magnetotransport measurement of the Fe_{x}Ge_{1-x} nanolayer sample only showing a positive MR. The inset is the curves of MR versus (μB)^2.
saturated. In the high-temperature region, the magnetic ordering of the matrix is randomized, so we expect and indeed observe an enhancement of MR to dissipate following a true parabolic dependence on the external applied field. To further clearly understand this phenomenon, the curves of \((\mu_0 H)^2\) versus MR are plotted in the insets of figure 3(b). At a low temperature, the dependence of MR on \((\mu_0 H)^2\) exhibits two separate contributions: a linear dependence at a high field corresponding to the orbital MR and a nonlinear dependence at a low field corresponding to magnetization-enhanced MR, which disappears at a high temperature as well. All of the results further confirm our speculation about the transport mechanism.

4. Conclusions

FexGe1−x nanodots and nanolayers were successfully fabricated by engineering the Fe doping concentration in low-temperature MBE. A TEM observation finds that both FexGe1−x nanodots and nanolayers have a lattice-coherent structure with the surrounding Ge matrix. The magnetic property measurements reveal FexGe1−x nanodots and nanolayers have a superparamagnetic property at about 12 K and a Curie temperature below 200 K, while FexGe1−x nanolayers have no superparamagnetic particles. The MR measurement shows that the magnetoresistance property could be engineered through manipulating the FexGe1−x nanostuctures. The understanding and engineering of FexGe1−x nanostructures via the superlattice approach provide an important platform for the design of future spintronics and magnetoelectronics devices.

Acknowledgments

This work was supported in part by the FAME Center, one of six centers of STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA. We also gratefully acknowledge the financial support from the National Science Foundation through grant ECCS 1308358.

References

[19] Sze S M and Irvin J C 1968 Resistivity, mobility and impurity levels in GaAs, Ge, and Si at 300 °K Solid-State Electron. 11 599–602
[22] Babonneau D, Bricat J, Petroff F, Cabioc’h T and Naudon A 2000 Structural and magnetic properties of Fe1−x−C1−x nanocomposite thin films J. Appl. Phys. 87 3432–43
