MnGe magnetic nanocolumns and nanowells

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Abstract

We report a ‘superlattice’ growth method to produce well-aligned magnetic MnGe nanocolumns and nanowells by using low-temperature molecular-beam epitaxy. Both structural and magnetic properties show strong evidence of Mn\(_5\)Ge\(_3\) precipitates and lattice-coherent nanostructures with different blocking temperatures. Magnetotransport measurements reveal positive and negative magnetoresistances for the nanowells and nanocolumns, respectively. This distinction can be explained by different spin scattering mechanisms under magnetic fields. Our results suggest a new growth strategy to achieve reproducible MnGe nanostructures, which facilitates the development of Ge-based spintronics and magnetoelectronics devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of ferromagnetic order in MnGe magnetic semiconductors, incorporating the spin degree of freedom into conventional Ge-based semiconductor devices has been under extensive study \([1, 2]\). The availability of spin polarized carriers in a semiconductor may open new strategies for data processing and complement conventional charge based micro- and nanoelectronics \([3, 4]\). This advantage stimulates tremendous efforts in developing MnGe dilute magnetic semiconductors (DMSs) \([2]\). To date, much progress has been made to address the fundamental challenges in Mn doping and improve film quality \([1, 5–20]\). Unfortunately, the low solubility of Mn in Ge remains a key obstacle to further improving the Curie temperature \((T_c)\). Experimental data show that Mn has a strong tendency to aggregate to form metallic precipitates and nanostructures \([7]\). For example, under high-temperature growth conditions, Mn\(_{11}\)Ge\(_8\) \([17]\) and Mn\(_{11}\)Ge\(_8\) \([17]\), are developed and are responsible for the room-temperature ferromagnetism. In contrast, with low-temperature growth, lattice-coherent MnGe nanostructures with irregular shapes are often observed, most likely originating from spinodal decomposition \([13]\), similar to those of (Ga, Mn)N and (Zn, Cr)Te \([13, 21]\). While continuous efforts attempt to address the fundamental limitation of the Mn incorporation, the lattice-coherent nanostructures may facilitate spin injections into a traditional semiconductor because of less interface scattering and a small conductivity mismatch \([22, 23]\). In essence, a hybrid structure with a layer of a semiconductor and a ferromagnetic compound is needed to achieve spin injection. A precise control of the MnGe nanostructures may also enable the fabrication of nanodevices such as nanodot memories and nanochannels for spin injection. However, creating such hybrid systems is rather challenging, particularly considering the random nucleation of the MnGe nanostructures. Jamet \(et\ al\) \([7]\) recently employed a eutectoid growth method to fabricate self-organized MnGe nanocolumns. Other groups also tried various growth conditions to control the MnGe nanostructures by low-temperature molecular-beam epitaxy (MBE) \([10, 11]\). However, up to now, the controllability of these nanostructures still remains difficult and elusive. In this paper, we report a ‘superlattice’ approach by alternately growing MnGe and Ge layers with designated thicknesses. Well-controlled MnGe nanostructures can be obtained with excellent reproducibility when the growth temperature and thicknesses of MnGe and Ge are properly designed. Since the MnGe nanostructures are embedded in the Ge matrix, this material system combines...
Figure 1. Structural properties of the MnGe nanocolumns and nanowells. (a) A typical cross-sectional TEM image of nanocolumns; (b) EDS composition analysis taken from a MnGe nanocolumn, which shows Mn and Ge peaks; (c) an EDS line scan of Mn in the STEM mode, revealing the Mn distribution; (d) a high resolution TEM image of MnGe nanocolumns; (e) a typical TEM image of MnGe nanowells; (f) a high resolution TEM image of a single MnGe nanowell consisting of MnGe nanodots.

both the magnetic properties from the MnGe nanostructures and important semiconductor characteristics, providing an extraordinary material candidate for future spin electronics devices.

2. Experimental details

The ‘superlattice’ growth approach was carried out by alternating the growth of Mn-doped Ge and undoped Ge thin layers with a solid source MBE. High-purity Ge (99.9999%) and Mn (99.99%) sources were evaporated by conventional high-temperature effusion cells. During the growth, a Ge growth rate of 0.2 Å s$^{-1}$ with an adjustable Mn flux as the dopant source was used. A high-quality single-crystalline Ge buffer layer was first deposited at 250 °C with a thickness of about 50 nm. The growth temperature was then decreased to 70 °C for the subsequent ‘superlattice’ growth. Note that 70 °C was found to be the optimized growth temperature for the fabrication of the reproducible nanostructures. Ten periods of Ge and MnGe layers were grown for each case. By adjusting the nominal thicknesses of the Ge spacer layer from 6 to 25 nm while keeping the MnGe layer at about 4 nm, MnGe nanocolumns and nanowells were obtained, respectively. More than 90% of films in 50 runs exhibit the nanocolumn and nanowell structures, showing good reproducibility. All films were grown on semi-insulating GaAs substrates to avoid the substrate conducting effect. After growth, the structural and magnetic properties were conducted by transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), a superconducting quantum interference device (SQUID) and a physical property measurement system (PPMS).

3. Results and discussion

Figure 1(a) is a typical cross-sectional TEM image of the MnGe nanocolumns. From this figure, well-aligned
nanocolumns with dark contrast can be clearly observed. The composition of the dark nanocolumns was analyzed by the EDS experiments in the scanning TEM (STEM) mode and the result is shown in figure 1(b). It should be noted that the EDS result taken locally from one nanocolumn as the beam probes can be down to 1 nm in the STEM mode. The Mn and Ge peaks are clearly seen and the Mn concentration is determined to be up to 19%. Figure 1(c) is the EDS line scan of Mn, which clearly shows the Mn distribution and the size of the MnGe nanocolumns. To reveal the detailed lattice structure of the nanocolumns, high resolution TEM (HRTEM) experiments were carried out and the result is shown in figure 1(d). Careful examination of the HRTEM image verifies that the MnGe nanocolumns have the same diamond structure as that of the Ge matrix, showing a coherent growth. A similar phenomenon was previously reported in MnGe nanocolumns [7] and nanodots [9]. Figure 1(e) shows a typical TEM image of MnGe nanowells with ten periods. Noticeably, the nanowell is composed of dense MnGe nanodots, as shown in figure 1(f). Like the nanocolumn case, the MnGe nanodots inside the nanowells are also coherent with the surrounding Ge matrix. The diameter of these nanostructures has a typical range of 4–10 nm; and the Mn concentration can be tuned from 11% up to 19% in different samples, depending upon the nominal Mn concentration.

It should be noted that, other than the coherent MnGe nanostructures, some metallic precipitates can occasionally be found in our films. These precipitates are most likely attributed to the formation of the Mn$_5$Ge$_3$ phase [11]. The SQUID measurements, however, are much more sensitive to the presence of Mn$_5$Ge$_3$ clusters even at very low concentration [13]. Indeed, our magnetic measurements show strong evidence of both the Mn$_5$Ge$_3$ precipitates and the lattice-coherent Mn-rich nanostructures, which are responsible for the ferromagnetic properties in different temperature regions. These observations are in excellent agreement with Devillers et al. [13] and Ahlers et al. [18]. Due to the similarity of the magnetic properties, we take the case of the MnGe nanowells as an example. The film exhibits a saturation moment of 104 kA m$^{-1}$ (figure 2(a) at 10 K) compared with the reported value of 120 kA m$^{-1}$ for MnGe$_2$ nanocolumns [7]. The magnetic moments per Mn atom can be estimated to be $0.24 \mu_B$. Provided that each Mn has a theoretical moment of $3 \mu_B$ [1, 24], this gives a fraction of roughly 8% of Mn being activated in the MnGe layer.

Zero-field cooled magnetization (ZFC) experiments were performed by cooling the sample under zero magnetic field from 350 to 10 K, and subsequently measuring the magnetic moments while the sample was warmed up under a field of 200 Oe. For the field cooled magnetization (FC) process, however, the sample is cooled through its Curie temperature in the presence of a magnetic field (200 Oe). The difference between these two processes gives an insight into phase transformation, the blocking temperature ($T_b$), and the Curie temperature. As shown in figure 2(b), the MnGe nanowells display a substantial difference between the ZFC and FC curves, which is interpreted by blocking transitions of superparamagnetic particles [13], i.e., $T_b$ is associated with the lattice-coherent nanostructures and $T_{52}$ corresponds to the Mn$_5$Ge$_3$ precipitates. The anisotropy energy $E_A$ can be
magnetic components [26], a hard component (Mn5Ge3), and accordingly, we can fit the hysteresis loops as the sum of two lower blocking temperature because of a smaller volume ($V$) undergo a similar superparamagnetic transition, but with much lower blocking temperature because of a smaller volume ($V$) compared with Mn5Ge3 clusters [25].

The hysteresis loops in the temperature range between 25 and 100 K present a low-field narrowing (figures 2(a) and (d)). This is verified by anomalous behavior of the coercive field as a function of temperature, as shown in figure 2(c). The experimental coercive field decreases with temperature up to 50 K; however, the energy barrier ($E_A$) can block the magnetic moments in a direction either parallel or antiparallel to the easy axis [18]. Likewise, at a lower transition temperature of $T_{T1} = 25$ K, the lattice-coherent MnGe nanostructures would undergo a similar superparamagnetic transition, but with much lower blocking temperature because of a smaller volume ($V$) compared with Mn5Ge3 clusters [25].

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Here, $\beta = \mu H$. At zero magnetic field, $\beta$ vanishes. The conductivity tensor is diagonal when there is no magnetic field; and the current density can be simply described by $j = \sigma E$. Under this scenario, the current flowing through the material is concentrated in the metallic region, which behaves like a ‘short circuit’ [7, 30, 31]. However, at high magnetic fields ($\beta \gg 1$), the off-diagonal terms of $\tilde{\sigma}(H)$ dominate ($\tilde{j} \perp \tilde{E}$), and the current becomes tangent to the nanodots. The current is deflected to flow around the magnetic clusters, resembling an ‘open circuit’ state. The transition from the ‘short circuit’ at the zero field to the ‘open circuit’ at high fields produces an increase of resistance, i.e., a positive geometry-enhanced MR [30, 31]. The above explanation has been successfully applied to several material systems, including Au/InSb [29] and MnAs/MnGaAs [30]. Similarly, the geometrically-enhanced MR was identified in MnGe$_2$ nanostructures with a high Mn concentration of $\sim 33\%$ [7].

While the geometrical effect offers a good explanation for the positive MR (figure 3(b)), the reduced spin scattering would generate a negative MR, as observed in the nanocolumn case (figure 3(a)). Therefore, we anticipate that more than one mechanism may be relevant to MR at low temperatures. The final results could depend on the competition between different mechanisms [30]. The magnetotransport properties of the MnGe nanocolumns and nanowells suggest that, by manipulating the film structures, different MRs can be engineered. This property offers a great advantage for designing spintronics devices in which the direction of spin injection relative to the magnetic domain is critical.

4. Conclusions

In conclusion, we have fabricated MnGe nanocolumns and nanowells with a Curie temperature of $\sim 300$ K by low-temperature MBE. The magnetic property measurements revealed the presence of two phases in both nanocolumns and nanowells: the lattice-coherent nanostructures $(T_{b1} \sim 25$ K) and the Mn$_3$Ge$_3$ metallic precipitates $(T_{b2} \sim 250$ K). The MR measurements showed different magnetotransport mechanisms, involving both geometrical and spin scattering effects. The understanding and fabrication of MnGe nanostructures via the ‘superlattice’ approach provides an important platform for the design of future spintronics and magnetoelectronics devices.

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References