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Growth of Mn_5Ge_3 ultrathin film on Ge(111)

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The growth of Mn_5Ge_3 ultrathin films with different thicknesses, prepared by solid phase epitaxy, is studied. The results of scanning tunnelling microscopy and low energy electron diffraction studies show that the film can be formed and it is terminated with a $(\sqrt{3} \times \sqrt{3})$ R30° surface reconstruction when the thickness of Mn exceeds 3 monolayers. The magnetic properties show that the Curie temperature is about 300 K and the T^2-dependent behaviour is observed to remain up to 220 K.

Keywords: Mn_5Ge_3, magnetic semiconductors, scanning tunnelling microscopy, solid phase epitaxy
PACC: 7530T, 8115N

1. Introduction

The spin injection from metal into nonmagnetic semiconductors has recently aroused a great interest because it has potentialities for the next generation of spin-dependent electronic devices.[1] Owing to a large resistivity mismatch between metal and semiconductor, the efficiency of spin injection is very low. The diluted magnetic semiconductors (DMS) with both ferromagnetism and semiconducting properties, have made a unique opportunity for spin injection.[2,3] $Ga_{1-x}Mn_xAs$ films grown by using low temperature molecular beam epitaxy (MBE) technique, of which Curie temperature (T_c) has reached 200°C, is becoming a hot point of recent research both in theory and in experiment.[3] Compared with the GaAs system, the group-IV ferromagnetic semiconductor Mn_xGe_{1-x} may have a great potential for the silicon electronics due to the complete compatibility between of Si and Ge. It is reported that the value of T_c for Mn_xGe_{1-x} increases linearly with the concentration of manganese (Mn) from 25 K to 116 K. [4] It is [5–7] found Tsui etc. that the T_c can reach 270 K through the combination growth of Mn, Co and Ge. The current rectification of Ge-based magnetic heterojunction diode can been controlled either by the bias voltage or by the magnetic field, which proves the possibility of producing fully electronic spin devices.[8]

A common viewpoint is that the magnetism in Mn_xGe_{1-x}DMS originates from the magnetic phase Mn_5Ge_3, and the interface between Mn_5Ge_3 and Ge substrate plays an important role in magnetic and electronic properties.[9–12] In this paper, we report on the growth of Mn_5Ge_3 ultrathin films with different thicknesses prepared in an MBE system. The morphology and the structure of the samples are characterized by using a scanning tunnelling microscope (STM) and low-energy electron-diffraction (LEED) method. In addition, the magnetization is measure by a superconducting quantum interference devices magnetometer (SQUID, Quantum Design) at a temperature varying from 300 to 2 K.

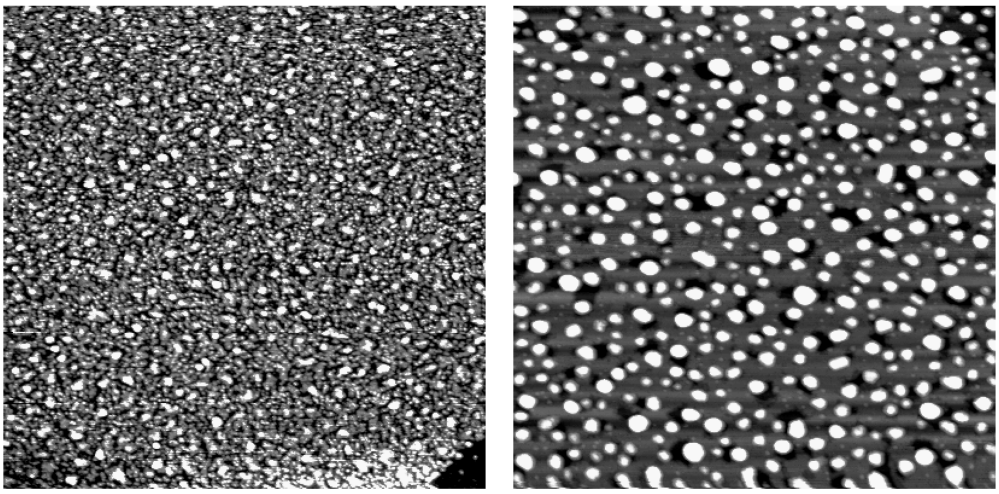
2. Growth procedure and characterization

All Mn_5Ge_3films were prepared at an ambient temperature in an MBE system with different growth times at a base pressure of 2×10^{-8} Pa. Firstly, commercial n-type Ge(111) wafers were cleaned *in situ* by Ar-ion sputtering and by annealing at 650°C alternatively. Then, the STM image showed a perfect Ge(111)-c(2×8) reconstructed surface structure, in accordance with the $\sqrt{3}\times\sqrt{3}$ LEED patterns. Secondly, Mn was deposited on the Ge(111) surface with a constant flux by K-cell, a process known as solid-phase epitaxy.[13] Finally, the alloy films were annealed at

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450°C for several minutes, and then the LEED patterns were observed. The structural evolution of a vicinal Ge surface, developing upon low coverage deposition of Mn from 0.4 to 192 ML, was carefully studied as a function of the growth time by using an STM.

Figure 1(a) is the STM image of the sample with 0.4 ML Mn deposited at an ambient temperature before annealing. It is found that the Mn atoms distribute randomly on the Ge(111) surface, and some of them have aggregated into small clusters with about one monolayer in height and 3–5 nm in diameter. As reported in Ref.[14], the larger clusters on the as-sputtered sample are of Mn-Ge alloy, and the smaller ones are were probably of pure Mn. The LEED result shows that there are weak $\sqrt{3} \times \sqrt{3}$ spots, which means that the partial amorphization of Ge surface results from the reaction between Mn atoms and Ge substrate. Figure 1(b) shows the STM topographic image (200×200 nm) of the sample after annealing at 450°C for 30 s. It can be found that some irregular islands with concaves distribute on the Ge surface. The statistical data show that the average height of these Mn-Ge alloy islands is about 3.5 nm and the diameter is in a range of 3–5 nm. The LEED pattern shows quite weak $\sqrt{3} \times \sqrt{3}$ spots, which means that some of Mn atoms have reacted with Ge substrate.

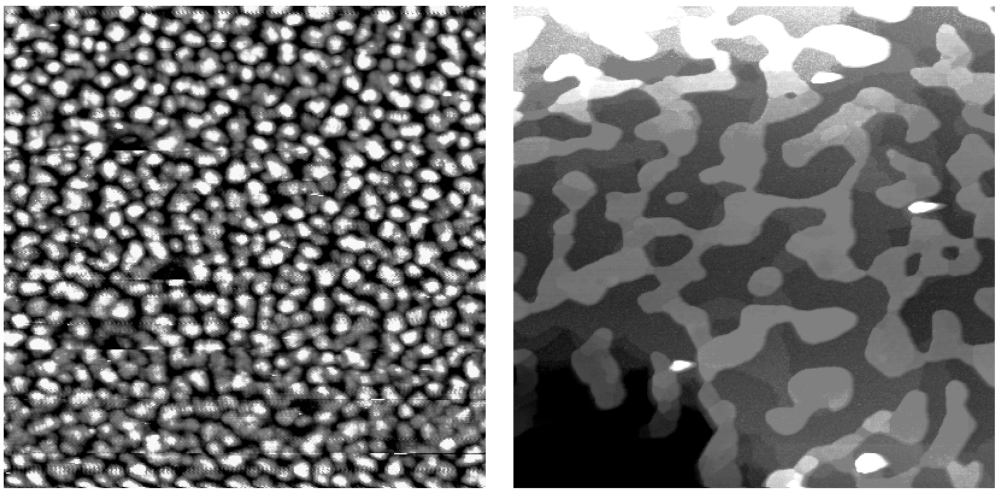


(a) (b)

Fig.1. STM topographics image (500×500 nm) of the sample with 0.4 ML Mn before annealing (a) and after annealing (b).

Figure 2(a) exhibits the STM topographic image of the sample with 3 ML Mn on the Ge(111) substrate before annealing. From this image, it is found that these clusters have a tendency to grow larger with the number of Mn atoms increasing, of which the diameter is about 3–8 nm, and the Ge(111) substrate cannot be seen. It is also confirmed by the LEED patterns where either the surface $\sqrt{3} \times \sqrt{3}$ spots or additional phase diffraction is visible. After annealing at 450°C, some islands are connected together, forming irregular agglomerates, just like the bridge crossing over the water surface, of which the width is about 10 nm, as shown in Fig.2(b).

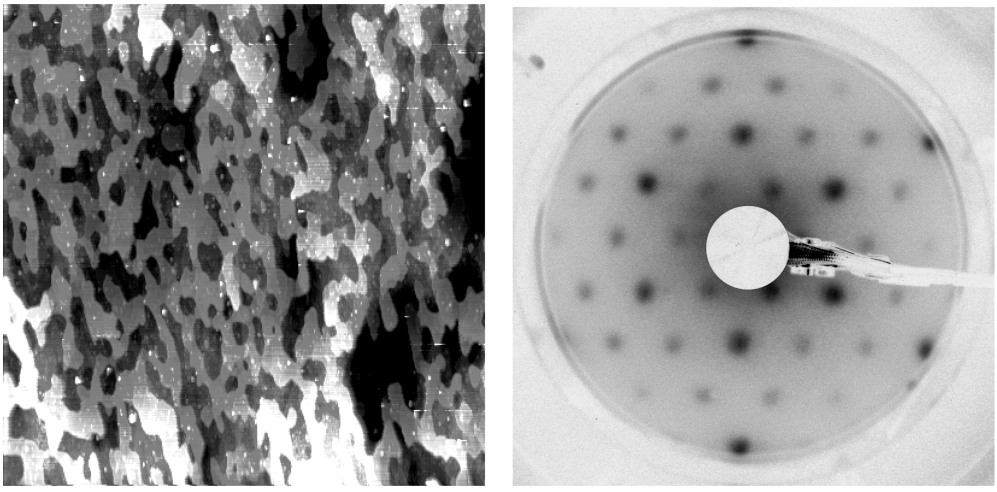
Figures 3(a) and 3(b) show the STM image and the LEED patterns of the sample with 12 ML Mn after annealing respectively. It is found that these islands are connected together completely, forming a poriferous film, which looks like a grid on the Ge surfaces. The STM image shows that the height of the film is about 2 nm, and the surface is relatively smooth. The LEED patterns show that the Ge (111) -c (2×8) structure completely disappear, and the clear $(\sqrt{3} \times \sqrt{3})$ R30°C spots occur, which confirms that the coverage is of a Mn_5Ge_3 film.[15]



(a) (b)

Fig.2. STM topographic images (200×200 nm) of the sample with 3 ML Mn before annealing (a) and after annealing (b).

Mn_5Ge_3has a hexagonal crystal structure of $D8_8$-type (space group $P6_3/mcm$, space group 193) with experimental cell dimensions at room temperature: a=7.184 Å and c=5.053 Å.[16] The epitaxial orientation of the films is $Mn_5Ge_3(001)//Ge(111)$ with $[100]_{Mn_5Ge_3}//[110]_{Ge}$, and there is a mismatch of 3.7% between Mn_5Ge_3 and Ge surface.[13] The Mn_5Ge_3 phase grown on the Ge substrate is terminated with a $(\sqrt{3}\times\sqrt{3})$ R30°C structure, which means that the lattice length of Mn_5Ge_3 (100) face is $\sqrt{3}$ times the length of Ge(111) face. The reaction mechanism of Mn-Ge is assumed to be similar to that the one of Mn-Si.[17] As shown in Fig.1(a), the Mn atoms distribute randomly on the surface and a small number of atoms react with the substrate. When the sample is annealed, more Mn atoms can react with the surface so that the clusters grow bigger, forming Mn-Ge islands with the concaves left (Fig.1(b)). When more Mn atoms are deposited, they tend to gather into bigger clusters on the surface (Fig.2(a)). And more islands can form if the Mn-Ge ratio reaches a certain value after annealing. The unreacted Mn clusters subsequently merge into these islands to grow in lateral direction to form films (Fig.2(b)). As shown in Figs.3(a) and 3(b), the thicker films keep the same morphology and structure. If the Ge surface is covered with Mn_5Ge_3, we can calculate that 1ML Mn can form about 0.33 nm Mn_5Ge_3 films. By comparing with the height of Mn_5Ge_3islands and the Mn flux, we can find that the Ge(111) surface is covered by Mn_5Ge_3 completely.



(a) (b)

Fig.3. STM topographic image (500×500 nm) (a) and LEED patterns of the sample with 12 ML Mn (b) after annealing.

3. Magnetic properties

According to the bulk phase diagram, there exist many phases in Mn-Ge alloys such as Mn_5Ge_3, Mn_5Ge_2 $Mn_{3.4}Ge$, Mn_3Ge_2 and Mn_2Ge.[18−21] The values of T_c for Mn_5Ge_3, Mn_5Ge_2, $Mn_{3.4}Ge$, Mn_3Ge_2 are 300, 710, 920, and 300 K respectively, and the Néel temperature of Mn_5Ge_2 is about 390 K.[22] Regarding $Mn_{11}Ge_8$ as Mn_3Ge_2 formerly leads to the finding that it exhibits a ferromagnetic ordering temperature of approximately 300 K and possesses a pronounced second ordering temperature near 140 K.[23,24] The Mn_5Ge_3 phase is stabile for the Mn-Ge alloy films, which can form at an annealing temperature varying from 300°C to 650°C.[13]

The magnetic properties of our samples were directly measured by using a superconducting quantum interference devices magnetometer (SQUID, Quantum Design). Figure 4(a) shows the curves of temperature-dependent magnetization (M-T) of Mn_5Ge_3 films with different thicknesses: 4, 12, 24, 36, 48, 72, 96 and 192 ML separately. It is found that there exists an FM transition at about 300 K, but no transition appears from ferromagnetic to antiferromagnetic in a temperature range from 5 to 260 K. According to the T_c of samples and the surface $(\sqrt{3} \times \sqrt{3})$ R30°C LEED spots, it is confirmed that the phase is not $Mn_{11}Ge_8$ phase but Mn_5Ge_3 phase.[23] Furthermore, we find that the T_c of all samples is about 300 K, the same as the ever reported value.[13] The data of magnetization show a nearly perfect T^2 dependence up to about 220 K as shown in Fig.4(b). The T^2 fall of the magnetization arises from the long-wavelength, low-frequency fluctuations of the magnetization or multiple excitations of the interacting spin waves.[25]

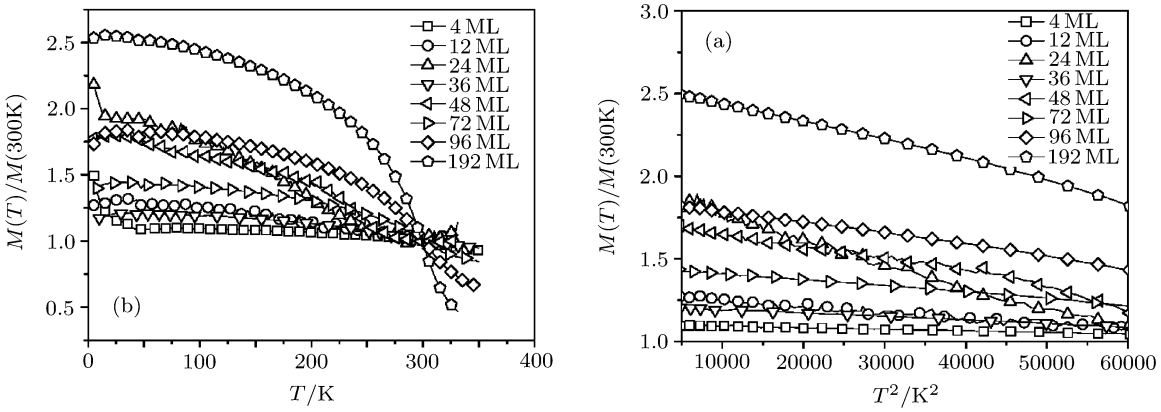


Fig.4. The normalized T-dependent (a) and T^2-dependent (b) magnetizations of Mn_5Ge_3 films with different Mn thicknesses: 4, 12, 24, 36, 48, 72, 96 and 192 ML separately.

4. Summary

Mn_5Ge_3 ultra thin films with different thicknesses have been prepared by solid phase epitaxy. The results of STM and LEED studies show that Mn atoms adsorbed by the Ge(111)-c(2×8) surface aggregate and react with the substrate to form Mn_5Ge_3 films with a $(\sqrt{3} \times \sqrt{3})$ surface structure. When the thickness of Mn exceeds 3ML, these islands are connected into a flat film. The magnetization results show that the T_c of all samples is about 300 K, which means that it may have great potentialities for Ge-base spintronic devices at room temperature.

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