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Suppression of Mn segregation in Ge/Mn_5Ge_3 heterostructures induced by interstitial carbon

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ABSTRACT

Mn_5Ge_3 compound, with its room-temperature ferromagnetism and possibility to epitaxially grow on Ge, acts as a potential spin injector into group-IV semiconductors. It is shown that the realization of Ge/Mn_5Ge_3 heterostructures is highly hampered by Mn segregation toward the Ge growing surface. The Mn segregation length can be estimated *in-situ* and in real time by means of reflection high-energy electron diffraction. We present here an approach allowing to greatly reduce or even to prevent the Mn segregation, whose principle is based on filling the Mn_5Ge_3 lattice with interstitial carbon atoms. In addition, we show that interstitial carbon in Mn_5Ge_3 allows to enhance not only the Curie temperature of $Mn_5Ge_3C_x$ layers but also in the whole Ge/Mn_5Ge_3/Ge heterostructures.

1. Introduction

In recent years, the epitaxial growth of intermetallic Mn_5Ge_3 thin films has received growing interest, work in this direction is motivated by the hope to find out an efficient spin injector into group-IV semiconductors [1–9]. Indeed, the use of standard ferromagnetic metals, such as Fe, Co or Ni, directly on Si and Ge is highly hampered by their reactivity with group-IV semiconductors to form interfacial silicides or germanides, which, for most of them, are not ferromagnetic (for example, $CoSi_2$ is metallic [10] while β-$FeSi_2$ is semiconducting [11]). It is also not trivial to obtain epitaxial growth of an oxide in between Ge (or Si) and a ferromagnetic metal, efficiency of spin injection is therefore limited by the interface roughness and the difference in materials conductivity.

The Mn_5Ge_3 compound exhibits numerous features, which may make it as a potential candidate for spin injection into Ge. First, this compound has a Curie temperature near room temperature [12], theoretical calculations predicted a high-spin-injection efficiency along its *c* axis [3] and a spin polarization up to 42% has been demonstrated [13]. Second, Ge_3Mn_5 films with thickness up to 165 nm can be epitaxially grown on Ge(111) substrates despite a misfit as high as 3.7% [6]. This feature is of particular importance with respect to the application of Mn_5Ge_3/Ge(111) heterostructures for the realisation of spintronic devices. Indeed, in a lattice mismatched heteroepitaxial system, a misfit as high as 3.7% often results in highly defected epitaxial layers. For example, Ge has a lattice parameter of ~4% larger than that of Si, pseudomorphic Ge growth is obtained only for a thickness smaller than 4 monolayers, beyond which islanding growth mode occurs [14]. For a Ge thickness of about some tens of nanometers, a threading dislocation density higher than 10^8 cm^{-2} is usually observed and the growth front becomes extremely rough. In addition, in the Ge–Mn phase diagram [15], the Mn_5Ge_3 compound is not the most stable phase but thanks to its hexagonal structure, which is similar to that of the Ge(111) surface, Mn_5Ge_3 is the unique epitaxial phase, which has been stabilized on Ge(111) [1,2,5,6].

In this paper, we report on the effect of Mn segregation occurred during Ge overgrowth on Mn_5Ge_3/Ge heterostructures. During the course of our experiments to produce Ge/Mn_5Ge_3/Ge multilayers for the realization of spin valves and giant magneto-resistance (GMR) structures, we have observed a long-range Mn segregation upwards the Ge growth front. We show that incorporating carbon atoms into the interstitial sites of the Mn_5Ge_3 lattice allows to prevent out-diffusion of Mn from Mn_5Ge_3. In addition, we show that interstitial carbon also allows to enhance the magnetic properties of Ge/Mn_5Ge_3/Ge multilayers.

2. Experimental details

Materials growth was performed in a molecular beam epitaxial (MBE) system with a base pressure better than 5×10^{-10} mbar. The MBE chamber is equipped with a 30-keV reflection high-energy electron diffraction (RHEED) apparatus allowing to monitor in real time

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the epitaxial growth process and the change of the film surface reconstruction. An Auger electron spectrometer is used to control the cleanliness of the substrate surface prior to growth and the film composition.

Standard effusion cells were used for Mn and Ge deposition, the Mn flux was measured by a quartz crystal microbalance and the Ge growth rate was deduced from measurements of RHEED intensity oscillations. The Mn and Ge growth rates used in this work are of 0.9 and 3 nm/min, respectively. Carbon evaporation was carried out using a sublimation source of high purity pyrolytic graphite, the carbon concentration was estimated by combining two approaches: for each sublimation current, it was estimated from δ-doping curves measured on GaAs surfaces and then corrected according to the change of Si(001) surface reconstructions from (2 × 1) to c(4 × 4) upon adsorption of a submonolayer of carbon [16]. The estimated error is about 10%. The substrate temperature was measured by a thermocouple in contact with the backside of the substrate.

Mn$_5$Ge$_3$/Ge(111) heterostructures were prepared by a room temperature Mn deposition onto Ge(111) substrates, followed by thermal annealing up to 430–450 °C, the temperature range at which the surface reconstruction characteristic of the Mn$_5$Ge$_3$ phase was generally observed. Structural analyses of post grown films were performed by means of high-resolution transmission electron microscopy (HRTEM) using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7 Å. HRTEM cross sections were prepared by mechanical polishing, followed by ion polishing (Gatan Precision Ion Polishing System).

Magnetic characterizations were carried out using superconducting quantum interference device magnetometer (SQUID) at temperatures ranging from 5 to 350 K. A magnetic field of 0.5 T is applied both in the plane of samples or perpendicular to it. The diamagnetic contributions of Ge substrates were subtracted from the measurements, leaving the magnetic contributions of grown films. More details of sample growth conditions can be found elsewhere [5,6].

3. Results and discussion

It is now well established that epitaxial Mn$_5$Ge$_3$ films on Ge(111) exhibit a $(\sqrt{3}x\sqrt{3})R30°$ surface reconstruction (denoted hereafter to as $\sqrt{3}$) with Mn termination [2]. From electron diffraction, such a reconstruction is manifested by the observation of 1 × 1 streaks along [1–10] azimuth and additional 1/3- and 2/3-ordered streaks between 1 × 1 streaks along [11-2] azimuth. The RHEED technique, thanks to its grazing incidence, allows to instantaneously reveal not only the change in the surface morphology but also the surface structure during film growth. To produce Ge/Mn$_5$Ge$_3$/Ge multilayers, we first grow a thin Mn$_5$Ge$_3$ layer on Ge(111), whose thickness ranges from 10 to 50 nm in order to insure a high crystalline quality and a smooth surface. Starting from those films, Ge overgrowth is carried out at temperatures ranging from 200 to 500 °C.

Fig. 1a shows a RHEED pattern taken along [11-2] azimuth of the starting surface of a 40 nm thick Mn$_5$Ge$_3$ layer prior to Ge deposition. Additional 1/3- and 2/3-ordered streaks between the bulk-like 1 × 1 streaks are clearly seen, confirming the Mn-terminated Mn$_5$Ge$_3$ surface. The observed long streaks in the RHEED pattern unambiguously indicate that the corresponding surface is highly smooth. Displayed in Fig. 1b is an example of the RHEED pattern observed after deposition of 5 nm of Ge (corresponding to a deposition time of 100 s) at a substrate temperature of 250 °C. Apart from a certain decrease of the RHEED intensity, which signifies an increase of the surface roughness, the 1/3- and 2/3-ordered streaks still remain visible. This clearly indicates that Mn has floated upwards the Ge growth front and reacted with deposited Ge to form a surface Mn$_5$Ge$_3$-like layer. To quantify the Mn segregation length, we have measured the RHEED intensity evolution as a function of the Ge deposition time of the specular streak (green curve) and of a 2/3-ordered streak. As can be expected, the intensity of both the specular and 2/3 streaks is found to decrease when increasing the Ge deposition time but the specular streak exhibits a decrease more abrupt. The Mn segregation length can be determined from the intersection of the slope of these two curves with the deposition time axis. Taking into account the Ge growth rate of 3 nm/min, the Mn segregation length is found to be of ~10 nm for the specular streak and of ~22.5 nm for the 2/3-ordered streak. Since the specular streak is in general more sensitive to the development of the surface roughness than any diffracted streak, we can deduce a value of the Mn segregation length of ~22.5 nm for the Ge overgrowth at 250 °C. It is worth noting that Mn segregation has been reported during Ge deposition on (001)-oriented Ge substrates and a segregation length larger than 20 nm was measured at a substrate temperature as low as 150 K [17]. We also note that *in-situ* analyses of the RHEED intensity evolution were used to determine the segregation length of In in III–V materials [18] and of Ge during Si growth in Si/Si$_{1-x}$Ge$_x$ heterostructures [19]. However, in those systems, the segregation length is only of some monolayers and the measurement of the segregation length was based on a RHEED intensity transient at the beginning of growth [18] or the change in the growth rate [19]. In our case, the appearance in RHEED patterns of an additional streaks characteristic of Mn$_5$Ge$_3$ allows a direct estimation of the Mn segregation length.

The structural properties of the Ge overgrown layer on Mn$_5$Ge$_3$/Ge(111) heterostructures are depicted in Fig. 2. Fig. 2a shows a typical cross-sectional TEM image of a 60 nm thick Ge layer grown on a

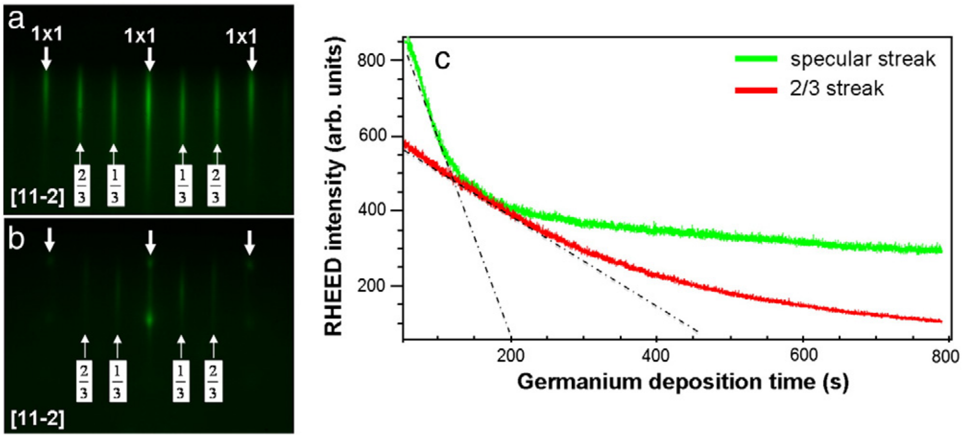

Fig. 1. RHEED patterns taken along the [2] azimuth: (a) of the $\sqrt{3}$ reconstruction of the Mn$_5$Ge$_3$ surface prior to the deposition of the Ge capping layers; (b): after deposition of 60 nm of Ge at a substrate temperature of 250 °C; and c) Evolution of the RHEED intensity of the specular streak (green curve) and a 2/3-ordered streak (read curve) with increasing the Ge deposition time. The dotted lines represent the slope of two curves.