Long range Mn segregation and intermixing during subsequent deposition of Ge capping layers on Mn_5Ge_3/Ge(111) heterostructures

M.-T. Dau, A. Spiesser, T. LeGiang, L.A. Michez, S.F. Olive-Mendez, V. Le Thanh *, M. Petit, J.-M. Raimundo, A. Glachant, J. Derrien

Abstract

We report on the Mn segregation and diffusion during the epitaxial overgrowth of Ge on Mn_5Ge_3/Ge(111) heterostructures. It is shown that the underneath Mn_5Ge_3 layers remain stabilized at the interface with the substrate while a small amount of Mn can leave the layers and floats at the Ge growth front. Mn can then act as a surfactant during Ge growth along the (111) orientation. The Mn segregation length and also the state of Mn atoms incorporated in the Ge layers are found to depend on the growth temperature. At a growth temperature of 250 °C, a segregation length of ~10 nm is observed and Mn atoms incorporated in the Ge layers are uniformly distributed. At 450 °C, segregated Mn atoms can react with Ge to form Mn_5Ge_3 clusters inside the Ge overgrown layer. Such Mn_5Ge_3 clusters display random orientations and induce modification of the magnetic anisotropy of the whole film.

Introduction

In recent years, there has been a growing interest in synthesizing diluted magnetic semiconductors (DMS), motivated by the hope to significantly improve the efficiency of spin injection into semiconductors [1–3]. Among the various systems, which have been largely studied such as (Ga,Mn)As:Mn [4] or (II–VI):Mn DMS [5], Mn-doped Ge is of particular interest since it offers a direct route for integrating magnetism with existing silicon technology [2,3]. One of the major difficulties for getting high Curie temperature DMS is probably the very low thermodynamic solubility of magnetic elements in most semiconductors. In the case of Mn-doped Ge, when the Mn concentration exceeds about a few percents or when the growth temperature is higher than ~250 °C, the formation of Mn-rich phases and/or precipitates is generally observed [6,7]. Actually, all the previous studies agreed to indicate that these intermetallic precipitates are the room-temperature ferromagnetic Mn_5Ge_3 phase [8–11].

Intermetallic Mn_5Ge_3 thin films have been shown to epitaxially grow on Ge(111) substrates [12–15] and their electronic properties have been recently reported [16,17]. It has been predicted that high spin injection efficiency can be obtained along the c axis of Mn_5Ge_3 [16]. Furthermore, despite the fact that Mn_5Ge_3 is not the most stable phase in the Ge–Mn bulk phase diagram, recent experimental results revealed that Mn_5Ge_3 is the unique epitaxial phase which could be stabilized on Ge(111) [14]. The epitaxial Mn_5Ge_3 film surface was found to exhibit a $(\sqrt{3}\times\sqrt{3})R30$ surface reconstruction, which has been attributed to a Mn-terminated surface [13].

In this paper, we report on the first results of Mn segregation and diffusion during the Ge overgrowth on Mn_5Ge_3. Indeed, for spintronic research and applications such as spin valves or giant magnetoresistance (GMR) structures, it is desirable to achieve epitaxial growth of Ge on top of Mn_5Ge_3 films. During the course of our experiments to produce Ge/Mn_5Ge_3/Ge multilayers, we were aware of a long range Mn segregation during subsequent deposition of Ge capping layers on the top of Mn_5Ge_3/Ge heterostructures. For a Ge deposition carried out at a substrate temperature of 450 °C, we have observed, by means of reflection high-energy electron diffraction (RHEED), the phenomenon of Mn segregation with a length that can reach a value larger than 200 nm when depositing Ge capping layers. We have then combined RHEED, transmission electron microscopy (TEM) and magnetic characterizations via vibrating sample magnetometer (VSM) to investigate the Mn segregation at two substrate temperatures: 250 and 450 °C.

Experimental set-up and procedures:

Ge and Mn depositions were carried out by means of standard Knudsen effusion cells in a molecular-beam epitaxial (MBE) system with a base pressure better than 1×10^{-10} Torr. The MBE chamber is equipped with a RHEED apparatus to monitor the epitaxial growth process and an Auger electron spectrometer to control the cleanliness of the substrate surface.

Mn_5Ge_3/Ge(111) heterostructures were obtained by a roomtemperature Mn deposition followed by thermal annealing up to 430–450 °C, the temperature range at which a $(\sqrt{3}\times\sqrt{3})R30$ surface reconstruction characteristic of the Mn_5Ge_3 phase was generally observed. The chosen thickness of Mn_5Ge_3 films stays in the range of 10–30 nm to insure a good epi-layer and a smooth starting surface prior to the Ge overgrowth. In some samples, we have used a very thick initial Mn_5Ge_3 layer to compare the Ge growth mode. The Ge growth rate used in this work and determined from RHEED intensity oscillations is~3.3 nm/min. The substrate temperature was measured by a thermocouple in contact with the back side of the substrate.

Ge surface cleaning was carried out in two steps: the first was a wet chemical cleaning followed by an in-situ thermal annealing at 750 °C to remove the Ge surface oxides. More details of the Ge surface cleaning can be found in Ref. [14]. Structural analyses of post grown films were performed by means of high-resolution TEM using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7 Å. The magnetic properties were investigated with a VSM with a magnetic field of 1 T applied in the plane and of 2 T applied perpendicular to the sample surface. The diamagnetic contributions due to the Ge substrate were subtracted from the measurements, leaving the magnetic contributions of the Mn_5Ge_3 films.

Results and discussion

The phenomenon of Mn segregation has been the subject of several works and was mainly studied in a Ge(001) matrix during the growth of diluted $Ge_{1-x}Mn_x$ alloys. A typical example of the Mn segregation phenomenon is probably the formation of self-assembled Mn-rich nanocolumns, observed within particular growth conditions during Mn-doped Ge growth on Ge(001) [18–20]. These nanocolumns have been shown to exhibit a high Curie temperature and a giant magnetoresistance. Recently, when investigating the Mn growth mode on Ge, Zhu et al. [21], have predicted a surfactant effect of Mn during Ge epitaxial growth along the [001] orientation and this has been recently experimentally demonstrated [22]. However, concerning the [111] orientation of Ge, the authors has predicted a contrary effect that Mn would prefer to diffuse into the bulk via interstitial sites than to float toward the subsurface sites. Here, we show that Mn, during the epitaxial overgrowth of Ge on Mn_5Ge_3/Ge heterostructures, floats at the growth front and acts as a surfactant along the [111] orientation of Ge.

As it has been recently shown, room-temperature deposition of a 10–30 nm thick Mn layer on Ge(111) surface followed by a thermal annealing at the temperature range between 430 and 650 °C produces a (√3×√3)R30 surface reconstruction [12–14]. The corresponding phase has been unambiguously attributed both from the chemical, structural and magnetic properties, to the Mn_5Ge_3 compound [14]. In our experiments to produce Ge/Mn_5Ge_3/Ge multilayers, we first grow a thin Mn_5Ge_3 layer on Ge(111), whose thickness ranges from 10 to 30 nm in order to maintain a high crystalline quality and a smooth surface. When growing Ge capping layers on top of this Mn_5Ge_3 layer, we found out that the (√3×√3)R30 reconstruction persists up to a surprisingly high thickness, larger than 200 nm. Since the (√3×√3) R30 surface reconstruction is manifested by the observation of 1x1 streaks along [1–10] azimuth and additional 1/3 and 2/3 ordered streaks between 1×1 streaks along [11-2] azimuth, we have investigated the Mn segregation by measuring the evolution of the RHEED intensity of one of these ordered streaks. Such an evolution versus the Ge deposition time, depicted in Fig. 1, quantitatively reflects the Mn segregation length throughout the overgrown Ge. We show in the insert of the figure a RHEED pattern taken along the [11-2] azimuth in which one can observe the appearance of 1/3 and 2/3 ordered streaks characteristic of Mn_5Ge_3. The RHEED intensity measurements were taken in the dotted line region surrounding a 2/3 streak, as indicated in the pattern. The figure clearly reveals a long range Mn segregation on the Ge growing surface. The segregation length is about 10 nm for a Ge growth temperature of 250 °C and can be larger than 200 nm for a growth carried out at 450 °C. Note that the curve b) only represents a part of the RHEED intensity evolution, up to a Ge thickness of ~45 nm, the intensity of the 2/3 streak completely disappears after deposition of a Ge thickness much larger than 200 nm. Another feature that reveals the figure is that during Ge deposition a part of Mn has been incorporated in the Ge layers, a common behavior which has been observed for most of surfactant atoms in epitaxial growth [22]. Indeed, since RHEED patterns reflect the surface structure of the Ge growing front, the decrease of the RHEED intensity with increasing the Ge thickness implies that a part of Mn atoms has been incorporated into the grown layers. Work is now in progress to determine the spatial distribution of the Mn atoms throughout the Ge layers and will be published later.

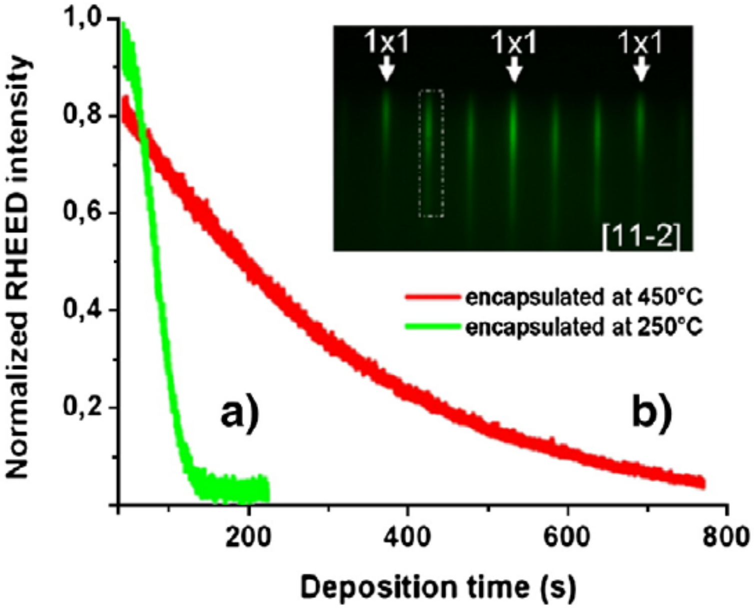

Fig. 1. Evolution of the RHEED intensity of a 2/3 streak along the [11-2] RHEED pattern characteristic of the Mn_5Ge_3 phase during Ge overgrowth at 250 °C (curve a) and at 450 °C (curve b). Shown in the insert is a RHEED pattern taken along the [11-2] azimuth characteristic of the Mn5Ge3 compound prior to Ge deposition. During Ge deposition, the RHEED intensity measurements were taken in a dotted line region surrounding a 2/3 streak, the Ge growth rate is 3.3 nm/min.

Different from a recent work reported in Ref. [22] in which a submonolayer amount of Mn was predeposited prior to Ge growth, the unique source of Mn atoms in our experiments stems from the Mn_5Ge_3 layers. To understand the segregation phenomenon observed from the above RHEED analysis, some questions which may arise: do the underneath Mn_5Ge_3 layers remain stabilized at the interface with the Ge substrate or are they dissolved in Ge overgrown layers? What is the state of Mn atoms incorporated in the Ge layers? To understand these features, we have combined structural and magnetic characterizations to investigate the corresponding samples. Fig. 2a shows a high-resolution crosssectional TEM image of the interfacial region of a Ge/Mn_5Ge_3 sample grown at 250 °C. The image reveals an atomically resolved Ge/ Mn_5Ge_3 interface, no trace ofMn is visible in the Ge overgrown layer. Mn_5Ge_3 layers with expected thickness are well present on the Ge substrate, indicating that Mn_5Ge_3 remains stabilized during the deposition of the Ge cap layers. It is important to emphasize that since epitaxial Mn_5Ge_3 layers have (001) hexagonal planes parallel to the (111) plane of the Ge substrate [14], the Ge overgrown layer is of (111) orientation. This orientation can be easily checked from RHEED patterns, which displayed well a three-fold symmetry characteristic of a hexagonal plane. For Ge deposition at 450 °C, we observe, in contrary, the presence of some Mn_5Ge_3 crystallites or clusters inside the Ge overgrown layers (Fig. 2b). The Mn_5Ge_3 crystallites are mono-crystalline and exhibit random orientations in comparison to the orientation of the underneath Mn_5Ge_3 layer.

We note that to better get out the existence of Mn_5Ge_3 crystallites inside the Ge cap layer in Fig. 2b, we have used a relatively thick area of the sample for TEM analyses. This makes the Ge overgrown layer becoming less defined, which appears to have an amorphous aspect. In every case, the Ge overgrown layer is not amorphous but monocrystalline as being revealed from RHEED patterns.

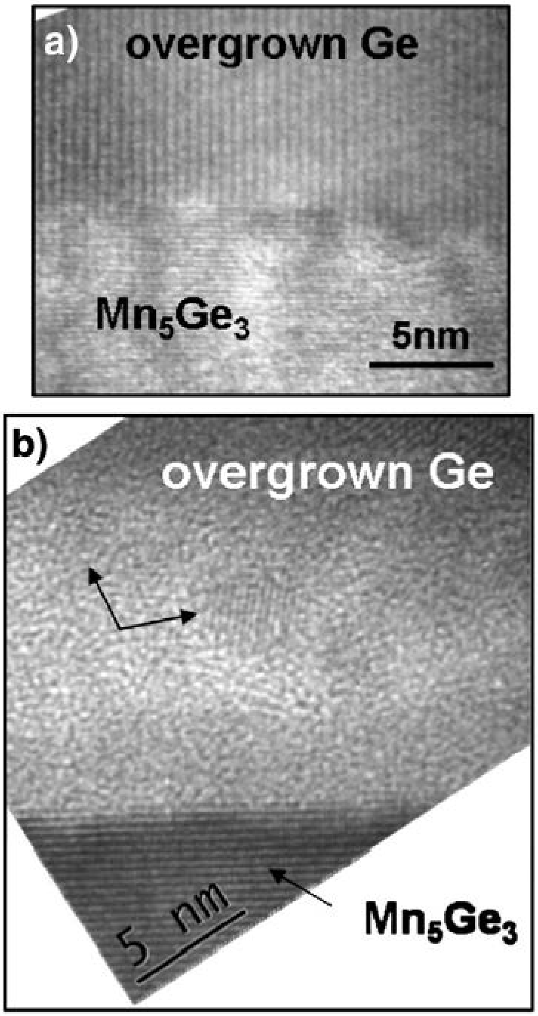

Fig. 2. Cross-sectional TEM images of the interfacial region of a Ge/Mn_5Ge_3 samples grown at 250 °C (a) and at 450 °C (b). Note that for Ge cap layers grown at 450 °C, some Mn_5Ge_3 crystallites, indicated by small arrows, are present in the Ge layers, the crystallites exhibits random orientations.

Fig. 3 displays hysteresis loops of samples corresponding to Ge cap layers grown at 250 and 450 °C, respectively. For comparison, we also report in the figure hysteresis loops of the reference sample, i.e., a simple Mn_5Ge_3/Ge(111) heterostructure which does not contain any Ge cap layers. The measurements were taken by VSM at 15 K with a magnetic field of 1 T applied in-plane (Fig. 3a) and of 2 T applied outof-plane of the sample (Fig. 3b). The hysteresis loops of the sample grown at 250 °C, measured both with magnetic field applied in-plane ($H_{//}$) and out-of-plane ($H_{\perp}$), are completely superimposed to those of the reference sample, exhibiting the same coercivity and the same magnetic anisotropy with an easy axis parallel to the interface. In other words, the magnetic signature of the Ge cap sample grown at 250 °C remains similar to that arising from a thin Mn_5Ge_3 film on Ge (111), the magnetic contributions coming from Mn atoms incorporated in the Ge layers and also from the topmost $(\sqrt{3}\times\sqrt{3})R30$ layer are neglected. This result supports TEM investigations shown in Fig. 2a in which no Mn_5Ge_3 crystallites are observable in the Ge layers.

For the sample grown at 450 °C, a reduction of the net magnetic moment is observed for both in-plane and out-of-plane measurements, as shown by the black triangle curves. More interestingly, the in-plane hysteresis loop (Fig. 3a) reveals that the easy axis of magnetization has slightly turned out of the sample plane while the hard axis still remains perpendicular to the sample surface (Fig. 3b).

Based on the above structural and magnetic results, we propose the following physical picture of the Ge capping process. Starting from the initial Mn_5Ge_3/Ge(111) surface characterized by a $(\sqrt{3}\times\sqrt{3})R30$ surface reconstruction, which is known to be rich in Mn (or Mnterminated surface) [13]. When depositing Ge on top of this surface, a sub-monolayer or even some monolayers of Mn can come away from the Mn_5Ge_3 surface and float on the top of the Ge growing front via interstitial diffusion. It is worth noting that within the resolution of TEM analysis, we did not observe any reduction of the thickness of the Mn_5Ge_3 layer before and after Ge capping. This probably implies that only excess Mn atoms on the Mn_5Ge_3 surface have left the initial Mn_5Ge_3 layer. The Mn floating phenomenon seems to be thermodynamically favorable since the Mn solubility in Ge is extremely low (less than 1% at the melting temperature). During this process, Mn atoms which failed to float on the growing front are incorporated In the Ge film. The Mn/Ge reactivity seems to depend on the substrate temperature: for a temperature of 250 °C, Mn atoms are likely uniformly distributed over the Ge layers, probably in both interstitial and substitutional sites. At this substrate temperature, Mn_5Ge_3 crystallites are not formed inside the Ge layers, as being revealed in Fig. 2a. We note that within the resolution of TEM analyses, we are not able to distinguish Mn atoms distributed over the Ge layer. On the other hand, Mn atoms which float at the growth front can react with Ge to form an ultra-thin Mn_5Ge_3 layer or an ordered surface alloy, giving rise to a $(\sqrt{3}\times\sqrt{3})R30$ reconstruction surface. It is interesting to note that recent results report on the stabilization of an ultra-thin Mn: Ge(111) surface alloy which is characterized by a $(\sqrt{3}\times\sqrt{3})R30$ reconstruction and exhibits magnetic properties similar to the Mn_5Ge_3 compound [23,24]. Therefore, the magnetic contribution of this surface layer should be an extremely small addition to that of the buried Mn_5Ge_3 film. Concerning Mn atoms incorporated in the Ge matrix, their magnetic contribution could be neglected in comparison with that of Mn_5Ge_3, since in the best case they lead to the formation of a Ge1−xMnx diluted material whose magnetic ordering is known to be at a very low temperature. The above analyses provide then a reasonable interpretation for the Ge/Mn_5Ge_3 sample grown at 250 °C whose magnetic properties behave as a single Mn_5Ge_3 layer formed on Ge(111) substrate.

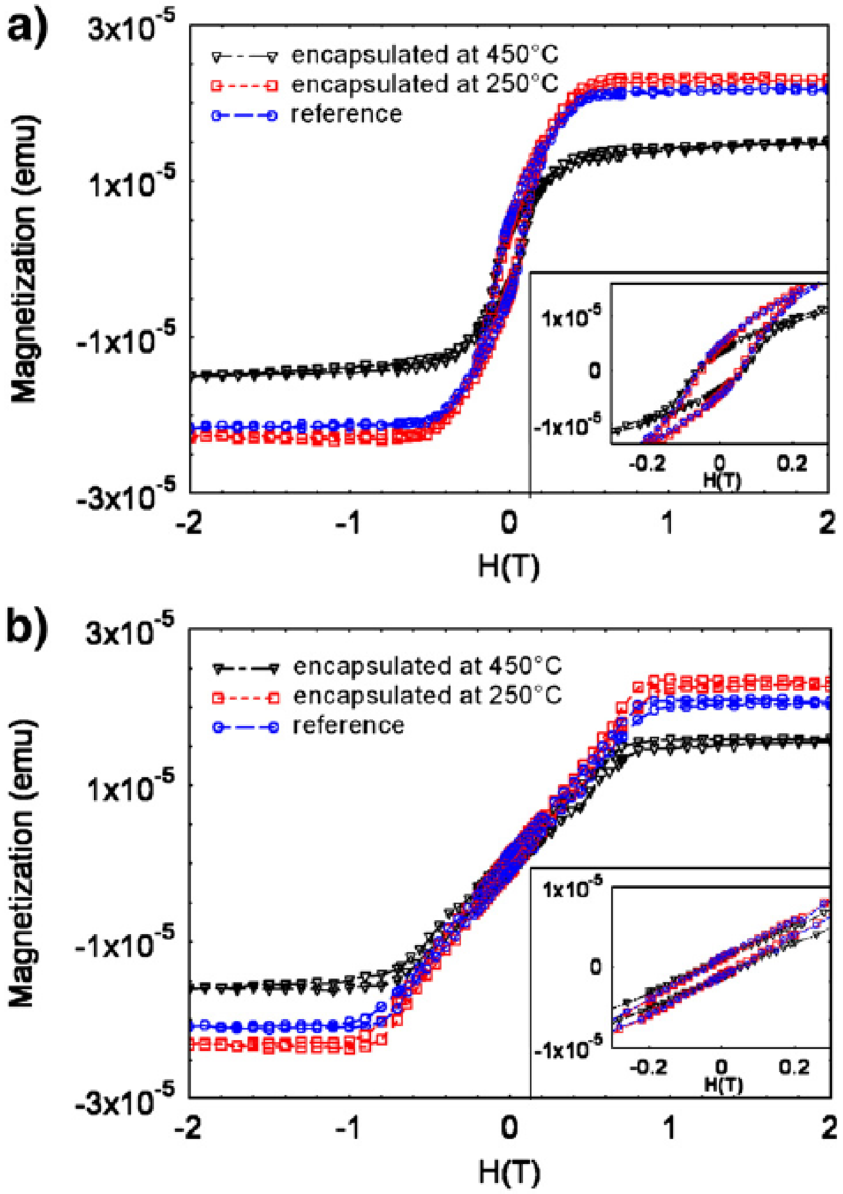

Fig. 3. Hysteresis loops of Ge/Mn_5Ge_3 samples grown at 250 and 450 °C, respectively. For comparison, we report in the blue-circle curve hysteresis loops of the reference sample, i.e., a simple Mn_5Ge_3/Ge(111) heterostructure not covered by Ge cap layers. The measurements were taken by VSM at 15 K with the magnetic field applied in-plane (a) and out-of-plane of the sample (b). Shown in insert are the magnifications of hysteresis loops around $H=0$(T).

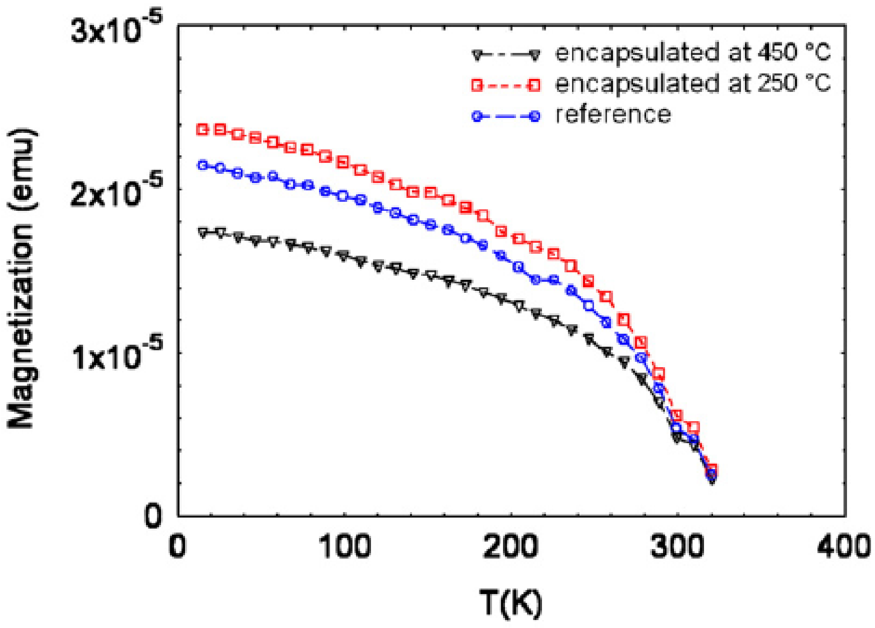

Fig. 4. Saturation magnetization as a function of temperature of Ge/Mn_5Ge_3 samples grown at 250 and 450 °C, respectively. For comparison, we report in the blue-circle curve saturation magnetization of the reference sample, i.e., a Mn_5Ge_3/Ge(111) heterostructure without Ge cap layers. Measurements have been carried out by VSM with a magnetic field of 1 T applied in the plane of the sample.

For the sample grown at 450 °C, TEM images reveal the formation of Mn5Ge3 clusters inside the Ge film. Since these clusters are randomly oriented, the variation of the preferential orientation of the clusters should induce a deviation of the hysteresis curve for the magnetic field oriented along this easy direction. This is exactly what has been observed in Fig. 3a. A decrease of the net magnetic moment can be explained by the fact that at this temperature, a larger amount of Mn can come away from the underneath Mn_5Ge_3 layer to float on the growth front and also to incorporate in the Ge layer. This idea may support the observation of a smaller saturation magnetization measured from the 450 °C cap sample as indicated in Fig. 4 (black triangle line). It is worth noting that both 250 and 450 °C cap samples exhibit a similar trend of the evolution of saturation magnetization versus the temperature and the same Curie temperature at ~330 K, as compared to the reference sample. However, the smallest value of the saturationmagnetization is observed for the sample grown at 450 °C. The 250 °C cap sample presents a slightly higher saturationmagnetization compared to that of the reference sample but the order of magnitude remains comparable.

Conclusion

In conclusion, by investigating the epitaxial overgrowth of Ge on Mn_5Ge_3/Ge(111) heterostructures we were able to characterize insitu and in real time the Mn segregation by means of RHEED. We have provided evidence that Mn acts as a surfactant during the Ge growth along the (111) orientation. The Mn segregation length is shown to depend on the growth temperature: at low growth temperatures, a short segregation length is observed but the growth front becomes rough. At high temperatures, Mn_5Ge_3 clusters have tendency to be formed in the Ge overgrown layers. To fabricate Ge/Mn_5Ge_3/Ge multilayers for spintronic applications, an intermediate range of the growth temperature, from 300 to 400 °C, seems to be needed. It remains also important to find out the ways to suppress or to reduce the Mn segregation in order to get high quality multilayers. Saturating the starting Mn_5Ge_3 surface by a small amount of carbon or atomic hydrogen mediated Ge growth would be alternative approaches to be investigated. Work in this direction is in progress.

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