An unusual phenomenon of surface reaction observed during Ge overgrowth on Mn$_5$Ge$_3$/Ge(111) heterostructures

Minh-Tuan Dau$^1$, Vinh Le Thanh$^1$, Lisa A Michez, Matthieu Petit, Thi-Giang Le, Omar Abbes, Aurélie Spiesser and Alain Ranguis

Aix Marseille Université, CNRS, CINaM-UMR 7325, F-13288 Marseille, France
E-mail: dautuan@gmail.com and lethanh@cinam.univ-mrs.fr

Abstract. The Mn$_5$Ge$_3$ compound, thanks to its room-temperature ferromagnetism, metallic character and ability to epitaxially grow on germanium, acts as a potential candidate for spin injection into group-IV semiconductors. Understanding and controlling Ge overgrowth behaviour on Mn$_5$Ge$_3$/Ge heterostructures represents a crucial step to realize Ge/Mn$_5$Ge$_3$/Ge multilayers for numerous spintronic applications. Here, we have combined structural and morphological characterizations with magnetic analyses to study the mechanisms of Ge overgrowth on epitaxial Mn$_5$Ge$_3$ layers in the temperature range of 450–550°C. It is found that deposited Ge instantly reacts with Mn to form a Mn$_5$Ge$_3$ surface layer, which, acting as a surfactant, continuously floats upwards from the growing surface to a distance larger than 70 nm. New Ge layers are successively formed underneath, allowing such a floating Mn$_5$Ge$_3$ surface layer to be stabilized by epitaxy. These observations can be considered as a typical example in which the stabilization of metastable thin films by epitaxy can overcome thermodynamic equilibrium. We have also investigated the effect of carbon adsorption on the top of the Mn$_5$Ge$_3$ layer prior to Ge deposition to control the Mn:Ge reaction. It is shown that adsorbed carbon effectively reduces...
the out-diffusion of Mn from Mn$_5$Ge$_3$, allowing Ge layers to stack up on top of Mn$_5$Ge$_3$. However, at temperatures of 450–550 °C, carbon may react with Mn to form manganese carbides and the resulting Ge overlayers are found to change their orientation from the (111) plane to the (001) plane, which has a higher surface energy. Finally, a strategy to realize Ge/Mn$_5$Ge$_3$/Ge multilayers will be addressed.

Contents

1. Introduction  
2. Experiment  
3. Results and discussion  
4. Conclusion  
References

1. Introduction

The development of active spintronic devices such as spin transistors or diodes requires materials, which are able to efficiently inject spin-polarized currents into standard semiconductors [1]. These materials should have a high Curie temperature ($T_C$), a high spin polarization and, in particular, are expected to be compatible with silicon technology. Because of the lack of high-$T_C$ diluted magnetic semiconductors [2–4], much effort has been recently devoted to the investigation of epitaxial ferromagnetic compounds [5–8]. Among these compounds, Mn$_5$Ge$_3$ has received particular interest since it exhibits a magnetic order up to room temperature [9], has a high spin polarization [10] and can be epitaxially grown on germanium [7, 11]. It has also been shown that epitaxial films with a thickness larger than 180 nm can be obtained and the epilayers exhibit a low density of threading dislocations [12]. In addition, the ferromagnetism of Mn$_5$Ge$_3$ could be increased up to ~450 K by carbon doping [13–15] and the resulting materials display excellent thermal stability [16]. It has also been demonstrated that the Mn$_5$Ge$_3$/Ge interface behaves as a Schottky contact [17, 18], thus opening up the route for spin injection into group-IV semiconductors via the tunnel effect through the Schottky barrier without needing an oxide barrier.

The epitaxial relationship and magnetic properties of Mn$_5$Ge$_3$ films grown on Ge(111) have been the subject of numerous investigations [7, 11, 12, 15, 16, 19–22] while the Ge regrowth on Mn$_5$Ge$_3$ has merely received little attention up to now. Understanding and controlling the Ge regrowth on Mn$_5$Ge$_3$ constitutes a vital issue for the realization of Ge/Mn$_5$Ge$_3$/Ge multilayers, which are the basis for numerous applications such as spin valves or the giant magnetoresistance effect. In recent reports, we have shown that for a growth temperature of 250 °C, the Mn segregation is a central problem that needs to be handled in order to get high-quality Mn$_5$Ge$_3$/Ge stacked layers [23, 24]. Here, we report on an unusual phenomenon that occurs during deposition of Ge on the top of a Mn$_5$Ge$_3$ surface at high substrate temperatures, i.e., within the range of 450–550 °C. We show that deposited Ge instantly reacts with Mn to form a Mn$_5$Ge$_3$ surface layer, which continuously floats up the growing surface, leaving behind new Ge layers that serve as a support to maintain the floating Mn$_5$Ge$_3$ layers by epitaxy. Unlike other elementary surfactant elements—such as As or Sb—where only a fraction of an atomic
monolayer floats on the growing surface, the Mn$_5$Ge$_3$ surface layer may have a thickness up to a few dozen nanometers. We also investigate the effect of carbon adsorption on the Mn$_5$Ge$_3$ surface prior to Ge deposition with the purpose of reducing the Mn out-diffusion from Mn$_5$Ge$_3$. It is shown that due to the Mn–C reaction in the surface region, the Ge overlayer changes its crystalline orientation from the (111) plane to the (001) plane.

2. Experiment

Experiments were carried out in two separate ultrahigh vacuum (UHV) systems with a base pressure better than $3 \times 10^{-10}$ mbar. One system was a standard molecular-beam epitaxial growth chamber, which was equipped with a reflection high-energy electron diffraction (RHEED) to monitor the growth mode of the growing film and an Auger spectroscopy to control the film chemical composition; the other UHV system was equipped with low-energy electron diffraction and Omicron room-temperature scanning tunneling microscope (STM). Ge and Mn evaporations were carried out using standard effusion cells; the Ge flux can be precisely measured using RHEED intensity oscillations ($5 \text{ nm min}^{-1}$) and the Mn flux, measured with a quartz-crystal microbalance, is $\sim 2 \text{ nm min}^{-1}$. Mn$_5$Ge$_3$ films were grown on Ge(111) substrates using the solid phase epitaxial (SPE) technique, which consists of Mn deposition at room temperature followed by thermal annealing at a temperature of $\sim 450^\circ$C. More details of film growth conditions can be found elsewhere [11]. The cleaning of the Ge surfaces was carried out in two steps: the first was a chemical cleaning, which begins with an ultrasonic rinsing of the samples in solvents (trichloroethylene, acetone and ethanol) to eliminate hydrocarbon contaminants that have been deposited on the substrate surface during its long storage in ambient air. Then, the Ge native oxide layers were etched in a diluted hydrofluoric acid solution (10%) for some minutes until a hydrophobic surface was obtained. The second step was an in situ thermal cleaning, which begins with an ultrasonic rinsing of the samples in solvents (trichloroethylene, acetone and ethanol) to eliminate hydrocarbon contaminants that have been deposited on the substrate surface during its long storage in ambient air. Then, the Ge native oxide layers were etched in a diluted hydrofluoric acid solution (10%) for some minutes until a hydrophobic surface was obtained. The second step was an in situ thermal cleaning, which consists of outgassing the sample for several hours at $450^\circ$C followed by flash annealing at $\sim 650^\circ$C to remove the Ge surface oxide, which can be formed during sample transfer into a high vacuum. After this step, the Ge(111) surface generally exhibits a relatively well-developed $c(2 \times 4)$ reconstruction. It is worth noting that during high-temperature flash annealing, if the vacuum in the chamber reaches a range of $10^{-7}$ mbar, C–Ge precipitates can be formed on the substrate surface. Those precipitates can be completely buried after the growth of some nm thick Ge buffer layers, giving rise to an atomically clean and well-developed, reconstructed surface. In this work, a 10 nm thick Ge buffer layer was systematically grown at $450^\circ$C to insure a good starting surface. The formation of C–Ge precipitates produces a darker contrast at the interface between the substrate and the Ge buffer layer and in some cases, as can be seen below, its presence is beneficial as it allows one to precisely measure the thickness of the upper layers.

Structural characterizations of grown films were performed by means of high-resolution transmission electron microscopy (HR-TEM) using a JEOL 3010 microscope operating at 300 kV with a spatial resolution of 1.7 Å. The magnetic properties of the films were probed with a quantum design superconducting quantum interference device (SQUID) magnetometer and the diamagnetic contribution arising from Ge was subtracted, leaving only the magnetic signal coming from Mn$_5$Ge$_3$ films. In situ, STM was used to characterize the initial stages of Mn$_5$Ge$_3$ and Ge overgrowth.
3. Results and discussion

To study Ge overgrowth on Mn$_5$Ge$_3$/Ge heterostructures, two issues regarding the starting surface need to be fulfilled: the Mn$_5$Ge$_3$ phase should not contain any mixture of other phases and its surface should be atomically smooth to avoid the influence of parameters such as surface roughness or the presence of clusters on it. Indeed, the bulk Ge–Mn phase diagram is relatively complex, as it contains, at standard temperature conditions, four phases when increasing the Ge concentration: Mn$_3$Ge, Mn$_5$Ge$_2$, Mn$_5$Ge$_3$ and Mn$_{11}$Ge$_8$ [25, 26]. The first two phases are ferrimagnetic, Mn$_5$Ge$_3$ is the unique ferromagnetic phase exhibiting a Curie temperature up to $\sim$296 K, while Mn$_{11}$Ge$_8$ is antiferromagnetic at low temperature, ferrimagnetic above 150 K and then becomes paramagnetic beyond 274 K. Note that Mn$_5$Ge$_3$ is also a unique phase, having a hexagonal structure similar to a threefold symmetry of the (111) plane of the Ge.

It is now well established that starting from a thin Mn film deposited on a Ge(111) substrate at room temperature, Mn$_5$Ge$_3$ is the unique epitaxial phase that can be formed upon annealing in the temperature range of 430–650 °C [7, 11, 12, 15, 16]. The Mn$_3$Ge$_2$ phase, which is the richest in Ge, is formed only when annealing at temperatures higher than 650 °C [16]. Below 650 °C, the coexistence of two phases, Mn$_5$Ge$_3$ and Mn$_{11}$Ge$_8$, may be observed, but only when the initial Mn film is thick enough ($\geq$ 210 nm) [27] or when films are grown on an amorphous oxide substrate [28]. Thus, according to the Mn–Ge phase diagram, Mn$_5$Ge$_3$ is not a stable phase, but can be stabilized on Ge(111) surfaces by the epitaxial effect because of the similarity between its crystal structure and Ge(111). It has been also established that the epitaxy of Mn$_5$Ge$_3$ on Ge(111) proceeds via the hexagonal (0001) plane of Mn$_5$Ge$_3$, being parallel to the (111) plane of Ge. Although we have shown that Mn$_5$Ge$_3$ films of a thickness up to 180 nm can be epitaxially grown on Ge(111) [12], we have chosen, here, a relatively small thickness ($\sim$25 nm) for the initial Mn$_5$Ge$_3$ film to ensure a high crystalline quality and a smooth surface. The structural and morphological properties of the Mn$_5$Ge$_3$ film prior to Ge deposition are thus displayed in figure 1. Figure 1(a) shows RHEED patterns taken along two main azimuths of a 25 nm thick Mn$_5$Ge$_3$ film, obtained after annealing at 450 °C for 10 min. Compared to the initial RHEED patterns of a clean Ge(111) $2 \times 4$ surface, the appearance of new 1/3 and 2/3-ordered streaks along the $[11\bar{2}]$ azimuth confirms the formation of a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction characteristic of Mn$_5$Ge$_3$. Furthermore, the observation of long streaks in the RHEED patterns indicates that the surface is highly smooth. An atomic-scale STM image of the corresponding surface is depicted in figure 1(b). The image displays highly ordered honeycomb-like arrays characteristic of a hexagonal symmetry of the Mn$_5$Ge$_3$ surface, in agreement with previous STM measurements [19]. The surface appears almost perfect, the only visible defects are some missing Mn atoms. We note that large-scale images (not shown here) reveal the presence of terraces with an average width of about 150 nm. A HR-TEM image taken near the interface region is shown in figure 3(c). The image clearly reveals atomic lattice planes of both the Ge substrate and Mn$_5$Ge$_3$ film. The film is highly ordered and the interface is atomically abrupt, no intermixing is observed. The above characterizations clearly indicate that the initial Mn$_5$Ge$_3$ film is of a high crystalline quality and its surface is atomically smooth.

Since the Mn$_5$Ge$_3$ surface gives rise to additional RHEED streaks compared to the Ge surface, it becomes possible to monitor, in real time and in situ, the Mn segregation process by measuring the intensity evolution of these streaks versus the Ge deposition time or the thickness. A typical result of intensity measurements of a 2/3 streak at three different substrate temperatures, 200, 450 and 550 °C, is reported in figure 2.
Figure 1. (a) Typical RHEED patterns taken along the [1−10] and [11−2] azimuths of a Mn$_3$Ge$_3$ surface. Additional 1/3 and 2/3 ordered streaks are observed along the [11−2] azimuth, defining a $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface reconstruction. (b) STM images of a surface of 25 nm thick Mn$_3$Ge$_3$ layer prior to Ge deposition, a surface unit cell of Mn$_3$Ge$_3$ is illustrated by a blue lozenge. Shown in the inset is a plane-view schema illustrating the epitaxial relationship between Mn$_3$Ge$_3$ and Ge(111). The blue and red lozenges represent a unit cell of Mn$_3$Ge$_3$ and Ge, respectively. Grey, orange-red and green balls represent Ge, Mn$_1$ (first, third layer), Mn$_2$ (second, fourth layer) atoms of Mn$_3$Ge$_3$ and the Ge substrate, respectively. An STM image was recorded with a negative bias (−0.8 V) and a current of 0.7 nA, Mn atoms are imaged as bright features (filled state images). (c) Atomically resolved cross-sectional TEM image taken near the interface region between the Mn$_3$Ge$_3$ and the Ge substrate.

Figure 2. The evolution of RHEED intensity recorded during Ge deposition at 200, 450 and 550 °C. Intensity measurements were taken in the region surrounding a 2/3 ordered streak (dotted line) along the [11−2] azimuth.
Two distinct behaviours regarding the scale of the deposition time of the Ge overlayers are clearly observed. At 200 °C, the intensity of the 2/3 streak vanishes at around 95 s, while at 450 and 550 °C it continues to a much higher deposition time and completely disappears only after a Ge deposition of more than 800 s. The corresponding Ge thickness is ~8 nm at 200 °C, while it is larger than 70 nm at 450 and 550 °C. It is worth noting that the surface segregation of an element during the growth of heterostructures or multilayers has been observed in many systems, including III–V materials [29] or Si on SiGe [30]. However, at usual growth temperatures (⩽600 °C), the segregation length does not, in general, exceed a dozen nanometers. To understand the different behaviour of Ge overgrowth observed at low and high temperatures as described above, we have systematically performed TEM analyses of samples at 450 and 550 °C. Figure 3(a) displays a typical cross-sectional TEM image taken after the deposition of 60 nm of Ge at 450 °C. To see the evolution of different layers in the final structure more clearly, we show, in figure 3(b), a schema of the designed sample in which the thickness of each layer is indicated. We also note that the Ge deposition rate was precisely measured from RHEED intensity oscillations (error <3%) and at 450 °C. RHEED oscillations of Ge growth on a Ge substrate (Ge homoepitaxy) confirm an almost perfect layer-by-layer growth mode. Contrary to the designed structure and also to TEM images obtained after Ge overgrowth at temperatures below 250 °C (see, for example, figure 1(c) in [24] for Ge overgrowth at 250 °C), the present image reveals that the sample surface is terminated by a Mn₅Ge₃ layer and no trace of Ge overlayers is detectable. Indeed, the observation in this TEM image of well-defined atomic rows, all being perpendicularly aligned to the interface, can be unambiguously attributed the hexagonal (0001) plane of Mn₅Ge₃, which is parallel to the (111) plane of Ge [11]. Thus, TEM analyses indicate that upon Ge deposition at 450 °C, it is not a Ge layer which is progressively formed on the surface as expected but the deposited Ge reacts with Mn to form the Mn₅Ge₃.
Figure 4. The evolution of surface morphology versus Ge deposition at 450 °C. The density of point defects is $6.3 \times 10^{12}$ and $1.1 \times 10^{13}$ cm$^{-2}$, in (a) and (b), respectively; (c) the step-bunched surface appears when increasing the deposited Ge to 15 ML. The inset shows a magnified image, the step height is a monoatomic layer; (d) for comparison, an STM image of a surface after the deposition of 15 ML of Ge on Mn$_5$Ge$_3$ at 200 °C. All images were obtained with a bias of $-0.8$ V and a current of $\sim 0.7$ nA.

The evolution of the Mn$_5$Ge$_3$ surface with Ge deposition has been probed using room-temperature STM (figure 4). Starting from a well-ordered Mn$_5$Ge$_3$ surface with large terraces (figure 1(b)), we have systematically undertaken surface imaging after deposition of every 2 monolayers (ML) of Ge. Two typical examples corresponding to the deposition of 2 and 4 MLs are shown in (a) and (b) respectively. Moreover, the step-bunched surface appears when increasing the deposited Ge to 15 ML as shown in (c).

Another interesting feature that can be seen from the image is the presence of Mn-rich clusters embedded inside the lower Ge layers. We notice that in standard Mn$_5$Ge$_3$/Ge heterostructures, Mn–Ge clusters are never observed in the Ge substrate after Mn$_5$Ge$_3$ growth at 450 °C [11, 12] or even after post-annealing up to 650 °C [16]. This point is also confirmed by the TEM image shown in figure 1(c). The formation of such clusters can be attributed to the fact that in the case of the Ge deposition on Mn$_5$Ge$_3$ at 450 °C, the initial epitaxial Mn$_5$Ge$_3$ film, because of its metastable state, is destabilized even at its interface with the substrate, which is 25 nm from the surface. Consequently, a part of Mn is detached around the interface region and diffuses into the substrate, resulting in the formation of Mn-rich clusters. This explains why the thickness of the final floating Mn$_5$Ge$_3$ film is slightly smaller than the initial one.
Figure 5. Hysteresis curves measured on the same surface area of a 25 nm thick Mn$_5$Ge$_3$ layer without Ge overgrowth (red curve) and after the deposition of 60 nm thick Ge at 450 °C (blue curve). Measurements were taken at 15 K with a magnetic field applied parallel to the surface of the sample. Shown in the inset is the evolution of magnetization versus temperature of a sample after deposition of 60 nm thick Ge on Mn$_5$Ge$_3$ at 450 °C, measurements were carried out with a magnetic field of 1 T applied parallel to the sample surface.

4 ML of Ge at 450 °C are shown in figures 4(a) and (b). Hexagonal honeycomb structures are clearly visible, confirming the formation of the Mn$_5$Ge$_3$ surface layer. Atomically-resolved surface analyses thus confirm the above RHEED and TEM results. The only parameter that changes with increasing Ge deposition is the density of point-defects, which is $6.3 \times 10^{12}$ cm$^{-2}$ at 2 ML, increasing to $1.1 \times 10^{13}$ cm$^{-2}$ at 4 ML and can go beyond $9.6 \times 10^{13}$ cm$^{-2}$ after the deposition of 10 ML of Ge (not shown here). This implies that upon Ge deposition, while the nature of the surface layer remains Mn$_5$Ge$_3$, the number of missing Mn atoms on the surface increases with increasing Ge deposition. When the deposited Ge reaches 15 ML, the density of point defects becomes so high that the corresponding surface exhibits terraces with much narrower widths (figure 4(c)). This phenomenon, which is similar to the well-known surface-step bunching that is usually observed when annealing metallic or semiconductor surfaces at very higher temperatures [32, 33], can then be attributed to the development of the surface roughness. To further illustrate the phenomenon of Ge:Mn surface reaction occurring during Ge deposition at 450 °C, we show in figure 4(d) an STM image of a surface obtained after deposition of 15 ML of Ge at 200 °C. The corresponding surface is highly disordered and no atomic resolution can be obtained in small-scale images. This implies that at low temperatures, deposited Ge covers the Mn$_5$Ge$_3$ layer and the observation of a disordered surface results from the low mobility of deposited Ge atoms. The Ge:Mn surface reaction forming a surface alloy, may occur but should have a very limited thickness. Finally, we note that for Ge deposition at 550 °C, almost the same behaviour of the Ge–Mn reaction is observed as that at 450 °C, the only noticeable difference is a slightly thicker Mn$_5$Ge$_3$ surface layer and STM investigations reveal a slightly smoother surface for the same deposited Ge thickness.

SQUID measurements have been undertaken to probe the collective magnetic properties of the whole sample. Figure 5 shows a comparison of hysteresis ($M$–$H$) curves measured at 15 K of a 25 nm thick Mn$_5$Ge$_3$ layer without Ge overgrowth (red curve) and after the deposition.
of 60 nm thick Ge at 450 °C (blue curve). The measurements clearly indicate that the Ge-overgrown sample remains ferromagnetic, confirming the above structural and surface analyses regarding the formation of the Mn₅Ge₃ surface layer. It is worth noting that, while magnetic measurements are undertaken on the same surface area in all samples, a slight decrease of both net magnetization and saturation magnetization is observed for the Ge-overgrown sample. The above reductions of magnetization can be unambiguously attributed to a decrease in the thickness of the Mn₅Ge₃ layer [12]. Displayed in the inset is a temperature-dependent magnetization of the corresponding Ge-overgrown sample. A Curie temperature around room temperature is observed, which again confirms that the surface layer consists of pure Mn₅Ge₃, ruling out the possibility of any mixture or coexistence with other Mn–Ge phases, in particular the antiferromagnetic Mn₁₁Ge₈ phase.

How can we explain the above phenomenon of the Ge–Mn reaction that leads to the formation of a Mn₅Ge₃ surface layer, which floats upwards from the growing surface at a distance as high as 70 nm while keeping the right stoichiometry and almost maintaining its initial thickness? Firstly, it is worth noting that the stoichiometry of the floating film, which was controlled by Auger spectroscopy, reveals that the intensity ratio between Ge and Mn is the same as the one before the Ge over-deposition (the intensity ratio between Ge and Mn peaks was found to be 1.6/1, a value similar to that reported in [11]). As mentioned above, in the low-temperature Ge–Mn phase diagram, Mn₅Ge₃ is not the most stable phase but the unique one, having a hexagonal structure. Due to the similarity between its hexagonal structure and the threefold symmetry of Ge(111), Mn₅Ge₃ films have been shown to be a unique phase that can be epitaxially stabilized on Ge(111). This also means that Mn₅Ge₃/Ge heterostructures can be destabilized if an adequate perturbation is applied. Previously, we have shown that post-thermal annealing can modify such equilibrium [16]. When depositing Ge on the Mn₅Ge₃ surface in the temperature range of 450–550 °C, it may be natural to expect that the Mn₅Ge₃ compound can be formed on the surface. Together with Ge atoms, which continuously arrive on the surface during the deposition, the formation of Mn₅Ge₃ requires the using up of Mn. As a consequence, the whole Mn₅Ge₃ layer floats upwards from the surface and leaves behind a new Ge layer, which allows the floating Mn₅Ge₃ layer to stabilize by the epitaxial effect. It is worth noting that the out-diffusion of Mn into the Ge substrate to form a cluster can be also considered as a destabilization of Mn₅Ge₃/Ge heterostructures. However, if the size and the density of Mn–Ge clusters are small and low enough, epitaxy between the Mn₅Ge₃ surface layer and the newly formed Ge layer can be maintained.

Another question that may arise is, over what distance can the floating of the surface Mn₅Ge₃ layer keep its integrity? This probably depends on the Ge growth rate and the Ge deposition temperature. These two parameters directly govern the upward Mn diffusion coefficient, the evolution of the surface roughness and the quality of the new Ge layer underneath Mn₅Ge₃.

The above results can thus be considered as a typical example in which the epitaxial relationship can counterbalance the formation of thermodynamically more stable phases. However, epitaxy leads to a metastable equilibrium, which can be broken under adequate perturbations. An example illustrating this point is that an epitaxial Mn₅Ge₃ layer with a thickness larger than 100 nm, can be kept stable for an almost unlimited time when annealing at 450–550 °C under vacuum but as soon as Ge deposits on its surface, a Mn out-diffusion from the interface region to the substrate is provoked.

In addition to contributing to fundamental research, the results obtained in this work also have practical implications. Based on the above results it becomes clear that any attempt to
Figure 6. Cross-sectional TEM images of a sample corresponding to adsorption of 8 ML of carbon on a 25 nm thick Mn$_5$Ge$_3$ layer followed by the deposition of 60 nm of Ge at 450 $^\circ$C; (a) a large-scale image and (b) atomically-resolved image taken at the interface region between the Ge overlayers and the Mn$_5$Ge$_3$ film. The Ge overlayers are found to be oriented along the $\langle 001 \rangle$ direction, which is rotated $\sim 54^\circ$ from the expected $\langle 111 \rangle$ direction.

produce Ge/Mn$_5$Ge$_3$/Ge stacked layers should avoid high-temperature Ge deposition to prevent a Ge:Mn reaction forming surface Mn$_5$Ge$_3$ layers. Recently, we have shown that adsorption of some MLs of carbon on the top of Mn$_5$Ge$_3$ followed by Ge deposition at 250 $^\circ$C, can greatly reduce Mn segregation [24]. The Ge overlayers were shown to be epitaxial with the (111) plane being parallel with the hexagonal (0001) plane of Mn$_5$Ge$_3$. We then applied this approach to the case of Ge deposition at 450 $^\circ$C. Numerous experiments have been systematically carried out with a carbon content ranging from 1 up to 12 ML. Up to a carbon content of 6 ML, TEM and SQUID characterizations indicate that most of the adsorbed carbon diffuses into the Mn$_5$Ge$_3$ lattice underneath and the formation of surface Mn$_5$Ge$_3$ layers is maintained. The only advantage is an increase of the Curie temperature of the whole structure up to 360–380 K, which can be explained by the diffusion of adsorbed carbon into interstitial sites of the Mn$_5$Ge$_3$ lattice [15]. Figure 6 shows cross-sectional TEM images of a sample corresponding to the adsorption of 8 ML of carbon on a 25 nm thick Mn$_5$Ge$_3$ layer followed by the deposition of 60 nm of Ge at 450 $^\circ$C. Unlike the case shown in figure 3(a), the large-scale image, presented in figure 6(a), clearly indicates that a Ge overlayer of 60 nm thick is now formed on the top of Mn$_5$Ge$_3$ and their interface is relatively smooth. However, when examining atomically-resolved images around the interface region (figure 6(b)), it is found that the Ge overlayer is epitaxial but has a new crystalline orientation. Instead of the expected (111) plane, we now find the (001) plane of Ge being parallel to the hexagonal (0001) plane of Mn$_5$Ge$_3$. The distance between the interreticular planes, measured along the [111] direction, is 3.2 Å, which is in agreement with the theoretical value. Note that the TEM images shown here have been taken along the [11−2] direction, allowing a direct measurement of the angle between the [111] direction and the normal of the layer surface. The measured angle is $\sim 54^\circ$, a value which is expected between these two directions. Taking into account the existence of a lattice mismatch as high as $\sim 11.1\%$ between twofold-symmetry Ge(001) and hexagonal Mn$_5$Ge$_3$(0001) [34], a very interesting feature observed here is that the Ge overlayers are two-dimensional and almost free of dislocations. Another noteworthy point is that a change of the crystalline orientation from the (111) to the (001) planes is not naturally expected since the (001) plane has a higher...
surface energy than that of the (111) plane (for example, in the case of silicon, the surface energy is 1467 mJ m\(^{-2}\) for the (111) plane while it is 2512 mJ m\(^{-2}\) for the (001) plane) \[35\]. The symmetry change of the Ge overlayers can be attributed to the fact that at a temperature as high as 450 °C, carbon atoms, which have not diffused into the lower Mn\(_5\)Ge\(_3\) layer due to a high concentration, react with Mn to form surface manganese carbides (MnC). Indeed, recently using thermodynamical calculations \[15\], we have shown that when doping Mn\(_5\)Ge\(_3\) with carbon, the Mn\(_5\)Ge\(_3\) lattice can host carbon into its interstitial sites up to a concentration \(x\) of about 0.5–0.6. We note that by considering the molecular formula of the Mn\(_5\)Ge\(_3\)C\(_x\) compound, the atomic concentration of carbon corresponding to \(x = 1\) is 11.11%. When the carbon concentration \(x\) becomes higher than 0.6–0.7, the formation of manganese carbide phases, such as Mn\(_7\)C\(_3\) and/or Mn\(_5\)C\(_2\), becomes energetically favourable. The darker contrast observed near the Mn\(_5\)Ge\(_3\) surface region (figure 6(b)) may arise from these Mn–C phases. However, due to the small size of this surface layer or also of clusters, analyses performed using \textit{in situ} Auger spectroscopy and energy dispersive x-ray spectroscopy from TEM microscopy, do not allow us, at present, to identify which MnC phase is formed at the interface region. Nevertheless, the above example confirms the limit of using the carbon-adsorption approach to realize multilayers at high growth temperatures. The window of processing is so narrow that a too small amount of carbon does not allow the prevention of the Ge–Mn surface reaction while a higher amount of carbon is conducive to the formation of manganese carbides on the surface, which modifies the orientation of the Ge overlayers and may prevent, in turn, the formation of epitaxial and two-dimensional second and upper layers of Mn\(_5\)Ge\(_3\).

4. Conclusion

To summarize, we have revealed an unusual phenomenon of a chemical reaction between deposited Ge and Mn out-diffusing from Mn\(_5\)Ge\(_3\) in the temperature range between 450 and 550 °C. While the detailed mechanisms of Mn diffusion and segregation remain to be understood, we have shown that not only a single element but also a compound having a thickness up to a few dozens of nm can float upwards from the growing surface, acting as a surfactant during epitaxial growth. The stabilization of the Mn\(_5\)Ge\(_3\) surface layer over a distance as high as 70 nm during its floating process, represents a typical example in which the epitaxial effect is the main driving force allowing the stabilization of the metastable phases. We have also shown that while epitaxial layers are crucial for device fabrication, adequate external perturbations like thermal annealing or the deposition of other elements can modify the stability of an epitaxial equilibrium. From a practical point of view, our results allow us to argue that any attempt to produce Ge/Mn\(_5\)Ge\(_3\) multilayered structures should be carried out at temperatures below 450 °C to prevent the Ge–Mn reaction. Our results also point out that while carbon adsorption on Mn\(_5\)Ge\(_3\) has been shown to be efficient in preventing Mn out-diffusion, experiments should be carried out at temperatures below 450 °C to avoid the formation of manganese carbides.

References

[1] Dietl T 2010 \textit{Nature Mater.} \textbf{9} 965
[2] Park Y D, Hanbicki A T, Erwin S C, Hellberg C S, Sullivan J M, Mattson J E, Ambrose T F, Wilson A, Spanos G and Jonker B T 2002 \textit{Science} \textbf{295} 651

\textit{New Journal of Physics} \textbf{14} (2012) 103020 (http://www.njp.org/)
[3] Stroppa A, Picozzi S, Continenza A and Freeman A J 2003 Phys. Rev. B 68 155203
[4] Stroppa A, Kresse G and Continenza A 2011 Phys. Rev. B 83 085201
[5] Jaafar R, Nehme Y, Berling D, Bubendorff J L, Mehdaoui A, Pirri C, Garreau G and Uhliaq-Bouillet C 2008 Appl. Phys. Lett. 93 033114
[6] Hamaya K, Itoh H, Nakatsuka O, Ueda K, Yamamoto K, Itakura M, Taniyama T, Ono T and Miyao M 2009 Phys. Rev. Lett. 102 137204
[7] Zeng C, Erwin S C, Feldman L C, Li A P, Jin R, Song Y, Thompson J R and Weitering H H 2003 Appl. Phys. Lett. 83 5002
[8] Picozzi S, Continenza A and Freeman A J 2004 Phys. Rev. B 70 235205
[9] Tawara Y and Sato K 1963 J. Phys. Soc. Japan 18 773
[10] Panguluri R P, Zeng C, Weitering H H, Sullivan J M, Erwin S C and Nadgorny B 2005 Phys. Status Solidi b 242 R67
[11] Olive-Mendez S F, Spiesser A, Michez L A, Le Thanh V, Glachant A, Derrien J, Devillers T, Barski A and Jamet M 2008 Thin Solid Films 517 191
[12] Spiesser A, Olive-Mendez S F, Dau M T, Michez L A, Watanabe A, Le Thanh V, Glachant A, Derrien J, Barski A and Jamet M 2010 Thin Solid Films 518 S113
[13] Gajdzik M, Sürgers C, Kelemen M T and Löhnseyen H V 2000 J. Magn. Magn. Mater. 221 248
[14] Slipukhina I, Arras E, Mavropoulos Ph and Pochet P 2009 Appl. Phys. Lett. 94 192505
[15] Spiesser A et al 2011 Phys. Rev. B 84 165203
[16] Spiesser A, Le Thanh V, Bertaina S and Michez L A 2011 Appl. Phys. Lett. 99 121904
[17] Nishimura T, Nakatsuka O, Akimoto S, Takeuchi W and Zaima S 2011 Microelectron. Eng. 88 605
[18] Sellai A, Mesli A, Petit M, Le Thanh V, Taylor D and Henini M 2012 Semicond. Sci. Technol. 27 035014
[19] Zeng C, Zhu W, Erwin S C, Zhang Z and Weitering H H 2004 Phys. Rev. B 70 205340
[20] De Padova P et al 2011 Surf. Sci. 605 638
[21] Stroppa A and Peressi M 2007 Phys. Status Solidi a 204 44
[22] Spiesser A, Virot F, Michez L A, Hayn R, Bertaina S, Favre L, Petit P and Le Thanh V 2012 Phys. Rev. B 86 035211
[23] Dau M T, Spiesser A, Le T G, Michez L A, Olive-Mendez S F, Le Thanh V, Petit M, Raimundo J M, Glachant A and Derrien J 2010 Thin Solid Films 518 S266
[24] Dau M T, Le Thanh V, Le T G, Spiesser A, Petit M, Michez L A and Daineche R 2011 Appl. Phys. Lett. 99 151908
[25] Gokhale A B and Abbasschian R 1990 Bull. Alloy Phase Diagrams 11 460
[26] Arras E, Caliste D, Deutsch T, Laçon F and Pochet P 2011 Phys. Rev. B 83 174103
[27] Abbes O, Xu F, Portavoce A, Girardeaux C, Hoummada K and Le Thanh V 2012 Defect Diffus. Forum 323–325 439
[28] Abbes O, Xu F, Portavoce A, Hoummada K, Le Thanh V and Girardeaux C 2011 Solid State Phenom. 172–174 579
[29] Moison J M, Guille C, Houzay F, Barthe F and Van Rompay M 1989 Phys. Rev. B 40 6149
[30] Ohtani N, Molder S M, Xie M H, Zhang J and Joyce B A 1993 Surf. Sci. 284 305
[31] Zeng C, Zhang Z, Van Benthem K, Chisholm M F and Weitering H H 2008 Phys. Rev. Lett. 100 066101
[32] Yoon M, Lee H N, Hong W, Christen H M, Zhang Z and Suo Z 2007 Phys. Rev. Lett. 99 055503
[33] Kandel D and Kaxiras E 1996 Phys. Rev. Lett. 76 1114
[34] Bihler C, Jaeger C, Vallatis T, Gjukic M and Brandt M S 2006 Appl. Phys. Lett. 88 112506
[35] Howe J M 1997 Interfaces in Materials (New York: Wiley)