Effect of thickness on structural and magnetic properties of Mn_5Ge_3 films grown on Ge(111) by solid phase epitaxy

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Abstract

We report on the structural and magnetic properties of epitaxial Mn5Ge3 films grown by molecular beam epitaxy (MBE) on Ge(111) substrates with film thicknesses ranging from 5 to ~185nm. It is shown that epitaxial Mn_5Ge_3 films with a thickness as large as 185 nm can be obtained despite a misfit of ~3.7% between two materials. Measurements of the in-plane lattice parameter carried out by means of reflection high-energy electron diffraction (RHEED) revealed that Mn_5Ge_3 films were fully relieved of strain after deposition of the first monolayer. For film thicknesses smaller than 50 nm, the easy axis of magnetization is found to lie in the hexagonal basal (001) plan, parallel to the interface and the hard axis is perpendicular to the layers. When the film thickness increases above 50 nm, magnetization measurements with magnetic field applied in-plane of the samples reveal that the easy axis of magnetization progressively turns out of the hexagonal basal (001) plan of Mn_5Ge_3. Even for Mn_5Ge_3 films with a thickness larger than 185 nm, the easy axis of magnetization never becomes perpendicular to the sample surface as being expected for bulk Mn_5Ge_3 materials.

Keywords: Spintronics, Intermetallic ferromagnetic compound, Spin injection.

Introduction

The emerging field of spintronics, which is regarded as nextgeneration electronics, would be dramatically boosted if roomtemperature ferromagnetism could be added to semiconductor devices and integrated circuits that are compatible with silicon CMOS technology. Two main approaches have been explored in order to inject spin-polarized current into semiconductors: use of ferromagnetic metal/semiconductor heterostructures via an insulator or a Schottky barrier [1] and use of ferromagnetic semiconductors (DMS) as a spin aligner [2]. For the first approach, if interesting results have been demonstrated in the Fe/GaAs system, the efficiency of spin injection into group-IV semiconductors remains very low due to the formation of interfacial silicides or germanides, which, for most of them, are not ferromagnetic. The second approach is hampered by low ferromagnetic ordering temperatures in most DMS investigated up to now. In the best case, the ferromagnetic order subsists up to a temperature of 170 K [3].

Recently, an alternative approach has been proposed in which defined ferromagnetic compounds, such as Fe_3Si [4,5], $Fe_{1.7}Ge$ [6] or Mn_5Ge_3 [7–11], were directly epitaxially grown on Si or Ge and act as a spin injector. Among these compounds, Mn_5Ge_3 is of particular interest since it is intermetallic and ferromagnetic up to room temperature. Theoretical calculations predicted a high spin-injection efficiency along the c axis of Mn_5Ge_3 [9] and a spin polarization up to 42% has been demonstrated. Mn_5Ge_3 thin films have been shown to epitaxially grow on Ge(111) substrates [7,8,11], allowing a direct injection of spin polarized current into a group-IV semiconductor. It is worth noting that it is possible to enhance the magnetic properties and spin polarization of Mn_5Ge_3 films by adding a small amount of carbon [12–14] or doping with iron in substitutional sites [15,16].

In a recent work [11],we have studied the epitaxial growth and the magnetic properties of Mn_5Ge_3 films on Ge(111) substrates. While Mn_5Ge_3 is not the most stable phase in the bulk Mn–Ge phase diagram, we have shown that Mn_5Ge_3 in the form of thin films is the unique epitaxial phase, which can be stabilized on Ge(111). We have also shown that in contrast to bulk Mn_5Ge_3 material which has its easy axis of magnetization along the c axis, epitaxial Mn_5Ge_3 films whose thicknesses are smaller than 50 nm have an easy axis of magnetization lying in the hexagonal basal (001) plane, parallel to the interface between the Mn_5Ge_3 films and the substrate.

The aims of the present work are to investigate the effect of the film thickness on the strain state and the magnetic properties of epitaxial Mn_5Ge_3 films grownon Ge(111).Weshowthat due to the existence of a misfit as high as ~3.7%, Mn_5Ge_3 films are fully relaxed of strain after deposition of the first monolayer. Interestingly, almost no threading dislocations are present in the films. For Mn_5Ge_3 films whose thickness is smaller than 50 nm, the easy axis of magnetization lies in the layers and the hard axis is perpendicular to the sample surface. For thicker films, the easy axis ofmagnetization seems to turn out of the hexagonal basal (001) plan but never becomes perpendicular to the sample surface as being expected for bulk Mn_5Ge_3 materials.

Experimental details

The samples were grown in a MBE chamber with a base pressure better than 1×10^{-10} Torr. The growth chamber is equipped with a RHEED technique to monitor the epitaxial growth process and an Auger electron spectrometer to control the cleanliness of the substrate surface and the stoichiometry of the grown films. Ge samples cleaved from Ge(111) epi-ready wafers with a nominal resistivity of 100 Ωcm were used. The

cleaning of Ge surfaces 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 oxide [11]. After this step, the Ge(111) surface generally exhibits a relatively welldeveloped c(2×4) reconstruction. To insure a good starting Ge surface prior to Mn deposition, a 30 nm thick Ge buffer layer was systematically grown at a substrate temperature of 600 °C followed by a thermal annealing at 700 °C for ~10 min.

Ge and Mn were evaporated from standard Knudsen effusion cells, the Ge deposition rate was obtained from RHEED intensity oscillations whereas the Mn deposition rate was determined from cross-sectional transmission electronic microscopy (TEM) images of a thick Mn layer deposited on Ge(111) at room temperature. The standard growth rates used is this work is ~3.3 nm/m for Ge and 0.4 nm/m for Mn. The Mn deposition was carried out at room temperature and subsequent thermal annealing was undertaken until the observation of the (√3×√3)R30 reconstruction characteristic of the Mn_5Ge_3 films. Such a growth technique is so-called solid-phase epitaxy (SPE).

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 vibrating sample magnetometer (VSM) with a magnetic field applied both in the plane and 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.

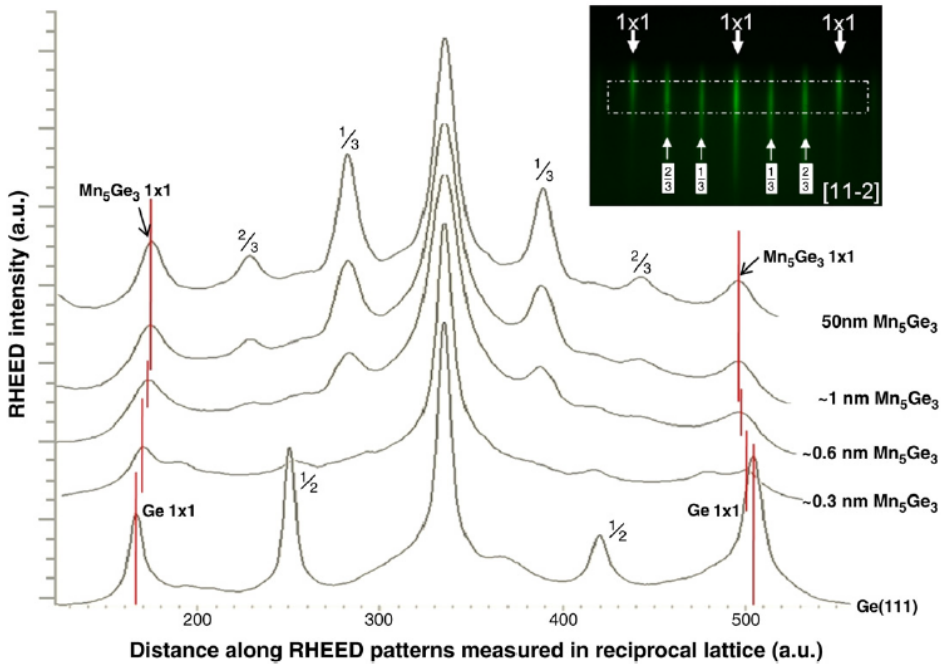

Fig. 1. Evolution of the in-plane lattice parameter of epitaxial Mn_5Ge_3 films with increasing the film thickness. Shown in the insert is a RHEED pattern along a [11–2] azimuth and RHEED intensity measurements were taken in the dotted line rectangle.

As we have indicated in a recent work [11], Mn deposition on Ge (111) at room temperature first results in the formation of a thin amorphous layer on which Mn crystallites are formed for deposition thickness larger than 2 nm. Thermal annealing of a room temperature deposited Mn layer at around 430–450 °C gives rise to a RHEED $(\sqrt{3}\times\sqrt{3})R30$ surface reconstruction, which has been attributed to the Mn_5Ge_3 compound. Such a reconstruction is characterized by the observation of 1×1 RHEED streaks along the [1–10] direction and 1/3- and 2/3-ordered streaks along the [11–2] direction. The epitaxial relationship between Mn_5Ge_3 and Ge(111) deduced from selected area electron diffraction (SAED) of transmission electron diffraction (TED) patterns implies that the hexagonal basal (001) plane of Mn_5Ge_3 is parallel to the (111) plane of Ge(111), which also has a pseudo-hexagonal symmetry [11]. The unit cell parameters of Mn_5Ge_3 are a_{hex}=7.184 Å and c=5.053 Å, the hexagonal (001) basal

plane of Mn_5Ge_3 matches the (111) plane of Ge to within 3.7% [a_{hex} of Ge(111)=6.919 Å]. Taking into account a such high misfit between two materials, some questions arise:what is the growth mode of Mn_5Ge_3 on Ge(111)? is it a two-dimensional (2D) or islanding (3D) growth?what is the strain state of the layer, is the layer pseudomorphic or strain relaxed?

RHEED technique is known to be a powerful tool to investigate the growth mode of epitaxial films. Thanks to the feature of glancing incidence, RHEED can reveal almost instantaneously changes either in the surface morphology or in the surface structure of the growing film. It is well established that a 2D growth is associated with streaky RHEED patterns due to reflection diffraction on a smooth surface, while a 3D growth is characterized by spotty patterns due to transmission diffraction through 3D islands. Fig. 1 displays the evolution of the in-plane lattice parameter of Mn_5Ge_3 films, measured by RHEED at different film thicknesses. The RHEED intensity was measured in a fixed region indicated by dotted lines on [11–2] pattern, displayed in the inset of the figure. We note that along this azimuth, 1/ 3- and 2/3-ordered streaks will appear when Mn_5Ge_3 compound is formed upon thermal annealing. The lowest curve in the figure corresponds to the clean Ge(111) surface prior to Mn_5Ge_3 growth. Taking the distance between 1×1 streaks on the clean Ge(111) surface as a reference, the figure reveals that a partial strain relaxation has occurred for film thicknesses as small as 0.3 and 0.6 nm. For a Mn_5Ge_3 film thickness of ~1nm, the strain accumulated in the grown film has fully released and the film in-plane lattice parameter becomes equal to that of the bulk material. In other words, by comparing the distance between 1×1 streaks of the Ge(111)

substrate with those taken from Mn_5Ge_3 films of 1 and 50 nm, one can find a difference of ~3.7%, a value expected from the misfit of two materials.

A feature of particular interest is that despite the fully relaxed strain state in Mn_5Ge_3 films, observed for a film thickness as small as 1 nm, Mn_5Ge_3/Ge(111) heterostructures exhibit in general a high crystalline quality and an interface atomically resolved. In ref. [11], we reported a TEM image of an epitaxial 10 nm thick Mn_5Ge_3 film in which almost no misfit dislocations were observable and the interface was smooth at the atomic scale. Guided by the aims to search the presence of misfit defects in Mn_5Ge_3 films, we have investigated TEM analysis at various areas of the sample and show in Fig. 2a an image in which typical defects are observed for a 10 nm thick film. Only misfit point defects are observable as can be seen in the dotted circle region, no threading dislocations are present in the whole film. These features are 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 4 monolayers, beyond which islanding growth mode occurs [17]. For a thickness of deposited Ge of about some tens of nanometers, a density of threading dislocations up to $108cm^{-2}$ can be observed and the growth front become extremely rough. While much still remains to study in order to understand the epitaxial growth of Mn_5Ge_3 on Ge, the above feature of Mn_5Ge_3/Ge heterostructures can be partially attributed to a high value of the elastic modulus of Mn_5Ge_3, which is 110 GPa as

compared to 77.2 GPa for Ge, allowing Mn_5Ge_3 films to be easily elastically deformed on Ge.

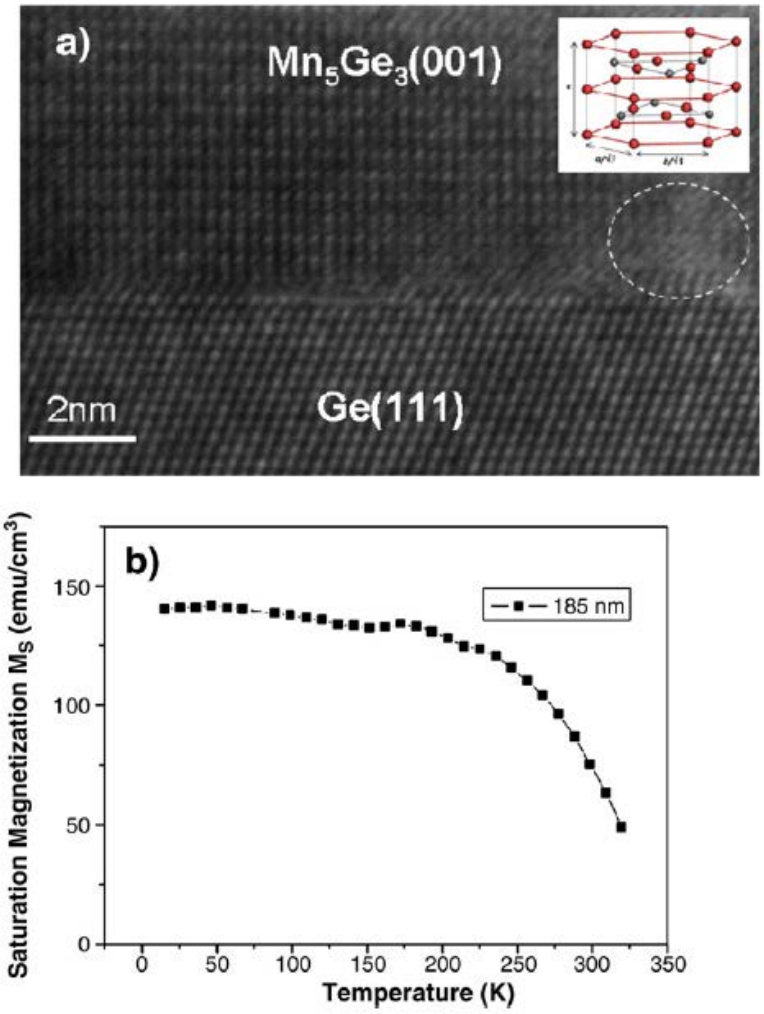

Fig. 2. a) High-resolution TEM image of a ~10nm thick Mn_5Ge_3 film epitaxiallly grown on Ge(111). Shown in the insert is the hexagonal structure of Mn_5Ge_3. The interface between film and substrate is sharp at the atomic scale and no threading dislocations are visible despite a misfit of 3.7%. Only some point defects are observable in the region indicated by the dotted line circle. b) Temperature dependence of the saturation magnetization of a 185 nm thick Mn_5Ge_3 film measured with a magnetic field of 0.5 T applied in the plane of sample. The Curie temperature is observed up to ~330–340 K, compared to 296 K for the bulk material.

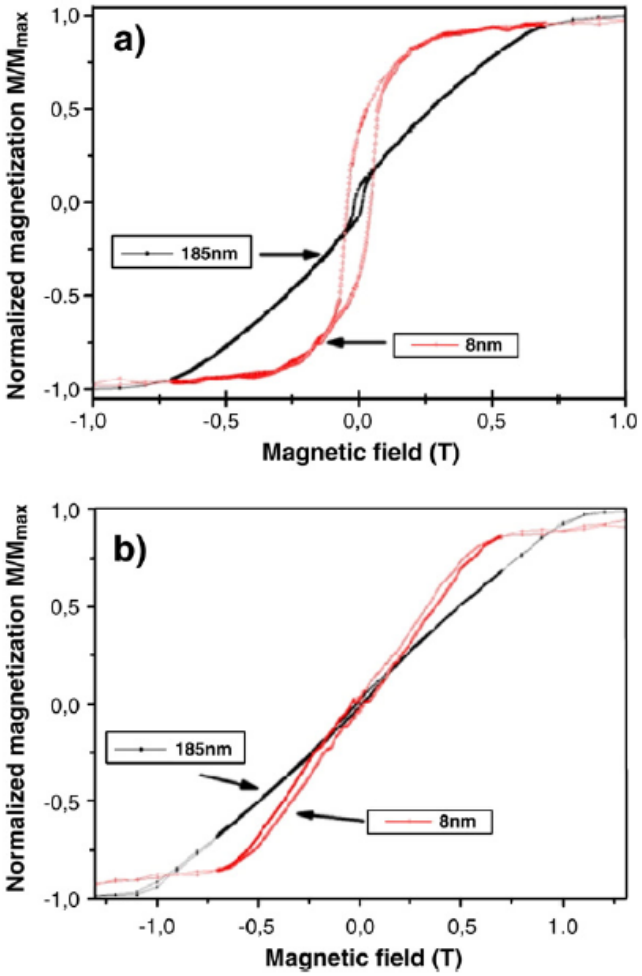

Fig. 3. Hysteresis loops of a 8 nm-thick (red line) and a 185 nm-thick (black line) Mn_5Ge_3 films measured at 15 K; Graph (a) correspond to a magnetic field applied in the plane and (b) perpendicular to the plane of the films.

The temperature dependence of the magnetic properties has been analyzed by using VSM with a magnetic field of 2 T applied out-of plane and of 1 T applied in-plane of samples. Magnetization measurements at saturation have been carried out from 15 K to 350 K. In the range of the investigated film thickness varying from 5 to 185 nm, the overall magnetic moment of Mn_5Ge_3 is found to increase linearly with the film thickness. The saturation magnetizations, i.e. the magnetic moment per volume unity, of all films are then superimposed. We show in Fig. 2b an example of the temperature dependence

of the saturation magnetization of a 185 nm thick film. The Curie temperature is observed up to ~330–340 K, compared to 296 K of the bulk material. It is worth noting that in the previous work [11], a Curie temperature of only ~296 K was observed for epitaxial Mn_5Ge_3 films. Indeed, we found that the Curie temperature of Mn_5Ge_3/Ge heterostructures depends on parameters such as the surface preparation prior to growth, the annealing procedure and the film crystalline quality.

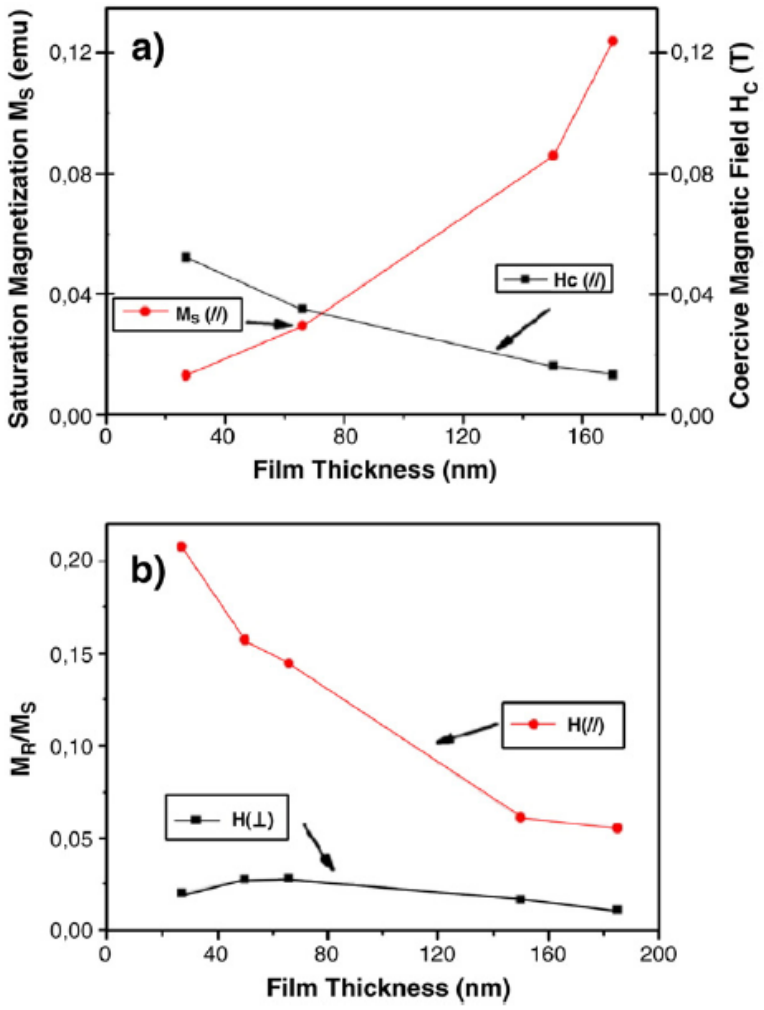

Fig. 4. a) Thickness dependence of the saturation magnetization (M_S) and the coercive field (H_c) of Mn_5Ge_3 films measured at 15 K. b) Thickness dependence of the remanent magnetization (M_r) on the saturation magnetization (M_s) of Mn_5Ge_3 films measured at 15 K. The magnetic field is in the plane (red dots) and perpendicular to the plane of the films (black squares).

To better take notice of the effect of the thickness on the magnetic anisotropy of Mn_5Ge_3 films, we present in Fig. 3 hysteresis loops measured at 15 K for two film thicknesses of 8 and 185 nm. Fig. 3a corresponds to in-plane measurements ($H_{//}$) and Fig. 3b to out-ofplane measurement ($H\perp$). The red curves arise from a thin Mn_5Ge_3 layer of 8 nm thick. The shape of the hysteresis loops measured inplane and out-of-plane of the 8 nm thick sample clearly indicates that the direction perpendicular to the film surface is a hard axis and the easy axis of magnetization lies in the hexagonal basal (001) plane. This is correlated with the magnetic field required to saturate the film magnetization, which is about 0.3 T for the in-plane magnetization, whereas it is twice larger for out-of plane magnetization. It is worth noting that the same behaviour is observed for all films whose thickness is smaller than 50 nm. While in bulk Mn_5Ge_3 material, the easy axis of magnetization is along the c axis, the above feature of the magnetic anisotropy observed in thin films could be attributed to the shape anisotropy.

When increasing the film thickness, the coercive field becomes smaller, but more importantly, the easy axis of magnetization is progressively getting out of the plane of the sample. The black curve shown in Fig. 3a and corresponds to a 185 nm thick film clearly illustrates this evolution. It can be also seen that squareness of the inplane hysteresis loop is decreased and the magnetic field required to saturate a 185 nm film is greatly increased.When comparing in-plane and out-of-plane hysteresis loops shown Fig. 3a and b, one can state that it still exists a difference between easy and hard axes and hard axis always remains perpendicular to the sample surface. However the easy axis is no longer locked in the layer, it turns out of the sample plane. It seems likely that

the shape anisotropy becomes less and less dominant when the film thickness increases.

We summarize in Fig. 4 the effect of the film thickness on the saturation magnetization (M_S), the coercive field (H_c) and also on the ratio between the remanent magnetization (M_r) and the saturation magnetization (M_s) ofMn5Ge3 films. As being expected, the saturation magnetization is found to increase with increasing the film thickness. Indeed, since M_S depends on the volume of the sample, a linear increase of M_S upon the film thickness is expected. The coercive field H_c is found to monotonously decrease with increasing the film thickness. At present, the origin of the thickness dependence of the Mn_5Ge_3 coercivity is not clearly understood. In general, for polycrystalline films the decay of coercivity with increasing the film thickness t can be described by the well known Néel formula involving the domain wall motion theory, $H_c \propto t^{-4/3}$ [18]. In practice, coercivity of polycrystalline films can be influenced by a variety of parameters, such as the film microstructure, the nature of the substrate, the surface roughness and the film composition. Experimentally, coercivity of polycrystalline films has been shown to exhibit a complex behaviour as a function of the film thickness [19]. Further studies are in progress to clarify the detail of the magnetic interactions in epitaxial Mn_5Ge_3 films. The thickness dependence of the ratio of remanence to saturation moment, M_r/M_s, is illustrated in Fig. 4b. With a precision of the order of 10%, the out-of-plane M_r/M_s ratio remains nearly constant with increasing the film thickness. On the other hand, the in-plane M_r/M_s ratio displays a monotonous decrease with increasing the film thickness. As described above, such a decrease of the in-plane

M_r/M_s ratio results from the magnetic field required to saturate the in-plane magnetization which increases when increasing the film thickness.

Conclusion

In summary, we have studied the epitaxial growth and the magnetic properties of Mn_5Ge_3 on Ge(111) in a large range of the film thickness varying from 5 to ~180 nm. Despite the existence of a lattice mismatch as high as 3.7%, epitaxial Mn_5Ge_3 films with atomically smooth interface and high crystalline quality can be obtained. Furthermore, RHEED analyses during growth reveal that two-dimensional and epitaxial growth can be observed for a film thickness higher than 180 nm. In contrast to bulk Mn_5Ge_3 material which has uniaxial anisotropy along the c axis, epitaxial Mn_5Ge_3 films of thickness smaller than 50 nm exhibit an easy axis of magnetization lying in the hexagonal basal (001) plane, parallel to the interface between the Mn_5Ge_3 films and the substrate. When the film thickness increases above 50 nm, the easy axis of magnetization turns progressively out of the hexagonal basal (001) plan of Mn_5Ge_3. It is worth noting that even for Mn_5Ge_3 films with a thickness larger than 180 nm, the easy axis of magnetization never becomes perpendicular to the sample surface as being expected for bulk Mn_5Ge_3 materials.

References

[1] C. Timm, J. Phys. Condens. Matter 15 (2003) R1865.

[2] O.M.J. van't Erve, G. Kioseoglou, A.T.Hanbicki, C.H. Li, B.T. Jonker, R.Mallory, M. Yasar, A. Petrou, Appl. Phys. Lett. 84 (2004) 4334.

[3] Y.D. Park, A.T. Hanbicki, S.C. Erwin, C.S. Hellberg, J.M. Sullivan, J.E. Mattson, T.F. Ambrose, A. Wilson, G. Spanos, B.T. Jonker, Science 295 (2002) 651.

[4] K. Hamaya, K. Ueda, Y. Kishi, Y. Ando, T. Sadoh, M. Miyao, Appl. Phys. Lett. 93 (2008) 132117.

[5] Y. Ando, K. Hamaya, K. Kasahara, Y. Kishi, K. Ueda, K. Sawano, T. Sadoh, M. Miyao, Appl. Phys. Lett. 94 (2009) 182105.

[6] R. Jaafar, Y. Nehme, D. Berling, J.L. Bubendorff, A. Mehdaoui, C. Pirri, G. Garreau, C. Uhlaq-Bouillet, Appl. Phys. Lett. 93 (2008) 033114.

[7] C. Zeng, S.C. Erwin, L.C. Feldman, A.P. Li, R. Jin, Y. Song, J.R. Thompson, H.H.Weitering, Appl. Phys. Lett. 83 (2003) 5002.

[8] C. Zeng, W. Zhu, S.C. Erwin, Z. Zhang, H.H. Weitering, Phys. Rev. B 70 (2004) 205340.

[9] S. Picozzi, A. Continenza, A.J. Freeman, Phys. Rev. B 70 (2004) 235205.

[10] A. Stroppa, M. Peressi, Phys. Stat. Sol. A 204 (2007) 44.

[11] S. Olive-mendez, A. Spiesser, L.A. Michez, V. Le Thanh, A. Glachant, J. Derrien, T. Devillers, A. Barski, M. Jamet, Thin Solid Films 517 (2008) 191.

[12] M. Gajdzik, C. Sürgers, M.T. Kelemen, H. v. Löhneysen, J. of Magn, Magn. Mater. 221 (2000) 248.

[13] C. Sürgers, K. Potzger, T. Strache, W. Möller, G. Fischer, N. Joshi, H.v. Löhneysen, Appl. Phys. Lett. 93 (2008) 062503.

[14] I. Slipukhina, E. Arras, Ph. Mavropoulos, P. Pochet, to appear in Appl. Phys. Lett. 94 (2009) 192505.

[15] T.Y. Chen, C.L. Chien, C. Petrovic, Appl. Phys. Lett. 91 (2007) 142505.

[16] A. Stroppa, G. Kresse, A. Continenza, Appl. Phys. Lett. 93 (2008) 092502.

[17] V. Le Thanh, Surf. Sci. 492 (2001) 255;

V. Le Thanh, Physica, E, Low-Dimens. Dyst. Nanostruct. 23 (2004) 401.

[18] L. Néel, J. Phys. Rad. 17 (1956) 250.

[19] See, for example, and references therein: J.G. Kim, K.H. Han, S.H. Song, A. Reilly, Thin Solid Films 440 (2003)) 54; J. Islam, Y. Yamamoto, H. Hori, J. Magn. Magn. Mater. 310 (2007) 2234; J. Islam, Y. Yamamoto, E. Shikoh, A. Fujiwara, H. Hori, J. Magn. Magn. Mater. 320 (2008) 571; G. Goll, A. Breitling, Appl. Phys. Lett. 94 (2009) 052502; A.S. Dzhumaliev, Y.V. Nikulin, Y.A. Filimonov, J. Commun. Technol. Electron. 54 (2009) 331.