Magnetic anisotropy of (Ge,Mn) nanostructures

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Abstract. We present a correlation between structural and magnetic properties of different (Ge,Mn) nanostructures grown on Ge(001) and Ge(111) substrates. Thin films of Ge$_{1-x}$Mn$_x$ were grown by low temperature molecular beam epitaxy to favor the out-of-equilibrium growth. Depending on the growth conditions crystalline or amorphous (Ge,Mn) nanocolumns have been observed on Ge(001) substrates. The magnetic properties were probed by superconducting quantum interference device (SQUID), vibrating sample magnetometer (VSM) and electron paramagnetic resonance (EPR). With the help of these complementary techniques (SQUID and EPR), magnetic anisotropy in these nanostructures has been investigated and different anisotropy constants were calculated.

1. Introduction
The electric control of magnetic properties in Ferromagnetic Semiconductors (FMS) make them very interesting materials for their potential use in spintronics industry [1, 2]. Making a FMS with high Curie temperature ($T_c$) and compatible with mainstream silicon technology is highly desirable. Up to now major efforts have been focused on diluted magnetic semiconductors (DMSs) in which the host semiconducting matrix is randomly substituted by transition metal, the model system being Mn-doped III-V semiconductor GaAs [3]. However, $T_c$ in these DMSs remain rather low and increasing the transition metal concentrations further to increase the $T_c$ leads to precipitation of secondary phases. Moreover, the understanding of origin of hole-mediated ferromagnetism in (III,Mn)V DMS is still under debate.

Recently group IV semiconductor Ge doped with Mn is gaining attention as a FMS due to its high Curie temperature, compatibility with existing Si technology and reported to be half metallic from the band structure calculations [4, 5]. The first evidence of ferromagnetism in (Ge,Mn) was reported by Park et. al. where the highest $T_c$ was reported to be 116K [6]. Since then (Ge,Mn) system has been studied intensively and the solubility of Mn in Germanium has been enhanced by non-equilibrium growth techniques [7, 8, 9, 10, 11, 12, 13, 14, 15].

In our case we have Mn-rich nanocolumns in Ge$_{1-x}$Mn$_x$ films grown by low temperature molecular beam epitaxy (LT-MBE) on Ge(001) substrates [4, 11]. These self-organized nanocolumns exhibit high $T_c$ and are formed by 2D spinodal decomposition. This columnar growth forming transition metal rich nanostructures exhibiting high $T_c$ has been predicted by ab-initio calculations coupled with kinetic Monte-Carlo simulations [16, 17]. Also Ge$_3$Mn$_5$ thin-films on Ge(111) have been grown. In this paper, we discuss the structural and magnetic properties of these (Ge,Mn) nanostructures. We investigate the magnetic anisotropy and extract various anisotropy constants.
2. Sample growth and experimental details

The (Ge,Mn) films were grown by MBE on epi-ready Ge(001) substrates at low growth temperature $T_g$ to stabilize metastable nanocolumns which are either crystalline ($T_g$=100°C) or amorphous ($T_g$=150°C). The growth process is described in detail in Ref. [11]. Also epitaxial Ge$_3$Mn$_5$ films were grown at 250°C on Ge(111) substrates by co-depositing Ge and Mn atoms according to the Ge$_3$Mn$_5$ stoichiometry.

Superconducting quantum interference device (SQUID), vibrating sample magnetometer (VSM) and electron paramagnetic resonance (EPR) techniques were used to calculate the magnetic anisotropy constants. EPR is a very sensitive spectroscopy technique with high field resolution, where the magnetization dynamics is described by the Landau-Lifschitz-Gilbert equation [18]. However, it is much convenient to use Smit Beljers formalism [19, 20], where the equation of motion is expressed as a function of the total free energy density (equations are given in ref. [21, 22]). These equations are used to calculate the magnetic anisotropy fields. However, SQUID measurements are needed to obtain the saturation magnetization and hence calculate the anisotropy constants. This approach has proved very useful in studying magnetic anisotropy in metallic thin-films and (III,Mn)V DMS [22, 21]. However, in our case we have (Ge,Mn) nanostructures but still the same approach has been used. We have tested our method to determine magnetic anisotropy constants using both EPR and SQUID measurements on Ge$_3$Mn$_5$ films grown on Ge(111) substrates [23].

The EPR experiments were performed at $T = 5$ K using a Bruker ESP 300 spectrometer. The spectrometer was operating at X-band (9.4 GHz) and Q-band (34 GHz), with a modulation frequency of 100 kHz and a modulation amplitude of 10 Oe for lock-in detection. The measurements performed with the out-of-plane applied field swept from [001] to [100] crystal direction. In this paper, we denote the effective out-of-plane second-order anisotropy field by $\mu_0 H_{a2} = \frac{2K_2}{M_S} = \frac{2K_{2\perp}}{M_S} - \mu_0(N_{\perp} - N_{\parallel})M_S$ and fourth-order cubic anisotropy field by $\mu_0 H_{a4} = 2K_4/M_S$, here $M_S$ is saturation magnetization, $K_{2\perp}$ is uniaxial out-of-plane anisotropy constant, $K_4$ is fourth order cubic anisotropy constant and $N_{\perp}, N_{\parallel}$ are the demagnetizing factors parallel and perpendicular to the film plane respectively. Transmission electron microscopy was performed using a JEOL 4000EX microscope with an acceleration voltage of 400 kV.

3. Results and discussion

In (Ge,Mn) films grown on Ge(001) substrate, Mn-rich nanocolumns spanning the whole film thickness are observed as a consequence of two-dimensional spinodal decomposition [4, 11]. These nanocolumns are well crystalline and in perfect epitaxial relationship with the Ge matrix when grown at substrate temperature of 100°C. However if the growth temperature is increased, they starts to become amorphous and increase in diameter. The high resolution TEM images of these nanocolumns are shown in reference [4, 11]. If we assume that the Mn concentration in the Ge matrix is in between 0 and 1 %, the resulting Mn content in the columns is close to 50 %.

SQUID measurements performed on a Ge$_{0.9}$Mn$_{0.1}$ film having crystalline and amorphous (Ge,Mn) nanocolumns are shown in Fig. 1. We identify two different contributions: paramagnetic signal from Mn ions in the Ge matrix at lower temperatures and ferromagnetic signal from the nanocolumns. The curie temperature was found to be 150K for crystalline nanocolumns and 125K for amorphous nanocolumns. The ZFC-FC measurements show that crystalline nanocolumns are superparamagnetic with blocking temperature of 15±5K and the narrow shape of the ZFC peak is related to the narrow size distribution of nanocolumns grown in this temperature range [11]. The amorphous nanocolumns have a Curie temperature of 125 K. In ZFC-FC curves we see two peaks at around 27 K and 72 K corresponding to broken and continuous nanocolumns. These peaks are broad and in agreement with the broad size distribution observed by TEM [11]. For these nanocolumns, the susceptibility perpendicular to
the plane seems slightly higher than that in the plane but a strong diamagnetic signal from the substrate and paramagnetic signal from diluted Mn atoms makes it difficult to quantify precisely this anisotropy.

Figure 1. For $T_g=100^{\circ}$C: (a) Temperature dependence of the saturation magnetization (in kA/m) of a Ge$_{0.9}$Mn$_{0.1}$ film containing crystalline nanocolumns. The applied field is 5 T. (b) ZFC-FC measurements performed with the field of 15 mT parallel and perpendicular to the film plane. Inset: magnetic remanence after maximum field cooling under 5 T. For $T_g=150^{\circ}$C: (c) Temperature dependence of the saturation magnetization of a Ge$_{0.9}$Mn$_{0.1}$ film containing amorphous nanocolumns. The magnetic field is 5 T and applied in the film plane along the [110] direction. The Curie-Weiss plot for two identical samples is shown in the inset. (d) ZFC-FC measurements performed at 0.015 T. The ZFC-FC curve exhibits two peaks with blocking temperatures around 27 K and 72 K respectively.

EPR technique is hence used to differentiate the ferromagnetic signal of nanocolumns from the paramagnetic diluted Mn atoms and estimate magnetic anisotropy. The experiments were performed in Q-band (34 GHz) and the field was applied in out-of-plane geometry from the direction [110] to [\bar{1}10] direction. Fig. 2(a,b) shows the EPR spectra of a Ge$_{0.9}$Mn$_{0.1}$ film with crystalline nanocolumns and the angular dependence of the resonance field is fitted using the Smit-Beljers formalism [19]. We found the anisotropy fields: $\mu_0 H_a^{(2)} \approx 0.09$T for the second order and $\mu_0 H_a^{(4)} \approx -0.11$T for the fourth order. Hence, these nanocolumns exhibit a
perpendicular uniaxial anisotropy and a cubic anisotropy with easy axis along [111]. If we consider the saturation magnetization of these small nanocolumns $M_S = 140 \pm 20 \text{kA/m}$, we can derive the anisotropy constants to be: $K_2 \approx 0.63 \times 10^4 \text{J/m}^3$ and $K_4 \approx 0.77 \times 10^4 \text{J/m}^3$. The presence of cubic anisotropy supports the crystallinity of nanocolumns and the second order anisotropy well corresponds to shape magnetic anisotropy along the columns axis. The EPR spectra from amorphous columns and its angular dependence are shown in Fig. 2(c,d). A single perpendicular uniaxial anisotropy is found and the fit gives the corresponding anisotropy field to be: $\mu_0 H_{a2} \approx 0.09 \text{T}$. From the saturation magnetization of amorphous nanocolumns $M_S = 220 \pm 20 \text{kA/m}$, the anisotropy constant is calculated to be $K_2 \approx 1.1 \times 10^4 \text{J/m}^3$. This value corresponds to that of shape anisotropy $\mu_0 M_S^2/4 = 1.5 \times 10^4 \text{J/m}^3$ of nanocolumns. As expected for amorphous nanocolumns, no cubic magneto-crystalline contribution is found.

**Figure 2.** For $T_g=100^\circ\text{C}$: (a) The EPR absorption spectra at Q band (34 GHz) of Ge$_{0.9}$Mn$_{0.1}$ sample. (b) Angular dependence of the resonance field as a function of orientation of magnetic field. We observe two contributions: a ferromagnetic peak of weak anisotropy and six hyperfine peaks from diluted paramagnetic Mn ions. For $T_g=150^\circ\text{C}$: (c) The EPR absorption spectra at Q band (34GHz) of Ge$_{0.9}$Mn$_{0.1}$ sample containing amorphous nanocolumns. (d) Angular dependence of the resonance field as a function of orientation of magnetic field. (The angle is defined between the direction [110] and the applied magnetic field. The angular step in goniometer during measurement has been 5°).
4. Conclusion
In this paper, we have systematically investigated different (Ge,Mn) nanostructures. We find a good correlation between their structural morphology and the magnetic properties.

In Ge$_3$Mn$_5$ films epitaxially grown on Ge(111), shape anisotropy is dominating and overcomes the magnetocrystalline component. Furthermore crystalline (Ge,Mn) nanocolumns exhibit second-order perpendicular uniaxial anisotropy along with fourth-order cubic anisotropy along (111) direction. This cubic anisotropy has been expected because of the crystalline structure of nanocolumns observed in TEM. On the other hand, in amorphous nanocolumns grown at high temperature ($T_g=150^\circ$C), this cubic anisotropy is absent and only shape anisotropy is observed. The correlation between magnetization and the diamond lattice in these Mn-rich structures has never been evidenced before.

To conclude, the knowledge of magnetic anisotropy is important for future use of (Ge,Mn) material spintronics applications since it determines the direction of magnetization, coercive fields and domain sizes. For this purpose, using complementary experimental techniques has proven to be effective for investigating the magnetic properties of these nanostructures.

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6. References
[1] Zutić I, Fabian J and Das Sarma S 2004 Rev. Mod. Phys. 76 323–410
[2] Dietl T 2002 Semicond. Sci. Technol. 17 377
[3] Ohno H 1998 Science 281 951
[4] Jamet M, Barski A, Devillers T, Poydenot V, Dujardin R, Bayle-Guillemaud P, Rothman J, Bellet-Amalric E, Marty A, Cibert J et al. 2006 Nature Mater. 5 653–659
[5] Stroppa A, Picozzi S, Continenza A and Freeman A J 2003 Phys. Rev. B 68 155203
[6] Park Y D, Hambicki 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 Science 295 651–654
[7] Bougeard D, Ahlers S, Trampert A, Sircar N and Abstreiter G 2006 Phys. Rev. Lett. 97 237202
[8] Ottaviano L, Passacantando M, Verna A, Gunnella R, Principi E, Cicco A D, Impellizzeri G and Priolo F 2006 Journal of Applied Physics 100 063528 (pages 4)
[9] Jaeger C, Biehler C, Vallaitis T, Goennenwein S T B, Opel M, Gross R and Brandt M S 2006 Phys. Rev. B 74 045330
[10] Li A P, Zeng C, van Benthem K, Chisholm M F, Shen J, Nageswara Rao S V S, Dixit S K, Feldman L C, Petukhov A G, Foygel M and Weiting H H 2007 Phys. Rev. B 75 201201
[11] Devillers T, Jamet M, Barski A, Poydenot V, Bayle-Guillemaud P, Bellet-Amalric E, Cherifi S and Cibert J 2007 Phys. Rev. B 76 205306
[12] Pinto N, Morresi L, Ficcadenti M, Murrri R, D’Orazio F, Lucari F, Boarino L and Amato G 2005 Phys. Rev. B 72 165203
[13] Ahlers S, Bougeard D, Sircar N, Abstreiter G, Trampert A, Opel M and Gross R 2006 Phys. Rev. B 74 214411
[14] Morgunov R, Farle M, Passacantando M, Ottaviano L and Kazakova O 2008 Phys. Rev. B 78 045206
[15] Sugahara S, Lee K L, Yada S and Tanaka M 2005 Jpn. J. Appl. Phys. 44 L1426
[16] Sato K, Katayama-Yoshida H and Dederichs P H 2005 Jpn. J. Appl. Phys. 44 L948
[17] Zheng S, Zhu W, Gao Y F, Stocks G M and Zhang Z 2010 Applied Physics Letters 96 071913 (pages 3)
[18] Hillebrands B and Onnajdeka K (eds) 2002 Spin Dynamics in Confined Magnetic Structures I (Springer Berlin)
[19] Smit J and Beljers H 1955 Philips Res. Rep. 10 113
[20] Suhl H 1955 Phys. Rev. 97 555
[21] Liu X and Furdyna J K 2006 Journal of Physics: Condensed Matter 18 R245
[22] Farle M 1998 Reports on Progress in Physics 61 755
[23] Jain A, Jamet M, Barski A, Devillers T, Yu I S, Porret C, Bayle-Guillemaud P, Favre-Nicolin V, Gambarelli S, Maurel V et al. 2010 Phys. Rev. B submitted