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Effect of thermal annealing of high temperature growth $[(GaAs)_m(Fe)_n]_p$ composite films on GaAs(001) by molecular beam epitaxy

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Abstract : $[(GaAs)_m(Fe)_n]_p$ composite films on GaAs(001) substrates obtained by molecular beam deposition methods at T_s = 580°C have been thermally annealed, and magnetic/structural changes caused by the annealing have been measured to study the relation between room-temperature photo-magnetic effect and by-products in composite films. Annealing inhomogeneous $[(GaAs)_8(Fe)_5]_{20}$ film, prepared by alternate beam deposition of Fe and GaAs, results in an increase in saturation magnetization, whereas the room-temperature photo-enhanced magnetization (RT-PEM) vanishes. Metamagnetic Fe_3Ga_4 is suppressed with the formation of ferromagnetic $Fe_3Ga_{2-x}As_x$. Observed results suggest two important points : firstly, metamagnetic Fe_3Ga_4 compound is most likely meta-stable bi-product and may play a principle role for RT-PEM, and secondly, ferromagnetic Fe_3GaAs and its derivatives are the stable form in Ga-As-Fe ternary system.

Keywords : GaAs, iron, X-ray diffraction, photo-induced magnetism, molecular beam epitaxy, metamagnetism.

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1. Introduction

Metal/semiconductor granular systems composed of grains of a ferromagnetic element (such as Fe, Mn) immersed in a GaAs matrix have been extensively studied in the last few years, mainly because they can present unique magneto-transport properties that make them good candidates for future technological applications [1]. Granular solids can be easily obtained by molecular beam epitaxy (MBE) and theirs microstructures can be significantly altered by thermal treatment methods prior to or after its fabrication, thus allowing the production of a broad variety of granular structures, characterized by their particle size distribution and density. Shi *et al* [2] reported the formation of

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submicrometer GaMn ferromagnets in GaAs using Mn^+ ion implantation and the subsequent heat treatment at 800–920°C in a forming gas (90%N_2, 10%H_2). The enhanced positive magneto-resistance in GaAs with nanomagnet clusters embedded by Mn ion implantation under light illumination have been reported [3]. MnAs nanoclusters embedded in GaAs can be obtained by annealing MBE growth (Ga, Mn)As at 500–600°C [4–8]. The absorption and magneto-optical properties of GaAs : MnAs are strongly dependent on its cluster size. On the other hand, by annealing Fe/GaAs(001) films at above 500°C, precipitation of Fe_3GaAs is found with Fe_3Ga and Fe_2As compounds [9–12].

Recently, composite GaAs-Fe film shows room-temperature photo-enhanced magnetization (RT-PEM) [13,14]. Taking advantage of this unique property, an optically-driven micro-cantilever assembly has been demonstrated [15]. While this is a very encouraging achievement towards the future applications such as the wireless micro-electronic mechanical system and the information processing technology, it is necessary to improve the magnitude of PEM. But the origin of PEM has remained unclear. Hypothesis of the alteration of inter-particle interaction by the light illumination was introduced on the basis of magnetization curves when this effect was found. However, the identification of key compound and particles had not been accomplished, partly because of the fact that the first generation samples consisted of polycrystalline, granular structures whose constituent ingredients were neither well engineered nor controlled. In the ternary phase diagram of Ga-Fe-As [12], there are varieties of compounds with different magnetic properties : for example, diamagnetic $FeAs_2$, ferromagnetic Fe_3Ga and $Fe_3Ga_{2-x}As_x$, antiferromagnetic FeAs and Fe_2As, and metamagnetic Fe_3Ga_4. For realizing the problem we annealed various types of inhomogeneous $[(GaAs)_m(Fe)_n]_p$ films under different conditions for studying phase separation as well as RT-PEM. Magnetic/structural changes caused by the annealing have been measured.

2. Experimental details

The GaAs-Fe granular magnetic-semiconductor hybrid structures have been grown by alternate molecular-beam deposition of Fe and Ga+As on GaAs/GaAs(001) substrate at high substrate temperature T_s = 580°C. We describe the sample structure by the expression $[(GaAs)_m(Fe)_n]_p$. Here, $(GaAs)_m$ and $(Fe)_n$ represent the net volume of the constituent materials deposited at one cycle in the unit of monolayer of GaAs and Fe, respectively. p represents the number of processing cycles of the alternate deposition. The nominal structure of the sample $[(GaAs)_8(Fe)_5]_{20}$ was thermally annealed in the nitrogen atmosphere for 30–120 min at temperatures of T_A = 500–600°C, where the sample thickness was typically 74 nm and Fe content was about 60%.

The crystallographic evaluation of the deposited films were carried out by the powder X-ray diffractometer with the Cu-K_α (λ = 1.542 Å) radiation source. The scan rate of 0.05° s^{-1} was applied to record the pattern in the 2θ range of 25°–90°. The magnetic evaluation, including the experiments with the light illumination, was carried out by the radio frequency superconducting quantum interference device (SQUID) magnetometer. The data shown in this paper were obtained with magnetic fields applied perpendicular to the sample plane. The diamagnetic contribution of a GaAs substrate was carefully subtracted from the raw magnetization data.

3. Results and discussion

Figure 1 shows X-ray powder diffraction (XRD) pattern for as-grown and annealed samples. Besides the diffraction peaks 2θ = 31.6°(200) and 66.1°(400) from the substrate, five Bragg peaks are found for as-grown sample as shown in Fig. 1(a), which are located at 2θ = 33.9°, 34.7°, 43.2°, 44.2°, and 60.1° to the reflection of (221), (–222), (023), (–420), and (–2–15) planes respectively, indicating a single crystal phase of the base-centered monoclinic Fe_3Ga_4 crystal structure. It should be noted that the X-ray Bragg reflection from the (–2–15) plane gives rise to the diffraction peak at $2\theta \sim 60.1°$ with the Cu-K$_\alpha$ X-ray source (λ = 1.542 Å), which practically appears to be a very convenient signal to identify this compound among other candidate compounds in the ternary phase diagram [12]. We also note that peaks due to other compounds such as Fe_3Ga and Fe_2As are absent in the XRD data. The intensity of diffraction peaks is suppressed upon annealing with the appearence of another extra peak (2θ = 63.2° (202)), which indicates the hexagonal $Fe_3Ga_{2-x}As_x$ phase.

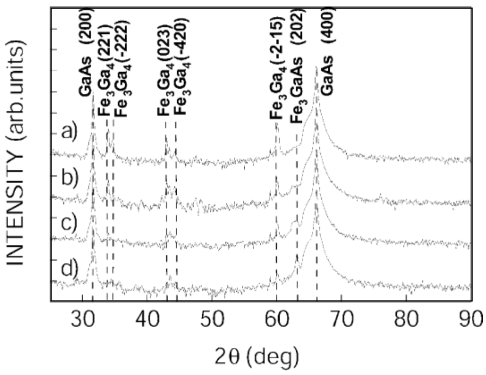

Figure 1. $\theta - 2\theta$ X-ray powder diffraction data for (a) as-grown [(GaAs)$_8$(Fe)$_5$]$_{20}$ and annealed samples at (b) T_A = 500°C for 30 min, (c) T_A = 500°C for 120 min, and (d) T_A = 600°C for 30 min.

Figure 2(a) shows high-field magnetization data (*M-H* curves) at 300 K for as-grown sample and annealed samples under various annealing conditions. Magnetization value is significantly large and starts to saturate at around H = 70 kOe for the as-grown sample. For the annealed samples, saturation tends to occur at lower fields, and the saturation value becomes even larger. The shape of *M-H* curve for as-grown sample is the same as the superparamagnetic-like magnetization curve of reported work [13,14]. But the temperature dependence of magnetization data (*M-T* curves) as shown in Fig. 3(a), a peak behavior is clearly observed at 360 K for as-grown sample under the external magnetic field of H = 50 kOe, which is relevant to the Neel temperature of metamagnetic Fe_3Ga_4 compound.

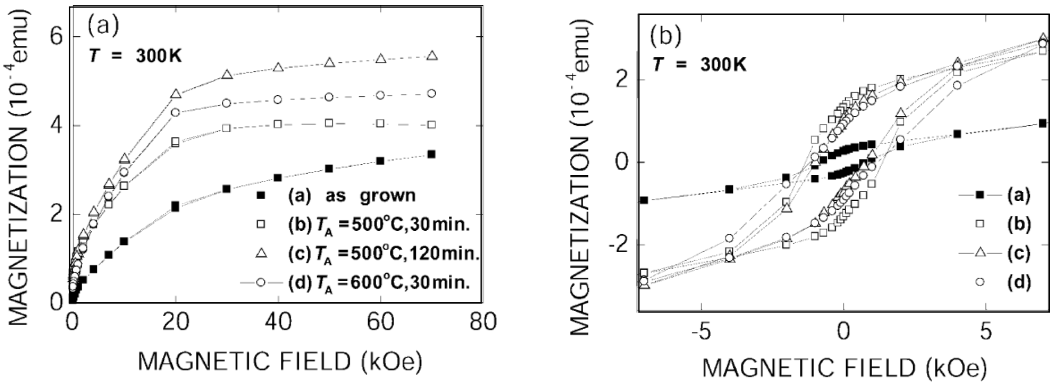

Figure 2. Magnetization data (*M-H* curves) at 300 K obtained from (a) high-field magnetization and (b) low-field magnetization for as-grown $[(GaAs)_8(Fe)_5]_{20}$ and annealed samples. Magnetic fields are applied perpendicular to the sample plane.

We are able to distinguish three different regions clearly (in *M-T* curves as shown in Fig. 3(b)) depending on the temperature under lower external magnetic field (H = 10 kOe) : the ferromagnetic-like region below 100 K, the antiferromagnetic-like region at 300–390 K, and the transition region in between the former two temperature regions. These complicated behaviors coincide fairly well with those found in the bulk metamagnet Fe_3Ga_4 [16] which was explained by the Moriya-Usami theory [17] in terms of the coexistence of ferromagnetic and antiferromagnetic interactions in itinerant electron systems. One of the essential points of the behavior of metamagnet is that, under some specific condition, the first order phase transition between antiferromagnetic and

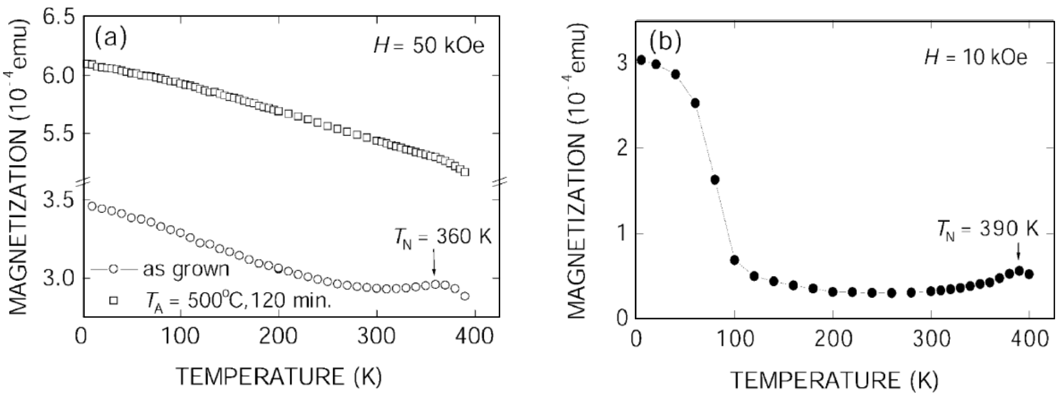

Figure 3. Temperature dependence of magnetization data (*M-T* curves) for (a) as-grown $[(GaAs)_8(Fe)_5]_{20}$ and annealed sample at T_A = 500°C for 120 min under the external magnetic field H = 50 kOe and (b) as-grown same sample under the external magnetic field H = 10 kOe. Magnetic fields are applied perpendicular to the sample plane. Neel temperatures, T_N, are 390 and 360 K for H = 10 and 50 kOe.

ferromagnetic state can be induced by an external magnetic field. The peak, representing the Neel temperature, shifts toward higher temperature with decreasing the field. This behavior, having been found also in the bulk crystal, can be viewed as the change in the balance between the antiferromagnetic and ferromagnetic interactions by an external magnetic field. It is worth noting that the Neel temperature of antiferromagnetic Fe_2As is 350 K [18], and this value does not shift by the application of a magnetic field [19].

Turning eyes on low-field magnetization data as shown in Fig. 2(b), we notice a clear hysteretic behavior obtained at 300 K for as-grown sample and this behavior increases with increasing annealing temperature, whereas hysteresis almost disappeared at high temperature (390 K), which is not shown here. As a whole, the observed behavior suggests that it is not ferromagnetic Fe but $Fe_3Ga_{2-x}As_x$ that is formed by annealing, since the Curie temperature of this compound is known to be 373 to 644 K depending as the value of x [20], whereas the Curie temperature of Fe is 1043 K [21]. It seems that formation reaction of $Fe_3Ga_{2-x}As_x$ is promoted by annealing. The amount of Fe that is estimated from the saturation value of this annealed (T_A = 500°C for 120 min) sample at 300 K is [Fe] = 3.87×10^{22} cm^{-3}, assuming 1.42 μ_B for Fe_3GaAs compound [20]. This value is comparable to the total Fe concentration (3.31×10^{22} cm^{-3}) in $[(GaAs)_8(Fe)_5]_{20}$.

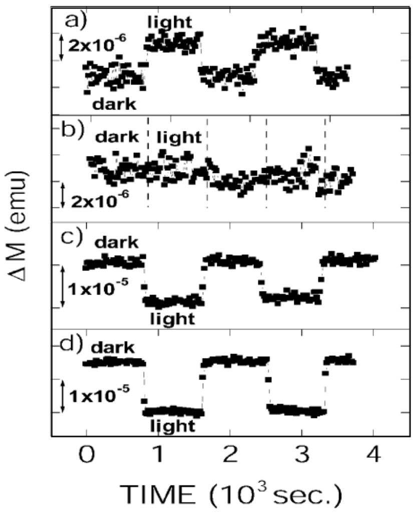

Figure 4. Change in magnetization profile with and without light illumination at room temperature for (a) as-grown $[(GaAs)_8(Fe)_5]_{20}$ and annealed samples at (b) T_A = 500°C for 30 min, (c) T_A = 500°C for 120 min, and (d) T_A = 600°C for 30 min. A magnetic field of 70 kOe is applied perpendicular to the sample surface.

Figure 4 shows the temporal profile of change in magnetization by switching the light on and off at room temperature under the magnetic field of 70 kOe for as-grown and annealed samples. Excitation power was 60 mW (156 mW/cm^2). The interval and duration of data sampling was 30 s and 1 s, respectively. It is clearly seen for as-grown sample that magnetization increases (ΔM_{PEM} = 3 x 10^{-6} emu) with illumination by light and returns back to the original level when the light is turned off indicating the positive change in magnetization with light *i.e.* occurance of RT-PEM. On the other hand, for the annealed samples, the negative change in magnetization is observed, which is most likely caused by the light-induced heating. The amount of negative change is increased with increasing annealing condition and the peak behavior disappears on annealing the sample as shown in *M-T* curves [Fig. 3(a)]. RT-PEM seems to disappear upon annealing in the case of ferromagnetic phase. This behavior may be explained again in formation of $Fe_3Ga_{2-x}As_x$ particles for lightly annealed sample. Particles can coalesce together by further annealing to form larger-size particles, which results in increased inter-particle distance and/or reduced surface-to-volume ratio. In either case, it would suppress the RT-PEM.

We also note here that enhancement in magnetization by the with light illumination was not observed in the antiferromagnetic Fe_2As compound [19], where the Neel temperature of this is 350 K. The origin of the PEM may be attributed to the metamagnetic character of Fe_3Ga_4. While the antiferromagnetic interaction is stronger than the ferromagnetic interaction at room temperature, the former interaction tends to be weakened by the external stimulation, as exemplified by the shift of Neel temperature to lower values by external fields [16]. While the understanding of this material is very limited at present, it is not unreasonable to infer that, in an itinerant electron system, the optical excitation may alter the balance between antiferromagnetic and ferromagnetic interaction, which in turn results in the change in magnetization or magnetic susceptibility.

4. Conclusions

In conclusion, the relation between room-temperature photo-magnetic effect and by-products in GaAs-Fe films has been studied by various types of thermally annealed films, and magnetic/structural changes caused by the annealing have been measured. XRD measurements reveal that Fe_3Ga_4 has been formed on top of the substrate which turn out to be a major by-product in $[(GaAs)_8(Fe)_5]_{20}$ films prepared by alternative beam deposition at relatively high substrate temperature T_s (*e.g*. T_s = 580°C). From the results of magnetization measurements, it has been found that Fe_3Ga_4 is a metamagnetic compound and the phase responsible for RT-PEM. Formation of ferromagnetic Fe_3GaAs or its derivatives is enhanced in thermally annealed samples, reflecting the equilibrium nature of this phase in ternary solid solution where RT-PEM vanishes.

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References

[1] H Akinaga *Semocond. Sci. Technol.* **17** 322 (2002)

[2] J Shi, J M Kikkawa, R Proksch, T Schaffer, D D Awschalom, G Medeiros-Ribeiro and P M Petroff *Nature* (London) **377** 707 (1995)

[3] Sh U Yuldashev, Y Shon, Y H Kwon, D J Fu, D Y Kim, H J Kim, T W Kang and X Fan *J. Appl. Phys*. **90** 3004 (2001)

[4] J De Boeck, R Oesterholt, H Bender, A Van Esch, C Bruynseraede, C Van Hoof and G Borghs *J. Magn. Magn. Mater.* **156** 148 (1996)

[5] H Akinaga, J De Boeck, G Borghs, S Miyanishi, A Asamitsu, W Van Roy, Y Tomioka and L H Kuo *Appl. Phys. Lett*. **72** 3368 (1998)

[6] H Akinaga, S Miyanishi, K Tanaka, W Van Roy and K Onodera *Appl. Phys. Lett*. **76** 97 (2000)

[7] M Tanaka, H Shimizu and M Miyamura *J. Cryst. Growth* **227** 839 (2001)

[8] M Moreno, A Trampert, B Jenichen, L Däweritz, and K H Ploog *J. Appl. Phys*. **92** 4672 (2002)

[9] B Lepine, S Ababou, A Guivarc'h, G Jezequel, S Deputier, R Guerin, A Filipe, A Schuhl, F Abel, C Cohen, A Rocher and J Crestou *J. Appl. Phys.* **83** 3077 (1998)

[10] M Rahmoune, J P Eymery, Ph Goudeau and M F Denanot *Thin Solid Films* **289** 261 (1996)

[11] M Rahmoune, J P Eymery and M F Denanot *J. Magn. Magn. Mater*. **175** 219 (1997)

[12] S Deputier, R Guerin, B Lepine, A Guivarc'h and G Jezequel *J. Alloys and Compounds* **262/263** 416 (1997)

[13] S Haneda, H Munekata, Y Takatani and S Koshihara *J. Appl. Phys*. **87** 6445 (2000)

[14] S Haneda, S Koshihara and H Munekata *Physica* **E10** 437 (2001)

[15] T Shinshi, F Kato, A Shimokobe, H Noguchi and H Munekata *Appl. Phys. Lett*. **83** 3425 (2003)

[16] N Kawamiya and K Adachi *J. Phys. Soc. Japn.* **55** 634 (1986)

[17] T Moriya and K Usami *Solid State Commun*. **23** 935 (1977)

[18] H Katsuraki and N Achiwa *J. Phys. Soc. Jpn*. **21** 2238 (1966)

[19] A T M K Jamil, H Noguchi and H Munekata *Thin Solid Films* **516** 3015 (2008)

[20] I R Harris, N A Smith, B Cockayne and W R MacEwan *J. Cryst. Growth* **82** 450 (1987)

[21] R M Bozorth *Ferromagntism* (ed.) W Perkin (New York : IEEE Press) p53 (1993)