Growth Direction Control and Magnetic Characterizations of MnAs Grown by Selective-Area Metal-Organic Vapor Phase Epitaxy

Toshitomo Wakatsuki¹, Shinjiro Harai², Shingo Ito¹ and Takashi Fukui¹

1. Research Center for Integrated Quantum Electronics Hokkaido University, North13, West8, Sapporo 060-8628, Japan
2. JST-PRESTO, 4-1-8 Honcho, Kawaguchi 332-0012, Japan
Phone: +81-11-706-7172, Fax: +81-11-716-6004, e-mail: wakatuki@rciqe.hokudai.ac.jp

1. Introduction
Position controlled and build-up fabrication of nanostructures with the hetero-structures between ferromagnetic and semiconductor thin films on semiconductor substrates by selective-area metal-organic vapor phase epitaxy (SA-MOVPE) is promising for the realization of future nano-spintronic devices utilizing characteristics of the spin-polarized carriers. Ferromagnetic MnAs layers, which serve as an electrical spin injection source into semiconductors, has been extensively investigated and demonstrated on GaAs substrates by molecular beam epitaxy. [1, 2] We have demonstrated the build-up fabrication not only of one-dimensional semiconductor nanowires [3] but also of ferromagnetic MnAs nanoclusters (NCs) [4] on (111) B semiconductor substrates by SA-MOVPE. It is crucial for realizing hetero-structures between ferromagnetic and semiconductor nanostructures with well-aligned crystallographic orientations to control the growth directions and the crystal facets of MnAs NCs because they strongly depend on SA-MOVPE growth conditions. In this paper, therefore, we report the growth direction control of MnAs NCs on partially SiO₂-masked GaAs (111) B substrates by SA-MOVPE. Structural and magnetic characterizations for the NCs are carried out, as well.

2. Experimental procedures
Before the MnAs growth, electron beam lithography and wet chemical etching were carried out to partially remove SiO₂ thin films deposited on GaAs (111)B substrates and make periodical mask openings. Diameter of the openings was about 300 nm. AsH₃ and (CH₂C₂H₄)₂Mn were used as source materials for the MnAs growth. The growth temperatures, Tg, were chosen from 750 to 850 °C. V/Mn ratios, that is, partial pressure ratios of p[AsH₃]/p[(CH₂C₂H₄)₂Mn], were varied from 375 to 3125. Growth time was changed from 10 to 60 minutes. MnAs NCs were observed by scanning electron microscopy (SEM). To closely investigate crystallographic structures of the NCs, cross-sectional lattice images and electron beam diffraction (ED) patterns were taken using transmission electron microscope (TEM). We observed magnetic domain structures of the NCs by magnetic force microscopy (MFM) at room temperature.

3. Results and discussion
Hexagonal MnAs NCs with well-defined crystal facets were formed only on GaAs surfaces of the mask openings. Typical NCs, which were grown at a V/Mn ratio of 2250 for 30 minutes, measured about 630 nm in diameter and 230 nm in height, as observed by SEM in Fig. 1. The hexagonal NCs had typically two types of crystal facets: One was parallel to the GaAs (111) B wafer plane on the top of the NCs, and others, which were formed around the top planes of the NCs as the six side-walls, were tilted by around 60° against the GaAs(111)B wafer plane. We observed six vertical facets at the bottom part of six side-walls of the NCs when the samples were grown at relatively high V/Mn ratios (> 1125) for longer growth time. This is presumably because the growth rates of the top planes of the NCs are enhanced under such growth conditions. When we decreased the V/Mn ratio of the NCs to 375 under the same growth time condition, the height of MnAs NCs were decreased. Furthermore, the vertical facets were disappeared. The measured size of the NCs was about 610 nm in diameter and 190 nm in height.

![Figure 1](image1.png)
**Figure 1**: (a) SEM image of MnAs NCs on GaAs (111)B substrates by SA-MOVPE. V/Mn ratio was 2250, and growth time was 30min. (b) Highly-magnified SEM image for one of the observed MnAs NCs.

![Figure 2](image2.png)
**Figure 2**: Growth time dependence of diameter and height of the MnAs NCs.
Under the V/Mn ratio condition of 375, we changed growth time from 10 to 60 minutes. The height of NCs was constant, though the diameter changed. Typical diameter of the NCs was about 850 nm from 480 nm, as shown in Fig. 2. Figure 3 (a) shows cross-sectional TEM image of the MnAs NC, which was grown at a V/Mn ratio of 2250 for 30 minutes. The surfaces of the NCs are atomically flat without any atomic step. As observed in SEM images in Fig. 1, we confirmed that vertical facets were at a lower part of the MnAs NC. However, unintentional GaAs layers were observed under the MnAs NCs. It is likely that GaAs layers were re-grown after the re-evaporations of GaAs surfaces because of the (CH$_3$C$_5$H$_4$)$_2$Mn source gas supply during the MnAs growth under high T$_g$ conditions. We conclude from the ED patterns that the MnAs NCs had hexagonal NiAs-type crystal structures, and that the c-axis (the [0001] direction) of the NCs was parallel to the [-1-1-1] direction of the ZB-type GaAs layers, as shown in Fig. 3(b). Therefore, the top surfaces, the six side-walls and the vertical facets at the bottom parts of the side-walls are attributable to {0001}, {10-11} and {10-10}, respectively. Next, we investigated magnetic domain structures of the MnAs NCs by MFM. First, we confirmed that MnAs NCs showed ferromagnetism at room temperature because we observed magnetic domain structures for as-grown samples, that is, for the samples without any external magnetic filed applications. After the external magnetic fields of 2500 Gauss were applied in the directions parallel to the wafer planes, we confirm that MnAs NCs behave as nano-magnets with single magnetic domain, as shown in Fig. 4, and that the magnetic easy axis, a-axis, of the NCs is in the wafer planes, which is consistent with cross-sectional TEM observation results.

Conclusions
We have fabricated MnAs NCs directly grown on partially SiO$_2$ masked GaAs (111)B substrates. Magnetic single domain structures were observed for the NiAs-type MnAs NCs with well defined crystal facets.

Acknowledgements
The authors would like to thank J. Motohisa, D. Kawamura, H. Iguchi and T. Sato for fruitful discussions and for supporting MOVPE experiments. This work was financially supported in part by JST-PRESTO and the Grant-in-aid for Scientific Research from MEXT in Japan.

References