# MnAs-based Magnetic Nanostructures

The materials such as diluted magnetic semiconductors (DMS) and semiconductor /magnetic hybrid systems have attracted much attention because of the combination of magnetic and semiconducting properties and hence high potential for new spin-electronic (or spintronic) device applications. Manganese-based ferromagnetic thin films such as MnAs and $Ga_{1-x}Mn_xAs$ have recently been epitaxially grown on GaAs substrates using molecular beam epitaxy (MBE). MnAs grows epitaxially onto GaAs in the hexagonal NiAs-type structure. For MnAs/GaAs, the interfaces are thermodynamically stable since the material shares As atoms and the growth process is completely compatible with the existing III-V MBE technology. Another attractive and prospective crystal structure for MnAs is the zinc-blende type structure. Recently, there were several reports on controlling nanoscale structures into zinc-blende type MnAs such as Mn $\delta$ doping in GaAs and MnAs/GaAs multilayer. The successful fabrication of the zinc-blende type MnAs nanoscale dots on sulfur-passivated GaAs (001) would open up the opportunities to investigate new spintronic devices. The density dependence of the dots is, however, strongly required to reveal the characteristics of the zinc-blende type MnAs because of the high-concentration limit of $Ga_{1-x}Mn_xAs$. Further progress in the research of the zinc-blende type MnAs is expected in the growth of thicker films, as suggested by hypothetical band-structure calculations. From this point of view, we have attempted the growth of the zinc-blende type MnAs films by increasing the MnAs dots density. It is expected that thicker layers may have crystalline structure of the thermodynamically stable NiAs-type bulk MnAs because of lattice relaxation. It has been reported that MnSb dots on sulfur-passivated GaAs surface maintain the NiAs-type structure because of the lattice mismatch of zinc-blende type MnSb with GaAs substrates. On the other hand, zinc-blende type CrAs has been grown on GaAs because of the small lattice mismatch although there is a critical thickness of 3 nm.

Another interesting MnAs-based nanostructure has been fabricated, that is a MnAs:GaAs granular film, consisting of MnAs nanoclusters embedded in GaAs, which has the advantage of being ferromagnetic and super-paramagnetic at room temperature depending on the cluster size. It is well known that the high-concentration doping of Mn into GaAs and the high-temperature annealing of $Ga_{1-x}Mn_xAs$ to more than 300℃, the NiAs-type MnAs nanoclusters are segregated in the size of about 10 nm in diameter. The granular material shows both positive and negative giant magnetoresistance controlled by carriers thermally or electro-optically generated in the semiconductor matrix.

For the investigation of electronic and magnetic properties of these MnAs-based nanostructures, X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) probing core levels are very powerful techniques. Here, we adopted the fluorescence yield method to detect signals, which enables us to obtain the information about not only the surface but also the bulk electronic structures because of the long probing depth of the photons. To investigate the magnetic properties, we performed XMCD measurement under 1000 Oe. It is difficult to distinguish the signal using superconducting quantum interference device (SQUID) because of the small amount of the magnetic compounds on/in the semiconductors. XMCD enables to detect the site-selective magnetic moments and the hysteresis curves.

In this article, we report on the morphology-dependent XAS and XMCD spectra in MnAs-based magnetic nanostructures.

The nanoscale MnAs dots were fabricated on

sulfur-passivated $n^+$-GaAs (001) substrates by a conventional solid-source MBE. It is well known that the GaAs substrates terminated by VI-element atoms such as sulfur or selenium have low surface energy, and thus enable a self-assembled growth of metallic clusters on the semiconductor. To terminate the surface of GaAs substrates by sulfur, the substrate was first dipped into an $(NH_4)_2S_x$ solution for 1 hour, and then rinsed by pure water. By heating the substrates up to 400℃, reflection high-energy electron diffraction (RHEED) pattern changed from a halo to a 1×1 streaky pattern, indicating the formation of flat surfaces. The growth of MnAs dots changed the streaky 1×1 RHEED pattern to a spotty pattern by the dot formation. The growth temperature of the MnAs dots on the substrate was set to 200℃. For the investigations of the density dependence of the MnAs dots, we prepared three samples with different dot densities of $3.5\times10^{12}$, $2.0\times10^{12}$, and $1.5\times10^{12}$ $cm^{-2}$ deduced by the atomic force microscopy (AFM) images as shown in Fig. 1. Hereafter we refer to the three samples as high-, medium-, and low-density MnAs dots. For all the dots, the diameter and the height of each dot were estimated to be about 10 nm and 5 nm, respectively, from the transmission electron microscopy (TEM) images.

The MnAs:GaAs granular films were obtained by a thermal annealing of diluted magnetic semiconductor $Ga_{1-x}Mn_xAs$ under As pressure following two different heat procedures; (I) 580℃×1 minute, and (II) 650 ℃×10 minutes. From the cross sectional TEM observation and the fitting of the magnetic-field dependence of the MCD signals by Brillouin function, the diameters of the clusters were estimated as (I) 6 nm and (II) 8 nm, respectively.

The XAS and XMCD measurements were performed using a Dragon monochromator installed at the beamline 11 of NSRRC. The XAS and XMCD spectra were measured by means of the soft X-ray fluorescence yield using a photodiode. In the case of XMCD measurements, we applied a magnetic field of 1000 Oe during the measurements at 100 K. As references, we measured the XAS spectra of a $Ga_{1-x}Mn_xAs$ film and a NiAs-type MnAs film.

Figure 2 shows Mn 2p XAS spectra of MnAs dots with various dot densities and those of $Ga_{0.96}Mn_{0.04}As$ as well as of NiAs-type MnAs film. The spectra of the low-density and medium-density MnAs dots are similar to that of $Ga_{1-x}Mn_xAs$, which indicates localized Mn 3d states. The spectrum of the high-density MnAs dots shows a line shape which is intermediate between that of $Ga_{1-x}Mn_xAs$ and that of the MnAs film. Many fine structures were observed in the localized cases, and can be analyzed using atomic multiplet theory. One can therefore speculate that there is a critical dot density below which the localized electronic structure of Mn 3d states is maintained in the zinc-blende MnAs dots. From

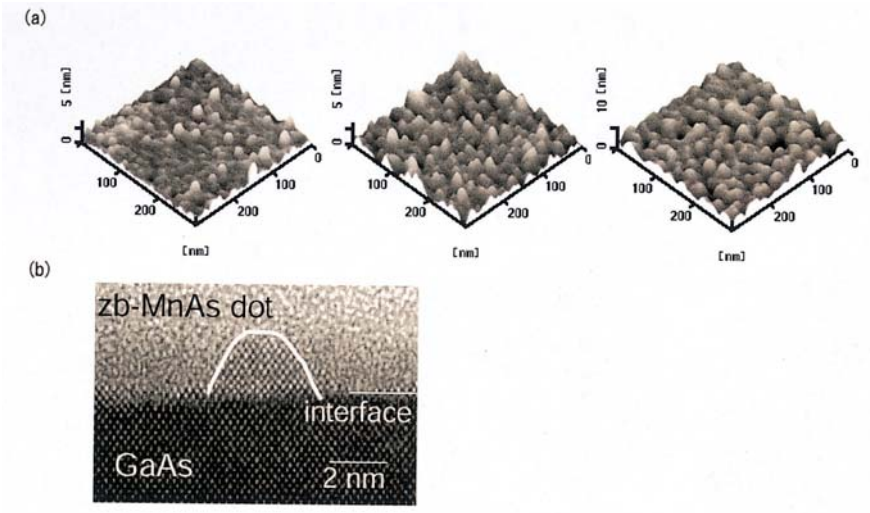


*Fig. 1: (a) Atomic force microscopy images of the zinc-blende type MnAs dots for different dot densities: low density (left), medium density (center), and high density (right). (b) Cross-sectional TEM image of a zinc-blende type MnAs dot (medium density).*

the AFM image of the high-density dots as shown in Fig. 1, dots cover almost all the substrate to the extent that the dots are connecting each other and behave as being metallic through the percolation, although the zinc-blende structure may be maintained at the center of each dot. Therefore, the broad XAS line shape of the high-density MnAs dots can be attributed to the metallic part of the MnAs dots, being most likely the NiAs-type structure.

To investigate the magnetism of MnAs dots, we performed XMCD measurements at the Mn 2p edges. Figure 3 shows XMCD spectra of the high-density MnAs dots. The magnetic field was reversed at every data point. Unfortunately, for the determination of the magnetic moment, the sum rules for Mn do not work, primarily because the separation of the $2p_{1/2}$ and $2p_{3/2}$ edges is too small. The inset of Fig. 3 shows the magnetic-field dependence of the XMCD at the $2p_{1/2}$ peak of $h\nu$=652.5 eV. A clear hysteresis was observed. In the case of the medium-density MnAs dots, XMCD signal was not observed, indicating the non-ferromagnetic behavior. To control the properties changing into ferromagnetic and metallic behaviors would be a key to fabricate the zinc-blende MnAs film.

Figure 4 shows Mn 2p XAS spectra of MnAs clusters. As a reference, the spectra of $Ga_{0.96}Mn_{0.04}As$ and MnAs films are also shown.

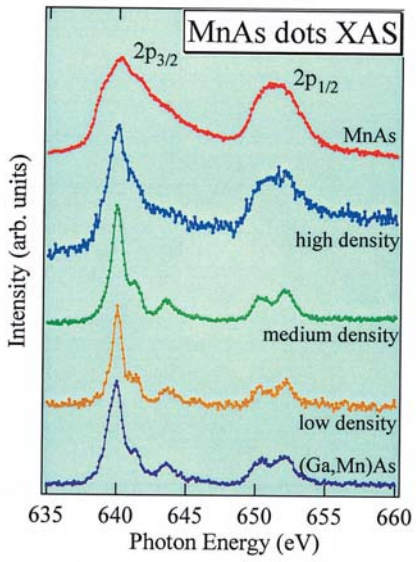


*Fig. 2: Density dependence of the Mn 2p XAS of MnAs dots compared with those of $Ga_{1-x}Mn_xAs$ and NiAs-type MnAs films.*

The XAS spectrum of $Ga_{1-x}Mn_xAs$ has the same line shapes as reported using the total electron yield method. After the annealing, Mn 2p XAS line shape changes from the localized Mn 3d states with the multiplet structures to the broad features coming from the itinerant NiAs-type spectrum. It is revealed that the nanoscale hexagonal NiAs-type MnAs clusters are formed in the GaAs matrix by phase separation due to the relaxation in the large compressive strain of the as-grown samples. We emphasize that XAS using fluorescence yield is the most suitable method to elucidate the bulk information such as MnAs clusters embedded in host matrix. Recently, it was reported that the crystalline structure of MnAs clusters is controllable by choosing the annealing conditions to form the zinc-blende type structure.

The XMCD spectra of the MnAs nanoscale clusters are shown in Fig. 5. Clear XMCD signal is obtained. The inset of Fig. 5 shows the magnetic-field dependence of the XMCD signal, where the photon energy was set at $h\nu$=652.2 eV. No hysteresis curve was observed, which means that no ferromagnetic ordering between the clusters occurs and indicates the super-paramagnetic behavior as reported in the magnetization measurement. We could deduce the site selective hysteresis curve from the XMCD magnetic field dependence.

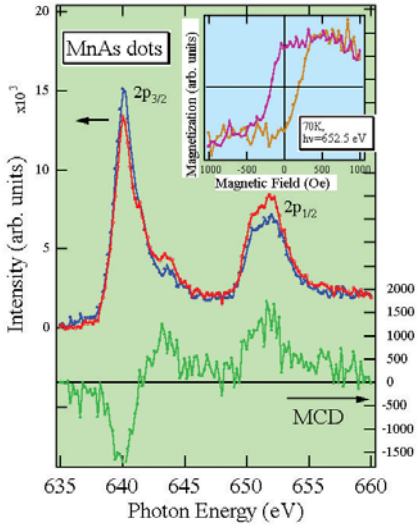


*Fig. 3: X-ray magnetic circular dichroism in the Mn 2p core-level region of high-density MnAs dots. Circular dichroism at 70 K is shown at the bottom. The inset shows the magnetic-field dependence of XMCD signals at photon energy $h\nu$=652.5 eV.*

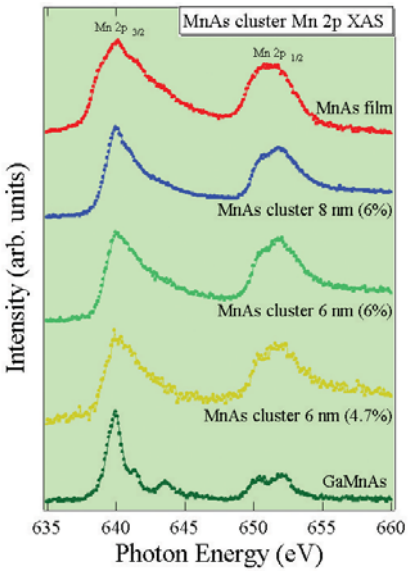


*Fig. 4: XAS spectra of nanoscale MnAs clusters compared with those of $Ga_{1-x}Mn_xAs$ and MnAs films.*

In summary, we have investigated the electronic and magnetic properties of MnAs-based nanostructures using XAS and XMCD. In the case of zinc-blende type MnAs dots, the density-dependent electronic structure through a percolation in each dot was revealed. By high-temperature annealing of $Ga_{1-x}Mn_xAs$, hexagonal NiAs-type MnAs clusters were segregated as MnAs:GaAs granular films and XAS spectrum drastically changed from the as-grown $Ga_{1-x}Mn_xAs$. No hysteresis curve in MnAs:GaAs granular films indicates the super-paramagnetic behavior.

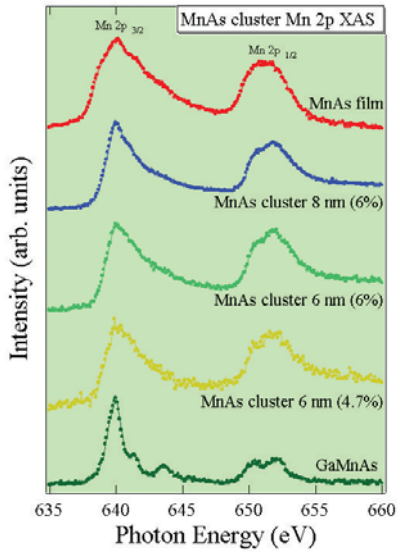


*Fig. 5: XMCD spectra of MnAs nanoclusters. The inset shows the magnetic field dependence of XMCD signals at hν=652.2 eV.*

## Beamline:

11A1 Dragon beamline

## Experimental Station:

XAS and XMCD measurements end station

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## Publications:


- K. Ono, J. Okabayashi, M. Mizuguchi, M. Oshima, A. Fujimori, H. Akinaga, J. Appl. Phys. **91,** 8088 (2002).
- H. Akinaga, M. Mizuguchi, K. Ono, and M. Oshima, Appl. Phys. Lett. **76**, 357 (2000).
- J. Okabayashi, M. Mizuguchi, M. Oshima, K. Ono, A. Fujimori, and H.Akinaga, J. Mag. Mag. Mater. (in press).


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