Self-assembled and patterned Fe and Fe$_3$O$_4$ dots on III-V semiconductors

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Abstract. In this article we reviewed the experimental results of self-assembled and patterned Fe and Fe$_3$O$_4$ dots on GaAs(100) and InAs(100) surfaces. Superparamagnetic nanoclusters were formed during the Molecular Beam Epitaxy (MBE) growth of the Fe on both GaAs(100) and InAs(100) substrates within 2.5 to 4.8 ML coverage. STM, MOKE and XMCD measurements were performed to characterize the structural and magnetic properties of these nanoclusters. These nanoclusters exhibit strong uniaxial anisotropy of the order of $6.0 \times 10^5$ erg/cm$^3$. Magnetic domain structures and coercivities of the epitaxial Fe films grown on GaAs(100) and patterned into arrays of circular dot were also investigated. MOKE and MFM studies revealed that the 1 µm diameter single domain dot arrays showed direct evidence of strong interdot dipolar coupling when the separation is reduced to 0.1 µm. The coercivities of the dots were also observed to be dependent on the separation and size of the dots indicating that interdot dipolar coupling affects the magnetization processes in these dots. Fe$_3$O$_4$ films grown on deformed GaAs(100) substrate formed nanostripes following the topography of the substrate. MOKE measurements showed that these nanostripes have uniaxial magnetic anisotropy with easy axis perpendicular to the length of the nanostripes. This suggests that the magneto-elastic coupling plays a more dominant role than that of the shape anisotropy in determining the magnetic properties of these nanostripes.

1. Introduction

Miniaturization of the electrical components becomes an obvious choice in device research and development because not only that, there is a strong demand to improve performance of electronic devices but also it can reveal phenomena those are unique from macroscopic length scale. However, miniaturization is also one of the fundamental challenges that the researchers are facing in the field of electronics as existing semiconductor based technology imposes constrains to the minimum achievable device size through the limitation of conventional lithography techniques. Consequently, novel technologies are demanded and new and exciting branches of technology are emerging. “Spintronics” [1-8] is such a potential concept. Within the context of spintronics, the electron spin, as well as the charge, is manipulated for the operation of information processing in electronic circuits, based on the fundamental fact that an electron contains “spin” as well as “charge”. These spintronic-devices, combining the advantages of magnetic materials and semiconductors, are expected to be non-volatile, versatile, fast and capable of simultaneous data storage and processing, while at the same time, consume less energy. They are playing an increasingly significant role in high density data storage, microelectronics, sensors, quantum computing, and Bio-medical applications.
The major challenge in developing next generation spintronics devices is the synthesis of high quality materials with Curie temperature above room temperature, capable of producing large spin polarization at the Fermi level and matched conductivity between the magnetic material and semiconductor. In this context the epitaxial ferromagnetic thin films grown on the semiconductors like GaAs, and InGaAs has already been put into test. Very recently half metallic magnetic oxides such as CrO$_2$, Fe$_3$O$_4$ etc. have drawn considerable attention as they could produce spin polarization of 100% at Fermi level.

In this paper, we will review our work of a) the growth of Fe/GaAs and Fe/InAs heterostructures, and in particular, the nanoclusters formed at the initial stage, b) the magnetic and transport properties of these nanoclusters and the interface, c) patterned single crystal Fe dot arrays, and d) magnetite nanostripes on deformed GaAs(100) substrate.

2. Experimental
All the Fe films were grown in MBE systems using e-beam evaporators with the pressure below 5x10$^{-10}$ mbar with a deposition rate of approximately one monolayer (ML) per minute. The InAs (100) substrates were cleaned using a combination of oxygen plasma etching and wet etching (HCl:H$_2$O=1:4) before loading into the UHV system and annealing in the chamber at 510$^\circ$ deg C for 0.5 h before growth. The GaAs(100) substrates were chemically cleaned with an H$_2$SO$_4$:H$_2$O$_2$:H$_2$O (4:1:1) solution for 30 sec, followed by de-ionized water rinsing and isopropyl alcohol (IPA) vapour cleaning. To reduce the intermixing of Fe with Ga, In, or As at the interface, the films were grown at room temperature rather than elevated temperatures. The epitaxial growth of the films was monitored with both LEED and RHEED. Clear diffraction patterns from the Fe overlayers were observed after about 3-5ML of deposition. STM measurements further confirm that the growth in both system proceeds via the three dimensional Volmer-Weber growth mode with nanoscale island formed at the initial growth stage. MOKE measurements were done in-situ during the growth to monitor the evolution of the magnetic properties of these films.

On the other hand in order to obtain Fe$_3$O$_4$ films, Fe films were grown epitaxially on GaAs(100) substrates and then oxidized in an UHV chamber. The substrate was annealed at 830 K for 30 minutes prior to film growth. The films were then oxidized in an oxygen environment of 5×10$^{-5}$ mbar for 180 seconds at 500K. Details of film structures and magnetic properties would be found elsewhere [9]. The Fe dot arrays were fabricated using electron-beam lithography operated at 50 KeV followed by ion-beam etching through an intermediate Al-mask prepared by metallization and lift-off process.

3. Superparamagnetic Fe nanoclusters on GaAs and InAs
The magnetic properties of Fe thin films grown on both GaAs(100) and InAs(100) substrate at room temperature were observed to proceed via three phases: a non-magnetic phase, a short-range-ordered superparamagnetic nanocluster phase, and a ferromagnetic phase; the superparamagnetic phase forms in a narrow thickness range of 3.5 - 4.8 ML(mono layer) for Fe/GaAs and 2.5 - 3.8 ML for Fe/InAs, respectively [10-12]. However, there are other suggestions for the mechanism of ultra thin Fe growth on GaAs and the issue of formation of superparamantic phase is still an active area of research [13]. Figure 1 and 2 are the STM micrographs of the formation of Fe nanoclusters on GaAs(100)-4 x 2 and InAs(100)-4 x 2 substrates, respectively. Figure 1(b) shows that even at a low coverage of 0.02 ML (monolayers) 3-D island of Fe are formed. Similar, features are also observed in case of the InAs substrate at a low coverage of 0.05 ML as shown in figure 2(a).
Figure 1: STM micrograph of (a) the GaAs(100) substrate, (b) – (d) growth of Fe nanoclusters on the GaAs(100) substrate. The thickness of the Fe growth is shown on the bottom left hand corner of the micrographs. The crystallographic directions are shown schematically in the inserts. The dimensions of (a) is 12.5 x 10 nm², while the others are 20 x 20 nm².

Figure 2: STM micrograph of the growth of Fe nanoclusters on the InAs(100) substrate at different thickness. The thickness of the Fe growth is shown on the bottom left hand corner of the micrographs.

Figure 3 depicted the trend of the magnetic phases in terms of MOKE measurement as the film coverage increases for Fe grown on GaAs(100) substrate. No MOKE signal was observed from the substrate in figure 4(a). Significant MOKE signal was first detected at a thickness of 3.5 ML. So for the coverage (x) for 0 < x < 3.5 ML there exist no magnetic phase. With further deposition the MOKE loops assumed s-shape at 4.3 ML. In these loops the lack of hysteresis is the indication that the ferromagnetic phase has not yet been developed and these loops represent either paramagnetic or superparamagnetic phases. The onset of ferromagnetic phase began at the thickness of 4.8 ML because
the loops at this thickness contained hysteresis. Considering figure 3 we could say that the magnetic properties of these clusters come from the exchange interaction within them, which becomes stronger, and leads to internal ferromagnetic ordering, giving rise to the well-known superparamagnetic phase. With further increase in the coverage, the islands coalesce and long range ferromagnetic ordering develops. The scenario has been schematically shown in figure 4.

Fitting the MOKE curves with a Langevin function, the average values of the effective magnetic moment per cluster are obtained to be \((1.05 \pm 0.15) \times 10^4 \mu_B\) and \((4.40 \pm 0.65) \times 10^4 \mu_B\), respectively, for the films of the coverage of 4ML and 4.3ML. We have also measured the XMCD spectra of both Fe/GaAs and Fe/InAs. The spin moments were found to be about \(2.0 \mu_B\) close to that of the bulk value and the orbital moments enhanced by about 200-300\% [14, 15]. This may be partially due to an increased degree of localization of electronic states at the interface related to the atomic scale structures of the reconstructed semiconductor surfaces. Temperature dependent magnetoresistance measurements were carried out on these cluster ultrathin films of 1.0-8ML thick on intrinsic GaAs. It is found that for films thinner than 3ML the temperature dependence of the zero field resistivity is consistent with electrons tunnelling between Fe nanoclusters through the intrinsic GaAs substrate. When the nanoclusters enter the superparamagnetic phase around 250K, a negative magnetoresistance is observed indicating that the electron spin-polarisation "survives" in the tunneling process through GaAs [16].

![Figure 3](image)

**Figure 3:** _In situ_ MOKE hysteresis loops of the Fe films grown on GaAs (100) with 4 X 6 reconstruction at different Fe thicknesses with the magnetic field applied along the <0-11> direction.
Ferromagnetic resonance (FMR) measurements were also done on these samples. In figure 5 shows the experimental data of FMR field $H_{\text{res}}$ as a function of field orientation angle of a 4.1 ML Fe film on GaAs(100) substrate. The observation clearly indicates that the film has large uniaxial anisotropy with the easy and hard axes parallel to the [0-11] and [011] directions, respectively [17]. A proper theoretical fitting of the data provide the in-plane uniaxial anisotropy constant as high as 59 $\times$ 10$^4$ erg/cm$^3$ of for the 4.1 ML sample with zero cubic contribution for the superparamagnetic nanocluster [18].

4. Patterned single crystal Fe dot arrays
Patterning an epitaxial film into nano elements have the advantage of modifying micromagnetic structures via the competing magnetocrystalline anisotropy and dipolar fields. Important understandings, like the thickness dependency of the coercive fields has been demonstrated for
submicron epitaxial Fe (100) dots [19], effect of size and shapes on remanent domain structures and magnetic behaviour of square and rectangular shaped epitaxial Fe(100) elements has also been studied [20–22]. We have investigated epitaxial Fe(100) circular dot arrays of 30nm thick and of different diameters and separations grown on GaAs(100) have been patterned by e-beam lithography, and studied using magnetic force microscopy (MFM) and focused magneto-optical Kerr effect (focused-MOKE) [23, 24]. Figure 6 shows the SEM micrograph of a 1 mm dot arrays. The crystallographic directions are indicated with the arrows in the figure. The MFM images of the different dot size with interdot separation of 2d and 0.5d, where d is the dot diameter are shown in figure 7. Distinctively different domain structures and coercivities are observed in dot arrays depending on different separations. This provides with the evidence that interdot dipole coupling affects both the domain structure and the coercivity. The domain structure of the 1 µm diameter dot arrays shows the effect of

![Figure 6: SEM micrograph of a 1 µm dot arrays.](image)

![Figure 7: MFM micrographs Fe epitaxial dots with separation (a) s=2d and (b) s=0.5 d](image)
strong interdot coupling when the separation is reduced down to around 0.1 µm. As shown clearly in figure 8, the coercivity of the dot arrays is dependent on both separation $s$ and the diameter $d$, illustrating that both the dot diameter and separation are crucial parameters in patterned magnetic data storage media.

![Figure 8](image)

**Figure 8:** Effect of interdot separation on coercivity of the Fe dot array.

5. Magnetite nanostripes on deformed GaAs(100)

Very recently, we have demonstrated the synthesis of magnetite (Fe$_3$O$_4$) nanostripes on deformed GaAs(100) by controlling the substrate processing and post-growth annealing. Before growth the GaAs substrates were prepared by chemical and thermal treatments with a chevron-featured RHEED pattern observed when the electron beam was along the GaAs(100)[011] direction as shown in figure 9. Following the growth of Fe this chevron-like pattern becomes less prominent. This chevron-like pattern appears again after the oxidation of the Fe into magnetite in 5×10$^{-5}$ mbar oxygen at 500 K for 1200 seconds. This is due to the formation of the nanoscale magnetite stripes along the [011] direction. The SEM images show that the size of the nano stripes is around 100×600 nm², as shown in figure 10. MOKE measurements

![Figure 9](image)

**Figure 9:** RHEED patterns obtained along the [011] direction of (a) GaAs(100) substrate after preferential chemical etching, (b) after oxidizing a 4.2 nm Fe film at 300 K. The chevron-features are present in both patterns, only it is more enhanced in (b).
Figure 10: SEM micrograph of magnetite nanostripe formed on GaAs(100) substrate. The horizontal axis is parallel to the [011] direction.

Figure 11: MOKE loops of the Fe nanostripes obtained along four crystallographic directions for a coverage of 4.2 nm. reveal that the 4.2 nm sample exhibits a uniaxial magnetic anisotropy property with easy axis along the [0-11] direction which is perpendicular to the length of the nanostripes. The magnetic property of the nanostripes is attributed to the deformation of the Fe₃O₄ lattice. Relative compression of the deformed lattice along [011] and [0-11] directions is responsible for the magnetic behavior of these nanostripes [25].
6. Conclusions
We have demonstrated that ferromagnetic nanostructures are possible to grow/fabricate on semiconductor substrates both by conventional lithography and epitaxial self assembly techniques. These ferromagnetic nanostructures behaves in different ways depending on the detailed fabrication/growth process. These nanostructures should have potentials to become materials for future spintronics as they are integrated with semiconductors and their sizes could go down to nano/atomic scales.

7. References
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