CHAPTER 5

MORPHOLOGICAL AND MAGNETIC PROPERTIES OF CoFe/Si THIN FILMS GROWN UNDER THE INFLUENCE OF A DEPOSITION FIELD

In the previous chapter, the effects of field cooling on CoFe/Si thin film system are discussed in detail. There, the orientation of the deposition field as well as the field applied during field cooling was kept fixed along the sample normal. In the following chapter, the growth, morphology, composition and magnetic properties of CoFe/Si nanostructures in the presence of a deposition field oriented normal-to as well as in-plane to the sample normal is discussed in detail.

The synthesis of metallic monolayers and multilayers of ferrous group metals is of great interest because of their magnetic properties. They have found wide application in the field of magnetic data storage, especially for reading/writing elements in the hard drive heads [72-78].

As discussed in the introduction to this dissertation, vapors of heavy organic molecules like Bianthrone show paramagnetic nature in the presence of an external magnetic field. This is attributed to the current loops generated in them in the presence of the external magnetic field. These current loops are affected by a deposition field whereas most metal vapors are diamagnetic. As discussed before, it is expected that there is a tiny window for the field to influence the magnetic nanostructures before they become immobile over the substrate surface. Such a possibility has been probed and investigated in this section of the dissertation.

Ultra-thin CoFe films of about 100Å were deposited on silicon substrates using a standard electron beam evaporation system. Prior to deposition, the silicon substrates (1cm × 1cm) were thoroughly cleaned and degassed using high
In correlation with the SEM and AFM images, this can be attributed to the smaller size of the nanostructures in sample a. The higher saturation magnetization value of sample b and c indicates the presence of a larger quantity of magnetic material (iron and cobalt) in these samples (figure 5.6-c, d and figure 5.7-a, b, c). This is in good correlation with the EDS results. The saturation magnetization of sample b is comparable to that of the sample c (figure: 5.6- c, d and figure 5.7 a, b, c; 28 µemu and 29 µemu on an average). This may be attributed to the fact that even though the nanostructures in both the samples are having different morphologies, they are volumetrically similar. The nanostructures in both the samples (b and c) are oblong spheroids with average minor and major axes of 80 nm and 220 nm (figure 5.2-b and c), the only difference being their relative orientation with respect to the sample plane.

Further in the case of sample a, we can see that, there exists an easy axis of magnetization along the normal-to the sample (figure 5.6-a). The hysteresis loop of sample b in figure 5.6-c also has an easy axis of magnetization along the normal-to the sample. In correlation with the AFM images (figure 5.2 – a and b) these observations can be attributed to the shape dependent magnetic anisotropy in which, typically the easy axis is along the longest dimension of the nanostructures [80]. This may also be attributed to the fact that the application of an external magnetic field during deposition results in a uniaxial easy axis parallel to the field direction, as pointed out in previous research by Hindmarch et al [81]. For similar reasons in the case of sample c, we can see that the easy axis of magnetization is in-plane to the sample (figure 5.7: a, b and c). It can be observed that when the hysteresis loop was plotted by keeping the magnetizing field parallel to the major axis of sample c (figure 5.7-c) the value of coercivity was slightly more than the measurement done along the minor axis (figure 5.7-b). It may be postulated that this increase in the value of coercivity is contributed to by an increased edge roughness in this particular
sample. It can also be observed that the easy axis of magnetization is oriented parallel to the major axis of the nanostructures in sample c.

The above observations indicate the significance of an external magnetic field during the growth of CoFe magnetic nanostructures. The relative orientation of the easy axis of magnetization with respect to the substrate plane is an important factor in the application of CoFe and similar magnetic systems in high density data storage media, read/write devices and MRAMS. From the observations discussed in this dissertation, it is evident that, having a calibrated external magnetic field with a suitable orientation can be used as a convenient method of controlling the size and magnetic orientation of the nanostructures in such systems.
temperature ultra-sonication. The base pressure of the high vacuum system used was $5 \times 10^{-8}$ mbar. A bulk mixture of Co and Fe (Co:Fe = 1:1) was evaporated onto the substrate at room temperature at a typical rate of $0.1 \AA/s$ under a working pressure of around $1 \times 10^{-7}$ mbar. The thickness of the deposited films was approximately determined using a quartz crystal monitor interfaced to an Inficon sigma controller. The substrates were aligned with respect to commercially procured NdFeB permanent magnets having calibrated field strength of 0.2 Tesla in order to achieve the normal-to and in-plane lines of force (Figure 5.1). The field was found to be uniform for a 2cm X 2cm area in both the arrangements (normal-to and in-plane).

**Figure 5.1**: Arrangement for obtaining lines of force normal-to to the substrate using a circular magnet (A) and arrangement for obtaining lines of fore in-plane to the substrate using a bar magnet (B).

Morphology of the samples was studied using Agilent Technologies’ AFM. All images were taken in contact mode using silicon cantilevers with force constant of 0.02–0.77 N/m, tip height 10–15 nm. Field emission scanning electron microscopy (FESEM) images taken using a FEI Quanta 200 FEG were used to
correlate and confirm the morphological features of the synthesized nanostructures. The elemental composition of the samples was analyzed using Oxford’s energy dispersive x-ray spectrometer (EDS). The samples were studied using vibrating sample magnetometer (VSM) to understand the changes in magnetic properties due to the influence of the magnetic lines of force. The magnetic studies were typically done at room temperature and all the samples were analyzed with magnetizing fields of the instrument normal to and in plane to the sample.

Figure 5.2-a: AFM images of sample synthesized in the absence of any fields.

Figure 5.2 (a-c) shows the AFM images of the sample synthesized in the absence of magnetic lines of force (sample a), sample plane oriented perpendicular
and parallel to the magnetic lines of force (samples b, c) respectively. The respective surface profiles are given in figure 5.3 (a-c).

**Figure 5.2-b:** AFM images of sample oriented perpendicular to an external magnetic field. The x marks in b indicates the direction of the magnetic lines of force which are oriented normal-to the sample.
Figure 5.2-c: AFM images of sample oriented parallel to the external magnetic field. The arrows indicate the direction of the magnetic lines of force which are oriented in-plane of the sample.

It is evident from the AFM images and the surface profiles that, for the Volmer Weber type islands formed in samples a, b and c, there is a high aspect ratio. These are typical of CoFe/Si system because of their slight lattice mismatch (~ 2%). This type of agglomeration also accounts for the significantly larger size of the nanostructures formed when compared to the thickness of the films deposited (100Å). The nanostructures in sample a has an ellipsoid or oblong spheroid kind of shape, with the longest dimension of the nanostructures oriented normal-to the sample plane.
Figure 5.3: Line profiles taken for AFM images of (a) sample synthesized in the absence of any fields, (b) sample oriented perpendicular to an external magnetic field and (c) sample oriented parallel to the external magnetic field.

The AFM images of sample a and b indicate similar growth morphologies. The only noticeable difference between samples a and b is that the minor and major axes of the nanostructures in sample a (~ 60, ~ 160 nm) is typically smaller than the minor and major axes of the nanostructures in sample b (~ 90, ~ 250 nm). This may
be attributed to the fact that when depositing in the presence of a magnetic field, the metal adatoms come very close to the substrate (before the substrate-metal bond is formed), the mobility of the Fe and Co atoms over the sample is affected by the lines of force passing through them. This would cause the metal adatoms to be mobile on the substrate and get deposited based on the applied magnetic field rather than the normal thin film growth dynamics. It can be postulated that the adatoms of the ferromagnetic metals will get deposited in a region where the magnetic flux density is more compared to the surrounding region, thereby forming larger clusters. Based on the postulation, it can be expected that the nanostructures would nucleate and grow along the direction of the applied magnetic field. Even though gaseous metal atoms are diamagnetic and are least affected by magnetic fields, it may be said that, as the atoms cool down from the gaseous state to the solid state during the deposition process, they regain ferromagnetic domain ordering while still retaining the surface mobility for a small period of time. We believe that the presence of these mobile ferromagnetic adatoms for a brief window of time results in the magnetic field influencing the growth of nanostructures.

Comparing the samples b and c; we can see that, in the latter case also the nanostructures have an ellipsoid or oblong spheroid kind of shape. This could be because of preferential growth of the nanostructures as the atoms would tend to align themselves favoring the direction of the orientation of the magnetic lines of force. This is in line with our earlier postulation. Further, this is also supported by the fact that the nanostructures in sample b were observed to be taller than their counterparts in samples a and c (Figure 5.2). The minor axis of the oblong spheroid structures formed in sample b is comparable to that of sample c. From the above observations, it can be concluded that the morphology of the nanoscale islands formed in both the cases are influenced by the direction of the magnetic lines of force passing through the sample during the time of growth.
Figure 5.4-a, b: FESEM images of (a) sample synthesized in the absence of any fields, (b) sample oriented perpendicular and (c) sample oriented parallel.
Figure 5.4-c: FESEM images sample oriented parallel.

Figure 5.4 (a-c) shows the FESEM images of sample a, b and c. The dimensions of the nanostructures grown in all the three samples correlate well with those estimated from the AFM images. This further confirms the fact that an external magnetic field can be used to control the shape, the structure and size of ferromagnetic nanostructures.

EDS spectra of the three different samples are given in Figure 5.5: a-c. The percentage composition of iron in samples a, b and c is 58, 55.25 and 56 and that of cobalt is 34.7, 37.3 and 38.1 respectively.
Figure 5.5: EDS spectra of (a) sample synthesized in the absence of any fields, (b) sample oriented perpendicular and (c) sample oriented parallel.
We can infer that the samples are richer in iron content compared to that of cobalt. This can be attributed to the fact that Fe, which requires a comparatively lesser heat of vaporization (340 kJ-mol\(^{-1}\)) gets deposited at a faster rate than Co (377 kJ-mol\(^{-1}\)). But, when we compare the sample synthesized in the absence of any fields with the ones subjected to the external magnetic fields (both parallel and perpendicular), the difference between the iron and cobalt content is lesser in the latter case (Figure 5.5-b and c). This may be attributed to the fact that, during the process of deposition, cobalt which has a higher magnetic susceptibility than iron is influenced more by the external magnetic field, which in turn leads to it aiding the deposition of cobalt adatoms from the evaporated adatoms to the substrate surface as compared to iron adatoms. It is also evident from the EDS spectra that the percentage composition of oxygen is very less when compared to iron and cobalt (5.6%, 2.4% and 3.2% in samples a, b and c respectively). Exposing the samples to ambient conditions for the magnetic measurement usually results in the formation of films covered with a thin layer of oxide (upto a few monolayers). The only effect this oxide layer has on the magnetic properties of the underlying ferromagnetic film is a decrease in the magnetic content of the film. If the film is thin enough, a decrease in the value of the saturation magnetization is observed. The samples studied in this experiment are well within the range of thickness that the effect of the oxide coating can be considered insignificant [79]. Also, since only trace quantities of surface oxides were formed, the use of capping agents for further characterizations is omitted. This was also done in order to prevent sample contamination from the capping agents. A characteristic peak for the substrate (Si) is also visible in the EDS spectra of each sample.

The hysteresis curves of the samples a, and b were measured with the magnetizing field of the VSM normal-to and in-plane to the sample are shown in figure 5.6 (a-d).
Figure 5.6: (a, b) Normal-to and in-plane VSM graphs of sample synthesized in the absence of any fields and (c, d) sample oriented perpendicular to an external magnetic field respectively.

For the sample c, one normal to the plane (figure 5.7-a) and two in-plane hysteresis loops were plotted; one with the magnetizing field parallel to the minor axis of the oblong spheroid (figure 5.7 –b) and the second one with the magnetizing field parallel to the major axis (figure 5.7 – c).
Figure 5.7: Normal-to VSM graph of (a) sample oriented parallel to the external magnetic field. In-plane VSM graphs of sample oriented parallel to the external magnetic field with the magnetizing field of the VSM parallel to the minor (b) and major (c) axes of the oblong spheroid nanostructures.

The analysis of data was done after subtracting the substrate and holder offset as described by Diaz-Castanon et al [49]. When the magnetic field of the VSM was applied normal-to and in-plane to samples a and b, the saturation magnetization value of the former (Figure: 5.6- a; 23 µemu) was found to be lesser than the latter.