Chapter 7: Plasma assisted synthesis and modifications of FePt nanostructures

In Section A of this chapter, an attempt to modify the surface of capped FePt nanoparticle using the H\(^+\) energetic beam produced by the Dense Plasma Focus is made. The effect of varying ion dose of highly energetic H\(^+\) ions on the structural and magnetic behaviour of the FePt nanoparticles is demonstrated. Controlled alignment of bimetallic FePt alloy nanoparticles (NPs) on platinized silicon using atmospheric microplasma (AMP) assisted chemical synthesis is also presented in Section B. Importance of the AMP in controlling the particle alignment is highlighted by performing experiments with various combinations of electrolyte concentration and discharge parameters. X-ray diffraction analysis reveals a 84% structural phase transformation from face centre cubic to face centre tetragonal phase post heat treatment. This structural transformation is accompanied with a change in the magnetic properties. The as prepared nanoparticles exhibit a soft ferromagnetic behaviour which turns in to hard magnetic phase with annealing. AMP discharge due to the high electric field shows ability for nanofabrication with a controlled alignment.
7.1 Introduction

The liquid phase chemical method such as co-reduction method and gas phase chemical method such as chemical vapour deposition (CVD) are preferred in order to maintain the purity of the prepared material (Sui et al. 2004). The physical method such as sputtering, physical vapour deposition (PVD), pulsed laser deposition (PLD), high energy density pulsed plasma deposition, and molecular beam epitaxy (MBE) are well known for the material deposition (Kim et al. 2007; Martins et al. 2001; Nakano et al. 2008; Schaaf et al. 2007; Konagai et al. 2007). The advantage of chemical methods over physical methods is the control on the grain growth and high yield of the material. Sun et al (Sun et al. 2000) demonstrated a control growth of FePt nanoparticles using chemical process and proposed a possible usage of these in data storage. These nanoparticles are capped with the organic capping of oleylamine and oleic acid for preparing the self assembled FePt nanoparticle with controlled particles size of narrow size distribution. However, the use of surfactant may result in the low value of magnetization. To retain the high value of magnetization, after chemical synthesis, organic capping of the nanoparticles needs to be removed.

The capping can be removed by various physical and chemical processes like chemical etching, thermal degradation, sputtering and different type of plasma treatment. The chemical methods involve the removal of capping using the suitable solvents which can dissolve organic capping. But the formation of the 2D self organization of the nanoparticles is not possible with chemical cleaning. The etching of the capping using the concentrated acid is another chemical approach. In the physical method the surface of the deposited film can be etch by the sputtering process using the massive gas ion like Ar. However, the etching process using the sputtering also results in the disturbance in the self assembly of the nanostructure. Plasma based irradiation is one of the best and fastest tool to clean the organic capping of FePt nanoparticles in ambient atmosphere.

In plasma processing, the energetic ion beam has been extensively used for the modification and synthesis of the nanoscale structures. The surface modifications of the nanostructures due to the ion beam can be understood in the form of inter particle
diffusivity and surface sputtering of atoms (Tang et al. 2011; Lee et al. 2012). The morphological and structural changes induced by the energetic ion irradiation can be observed in many materials, both in the crystalline and non-crystalline form, metals, semiconductors, organic or inorganic materials etc. The effect of energetic ions over the organic capping on the metal nanoparticle has not been studied earlier. Functionalised or capped nanoparticles need a thermal treatment for the degradation of organic capping from the surface of the particles. This conventional heat treatment used for removal of organic capping also disturbs the organization of the nanoparticles. Moreover the degradation of organic capping results in the carbonaceous layer over the nanoparticles on annealing. However there are other processes, used for the removal of organic shell of nanoparticles like hydrogen plasma treatment. A similar attempt has been made to remove the ligands using the dense plasma focus (DPF). Here the DPF which acts as a good source of H\(^+\) ions with very high energy may result in the surface modification of chemically prepared FePt nanoparticles. The aim of the present work is to use DPF as an excellent and elegant method for processing the long range self organization of the FePt nanoparticle up to few micrometer.

In the earlier chapters (3 to 6), attempts to prepare FePt monodispersed particles with a long range positional ordering by chemical methods were discussed in detail. However, annealing disturbs the monodispersity and positional ordering. Hence, a method to produce the nanostructures in the desired phase without the annealing process is required. The control of particle size using chemical synthesis has been achieved in the presence of the surfactant which results in the good control on the particle size (Sun et al. 2000; Medwal et al. 2013). However, chemical methods are inherently slow synthesis, and require high processing temperatures. The fast processing time and low processing temperature may be achieved by high energy plasma-based and plasma-assisted processes.

Plasma technology plays a vital role in the processing and synthesis of various types of the magnetic and nonmagnetic materials for a wide range of applications. At higher operating pressures, plasmas are generally more difficult to sustain and their
properties can change dramatically. The plasma assisted nanomaterial synthesis needs low pressure (<1mTorr) which requires expensive vacuum equipment. To eliminate the heavy infrastructure and maintenance costs associated with low vacuum process, the nanomaterial synthesis performed at the ambient pressure and temperature will be a huge industrial advantage. Therefore, one of the important challenges in plasma processing is the development of low-temperature plasma sources operated at atmospheric pressure (Mariotti et al. 2010).

The plasmas used in plasma nanotechnology are essentially the low temperature plasmas with electron kinetic energies ranging from fractions to few tens of eV. The condition of non-equilibrium plasmas is described by the relation $T_e >> T_i = T_g$, that are gaining considerable interest due to their extreme simplicity are atmospheric microplasma (AMP). The non equilibrium plasma is described by keeping in view temperatures of electrons ($T_e$), ions ($T_i$) and background gas ($T_g$) respectively (Karthikeyan et al. 1997; Kaneko et al. 2009; Feugeas et al. 1988; Rawat et al. 1993; Kant et al. 1997; Mariotti et al. 2010). The AMP are the one in which one of the dimensions of plasmas is reduced to micron size resulting in extremely high electric field leading to large increase in electrons kinetic energy. Microplasmas can be combined with electrochemical cell to reduce metal cations to synthesize nanoparticles (Mariotti et al. 2010). The AMP-assisted electrochemistry has been successfully used for self organized Mo-oxide nanoparticles (Mariotti et al. 2009). It is well established that plasma promotes nanostructure growth-rate and helps to increase the yield in low span of time. The production of nanostructures at atmospheric pressure with plasma treatment is an advantage to the scientific and industrial community as it does not involve the use of complicated infrastructure. The AMP coupled electrochemistry with tunable energy of the electron jet at the surface of the liquid is giving a new direction to the synthesis of nanostructured materials such as Ag, Au, CNT, FeNi, etc (Levchenko et al. 2008; Yang et al. 2007; Lin et al. 2011; Chiang et al. 2010; Hopwood et al. 2005). A gas-phase mode or plasma-liquid interaction mode for material synthesis has been employed. The bimetallic nanoparticle synthesis, such as that of FeNi etc, using AMP has been conventionally
done in gas-phase mode (Chiang et al. 2010). Both the solution based and the gas phase based AMP synthesis adds an additional step of the separation for the nanoparticles after synthesis.

In **Section A** of this chapter, an attempt has been made to modify the surface of organic capped FePt nanoparticle prepared by chemical co-reduction method using the H+ energetic beam produced by the DPF. The effect of varying ion dose of highly energetic H+ ions by varying the exposure shots on the samples is demonstrated. The structural and magnetic studies also been investigated as an effect of plasma dose. **Section B** deals with anodic AMP discharge to achieve the formation and controlled alignment of bimetallic FePt nanoparticles directly on the platinized silicon substrate (cathode) by coupling the high voltage AMP discharge with electrochemical process. In an electrochemical process deposition on suitable conducting substrates is achieved at low voltages, whereas AMP process involves high voltages for the plasma production and deposition which may possibly assist the formation of aligned nanostructures. An attempt to achieve aligned FePt nanoparticles was using the AMP coupled electrochemical technique is presented.

### Section A

**Effect of dense plasma focus on the chemically prepared FePt nanoparticles**

#### 7.2 Dense Plasma Focus Device

Dense plasma focus (DPF) device shown in Figure 7.1 mainly include the following parts:

(i) a capacitor bank with single or multiple switches

(ii) a focus vacuum chamber with desired gas at suitable working pressures

(iii) an electrode assembly with an insulator sleeve around the anode at its lower end and

(iv) a high voltage charger and a low jitter triggering electronics.
Figure 7.1: (a) block diagram (b) photograph of dense plasma focus (DPF) device

The plasma focus device deals with the storage of the electrical energy which is instantly transferred to the electrodes assembly inside the chamber using the fast switch. The high voltage is transferred from the capacitor bank to the electrodes and a plasma sheath is formed.

After formation of plasma sheath, the Lorentz force accelerates the conducting plasma sheath along the anode towards the end of the anode tube. At the top of anode, the plasma sheath compresses and form plasma pinch. The formed plasma pinch when interacts with the material changes its properties by means of transient thermal effects of dense plasma. When the current sheath reaches the top of the anode, it begins to compress in the radial phase and finally forms the pinched plasma column, which is accompanied by radiations like microwaves, infrared, visible, UV, soft and hard X-rays and particles like electrons, ions and neutrons emissions. This multiple radiation emission characteristics of DPF devices attract researchers to work on various possible applications. The thermal transient energy may also affect the surface morphology of the dispersed colloidal solution of FePt nanoparticles on the silicon substrate prepared by the chemical co-reduction. Plasma focus effect is investigated under hydrogen gas atmosphere, keeping the substrate and anode distance fixed.
The dynamics of plasma is divided into three phases

(a) **The breakdown phase**

(b) **The axial phase**

(c) **The radial phase.**

(a) **The Breakdown Phase:** When the pulsed high voltage is applied across the electrodes of the DPF device at a suitable gas pressure of a few mbar an electrical discharge is initiated. According to Paschen's law the values of the breakdown voltage with 1 - 10 mbar deuterium pressure are lower than 1 kV which is smaller than capacitor bank voltage normally used in the operation of these devices. At very low pressure, the discharge can achieved at the open end of the electrodes system or within the whole inter-electrode volume. However, at a very high pressure breakdown appearing in the space between the coaxial electrodes. Hence, very low or very high operating gas pressures result an unfocused and non uniform current sheath. Hence, a moderated and optimized filling gas pressures with different gases is needed to achieve the efficient and sufficient plasma sheath at the top of anode. It is to be mentioned that gases with higher molecular weight are used at the low gas pressures whereas the light gases gives the efficient focusing at higher gas pressure.

(b) **Axial phase:** The current sheath formed in the breakdown phase, is accelerated by Lorentz force \( \mathbf{J} \times \mathbf{B} \) towards the open end of the anode. The axial component of Lorentz force will drag the formed current sheath towards the open end of the co axial electrode. However, the force acting on the current sheath depends on the strength of magnetic field \( \mathbf{B} \) at the different radial positions. This force is inversely proportional to radial distance \( r \), from the center of the anode. Hence, the current sheath nearer to the inner electrode will move faster. The radial component of \( \mathbf{J} \times \mathbf{B} \) force pushes the current sheath in the outward direction to the outer electrode. Hence a gradient is generated in the magnitude of the Lorentz force, giving the uneven distribution of acceleration in current sheath.

(c) **Radial phase:** At the end of the axial phase, the current sheath pinches inwardly sweeping around the end of the inner electrode and finally collapses in about 10 - 200 ns. The radial phase, as the final stage of plasma compression, plays the most
important role in the plasma focus evolution due to its extremely high energy density, its transient character and for being a rich source of phenomena like the emission of intense radiation and high energy particles. Based on experimental observations, the radial phase can be subdivided into three sub-phases: (i) quiescent phase, (ii) unstable phase and, (iii) decay phase.

The quiescent phase marks the beginning of the expansion of the pinch plasma column. During this phase, the rate of the radial expansion is hindered by the confining magnetic pressure. But due to the "fountain" like geometry of the current sheath, the rate of the axial expansion is unhindered resulting in the formation of an axial shock front. The increase of the plasma column will result in the great change of plasma resistance and inductance, which in turn lead to sharp increase in voltage signal due to the changing current.

The sharp change in the plasma inductance induces electric field in the plasma column. This electric field accelerates the ions and electrons in opposite direction. The relative drift velocity between the electrons and ions increases and exceeds the electron thermal velocity, which is condition for the onset of the micro-instabilities (such as the electron cyclotron and the various forms of beam-plasma instability) in the focused plasma column. The sub-phase during which the instabilities occur and disrupt the pinch plasma column is called the unstable phase. The unstable phase is the richest stage of the plasma focus evolution and is associated with soft and hard x-ray emission, and also with the emission of fast deuterons/ions, electrons

The disruption of the plasma column which starts with instability continues until the whole plasma column has been broken up completely. This last phase of the radial collapse is the decay phase. The plasma density drops below $2 \times 10^{17} \text{ cm}^{-3}$. During the decay phase a large, hot and thin plasma cloud is formed due to the complete breakup of the plasma column. This plasma cloud emits a large amount of Bremsstrahlung and the line radiation. For UNU/ICTP DPF device, the uniform current sheath is found to form about 550 ns after the high voltage is applied across the electrode system, whereas the forming time for miniature plasma focus is 120 ns. The formation of uniform current sheath marks the end of the breakdown phase and the beginning of the axial acceleration phase.
7.3 Experimentation

In DPF, at the top of anode, the plasma sheath compresses and forms plasma pinch that interacts with the material and changes its properties by means of transient thermal effects of dense plasma. Chapter 4 describes the preparation of monodispersed FePt nanostructures on Si substrate, along with the structural and magnetic properties. Plasma focus effect is investigated under hydrogen gas atmosphere, keeping the substrate and anode distance fixed at 5 cm. The dense plasma gun, giving rise to the short lived hot and dense plasma ($10^{25} - 10^{26} \text{ m}^{-3}$) fire on the chemically synthesized FePt nanoparticles dispersed on the silicon substrate (Pan et al. 2009). The effect of dense hydrogen plasma on the assembly of FePt nanoparticles is investigated as a function of plasma shots. The substrates of size 1cm x 1cm containing FePt nanoparticles were loaded in the DPF chamber. The chamber is evacuated up to $10^{-3}$ mbar using a rotary pump. High purity hydrogen gas was flushed in the chamber. The chamber is filled up with hydrogen at a pressure of about 4 mbar. The plasma gun was triggered to fire a plasma shot. The samples were exposed to 1, 2, 3 and 4 plasma shots and used for further characterization. The morphological studies of chemically prepared FePt on the silicon substrate were invested by JEOL JSM – 6700F field emission scanning electron microscope (FESEM). The etching behaviour of hydrogen dense plasma on capped FePt nanoparticles has been demonstrated using Raman spectroscopy study.

7.4 Results and discussions

7.4.1 Effect of $H^+$ ions shots

Figure 7.2(a) shows the SEM image of oleic acid and oleylamine capped FePt dispersed on silicon substrates. This globule formation of FePt nanoparticles is due to the interaction among organic capping of oleic acid and oleylamine. The long chain of the hydrocarbon over the capped nanoparticles has strong interaction among themselves leading to the formation of the closed packed structure of FePt in the organic matrix. The inset shows the TEM image of monodispersed array (Figure 7.2(b)).
Figure 7.2: (a) SEM image of as dispersed FePt nanoparticles on the silicon substrate and (b) TEM image of nanoparticles showing array as an inset.

Figure 7.3 shows the effect of one shot of hydrogen plasma on the surface of as deposited film of nanoparticles on silicon. The SEM image clearly indicates that the energy transferred to the surface of the film is not sufficient to etch/remove the organic capping from the surface of the nanoparticle. However the increase in the globular size is observed with a random distribution over the silicon substrate. A layer of FePt nanoparticles is developed with the hydrogen shot.

Figure 7.3: SEM images of FePt nanoparticles exposed with one plasma shot
The samples exposed to two shots of H\(^+\) plasma ions as seen in Figure 7.4 shows the long range self-organization of the nanoparticles on the silicon substrate. Globules of almost uniform sizes ~ 220 nm is formed with 2 shots. These globules are agglomerated FePt nanoparticles, as seen from the inset, with particles size as small as 7 nm. Such agglomeration is due to the etching of the organic capping as a result of hydrogen plasma exposure. Hence two shots of hydrogen dense plasma are not enough to clean the surface of the capped nanoparticle, not in the favour of the organization. The increase in the particle size with the bilayer distribution is also observed from the SEM image due to the interparticle diffusion with high energy ion beam of pulsed plasma. The formation of bilayer is due to the high concentration of the FePt nanoparticles in that particular area. The enhanced grain growth of the nanoparticles is observed as a result of Ostwald ripening due to high energy of the ion bombarded to the samples. Samples exposed to 3 shots are shown in Figure 7.5. The sample exposures with 3 shots show the further enhancement in the particle size with the uniform arrangement of the FePt nanoparticles on the surface. Also the formation of droplets is observed.

![Figure 7.4: SEM images of FePt nanoparticles exposed with two plasma shot](image_url)
Figure 7.5: SEM images of FePt nanoparticles exposed with three plasma shot

As the specimen was exposed with 4 shots, the cracks on silicon are observed. However, the particles are still organized on the silicon substrate (not agglomerated). The cracks on the silicon are also very ordered as seen from Figure 7.6. The ions with high energy incident on the FePt nanoparticles result in the Ostwald ripening, giving the large particle size distribution. The high energy of hydrogen ion also etches the unwanted organic capping from the surface and may result in the interatomic particle diffusion.

Figure 7.6: (a) SEM images of FePt nanoparticles exposed with four plasma shot and (b) magnified image of (a) is shown as a inset
7.4.2 Raman studies

Raman spectroscopy of the FePt nanoparticles as a function of different number of shots has been investigated. As deposited nanoparticles capped with the oleic acid and oleylamine do not show Raman spectra corresponding to carbon and its other forms (allotropes). It has been observed from the Figure 7.7 that the nanoparticles exposed with the one shot of hydrogen plasma results in the formation of the carbonaceous layer with a G band centred at 1600 cm\(^{-1}\).

Figure 7.7: Raman spectra of FePt nanoparticles exposed with plasma shots

However, with 2 shots of H\(^+\) plasma, the Raman peak at 1340 cm\(^{-1}\) is also prominent with reduced intensity showing etching behavior of the hydrogen plasma. Furthermore, the intensity of the Raman peaks with 3 shots decreases and becomes completely invisible with 4 shots. Hence removal of the complete carbonaceous layer was seen with four shots.
7.4.3 Effect of H\(^+\) ions on the structural and magnetic behaviour

XRD measurement has been performed on as deposited and dense plasma exposed samples as shown in Figure 7.8. All the plasma exposed film shows the presence of the chemically disordered FCC phase. However, the FWHM of the peaks reduce on increasing the number of plasma shots indicating the grain growth. This is in conformity with the SEM result. Moreover, a peak corresponding to (002) is also observed for the sample exposed with 4 DPF shots indicating the induced asymmetry in the FePt unit cell.

![XRD pattern of FePt as a function of plasma shots](image)

**Figure 7.8: XRD pattern of FePt as a function of plasma shots**

The magnetic measurement has also been performed to observe the effect of plasma exposure on the nanoparticles and shown in Figure 7.9. Variation in the MH loop has been observed as a function of DPF shots, wherein an increase in the coercivity is observed. Coercivity \(\sim 500\) Oe is observed with 4 plasma shots. However, further magnetic measurement as a function of annealing temperature has been carried out at the sample exposed with 3 plasma shots for which the uniform assembly of nanoparticles is obtained. A plot of coercivity as a function of annealing temperature is given in Figure 7.10. At 400 °C, onset of magnetic phase transformation with a
coercivity of 2 kOe is observed. However, on further annealing, coercivity increases and reaches a value of 5.8 kOe at 600 °C.

Figure 7.9: MH loop of H⁺ ion exposed samples for (a) 1 shot (b) 2 shots (c) 3 shots and (d) 4 shots.

Figure 7.10: A plot of coercivity as a function of annealing temperature for sampled exposed for 3 H⁺ plasma shots.
Section B

Atmospheric plasma coupled chemical synthesis of FePt nanoparticles

7.5 Experimental

7.5.1 Experimental setup

The synthesis of FePt alloy nanoparticles is done using the microplasma discharge assisted chemical synthesis at atmospheric pressure. The chemicals viz. H₂PtCl₆ (98%), FeSO₄ (98%), HCl, Na₂SO₄ (99%) are required for the preparation of the electrolyte purchased from Sigma Aldrich and used without further purification. The experimental setup developed and designed at NIE-NTU, Singapore is shown in Figure 7.11.

![Experimental setup for atmospheric plasma](image)

Figure 7.11: Experimental setup for atmospheric plasma

A hybrid electrochemical cell with Pt coated silicon used as a cathode is immersed in the aqueous electrolyte solution containing the metals cations. A standard stainless steel capillary tube with the inner diameter ~ 180 µm and 5 cm length, purchased
from Sigma Aldrich, and placed at an optimised distance of 2 mm above the surface of the electrolyte solution served as an anode. A TREK 615-10, ±10 kV AC/DC generator in constant current mode was used for AMP discharge. It may be noted that the anodic AMP discharge was used to drag the metal cations to the platinized silicon. The distance between the anode (capillary tube) and cathode (platinised silicon) was kept > 3 cm. This was a critical distance arrived at after several attempts to avoid the self discharge between the electrodes. The stainless steel capillary tube was connected to the constant Helium gas flow with a flow rate of 50 cubic centimetres per minute (SCCM) at STP.

### 7.5.2 Synthesis of nanoparticles

The electrolyte solution was prepared using metal precursors H$_2$PtCl$_6$ and FeSO$_4$ as a source of Pt and Fe cations respectively. The pH of the electrolyte was controlled within 2.5-3 using HCl. The homogeneous mixing was done using a magnetic stirrer for 30 min before the electrolyte was exposed to the plasma. Much experimental iteration, in terms of (i) different molar concentration of metal precursors (ii) AMP discharge current and (iii) different discharge durations, were conducted to optimize FePt nanoparticle synthesis. The experiments were performed with the solution that contains 2 mM H$_2$PtCl$_6$, 10 mM FeSO$_4$, (or 100 mM FeSO$_4$) and 0.5 M Na$_2$SO$_4$ in 50 ml de-ionised water. A discharge current of 5 mA was used to produce the plasma. The prepared electrolyte was exposed to plasma discharge for 5 min and 15 min. This process is capable of generating suspension of nanoparticles in the solution as well as deposits on the substrates (platinized silicon currently). Annealing and further characterization was performed on the deposited substrates.

### 7.5.3 Post synthesis treatment

The substrates containing as-prepared FePt nanoparticles were immediately functionalized with amine using oleylamine to minimize surface oxidation of film. The amine functionalized nanoparticles were kept at 100 °C under 5% hydrogen +
95% argon for about one hour. This sample is hereinafter referred as “as-prepared” FePt nanoparticle sample. The as-prepared FePt nanoparticles were annealed at 600 °C using a microprocessor controlled furnace, for one hour, for desired hard magnetic phase transformation. This sample is hereinafter referred as “annealed” FePt nanoparticle sample. The annealing process was carried out under the presence of 95%Ar+5% H₂ to avoid oxidation. The morphological, structural and magnetic properties of as-prepared and annealed FePt nanoparticle samples were studied using Joel JSM-640F Field Emission Scanning Electron Microscope (FESEM), SIEMENS D5005 X-ray diffractometer (XRD) and Lakeshore 7400 Vibrating Sample Magnetometer (VSM) respectively.

7.6 Results and discussions

7.6.1 Morphological studies

The SEM images corresponding to the as prepared nanoparticles synthesized at different experimental conditions are shown in Figure 7.12. Figure 7.12(a) shows linearly aligned FePt nanoparticles on platinized silicon substrate, synthesized by 2 mM H₂PtCl₆ and 10 mM FeSO₄, for 5mA AMP discharge current exposed for 5 min. The SEM image recorded at higher magnification shows very small particles of ~ 15±1nm as shown in Figure 7.12(b). The Figure 7.12(c) shows SEM image, for 15 minutes AMP discharge time keeping all the other experimental condition same as mentioned for Figure 7.12(a). A non-aligned growth of nanoparticles is observed for higher discharge duration. Furthermore, an attempt to obtain the aligned nanoparticles with the higher AMP exposure time was done by increasing the relative molar concentration of the Fe and Pt ions (i.e 2 mM H₂PtCl₆ and 100 mM FeSO₄) in the electrolyte. However, huge clusters have been observed in the SEM image as shown in Figure 7.12(d).

Hence, a controlled aligned growth was observed only for a specific combination of AMP discharge current, discharge duration and molar concentration of solution. The plausible explanation for the controlled alignment of NPs on the substrate surface is given below.
The AMP discharge setup, shown in Figure 7.11, was used in constant current mode and the typical voltage applied was of the order of few kV. The high voltages involved in the experimentation lead to high electric field on the substrate surface which can result in alignment of NPs. The simplistic equivalent circuit of the setup is shown in Figure 7.13 which shows flow of AMP discharge current through two symbolic resistances Rp and Re. The Rp is the resistance offered by the plasma (the AMP formed between the tip of the anodic electrode and electrolyte surface) and Re is the electrolyte’s resistance. The equivalent resistance of the setup therefore can be written as $R = R_p + R_e$. The plasma resistance Rp may be taken as constant, under the operating conditions used during this investigation, as the discharge length and the
helium gas flow rate were kept fixed. The resistance of the electrolyte depends upon the concentration of the ions in the electrolyte which can be changed by varying the molar concentration of the solute in the solvent. Hence, the resistance \( (Re) \) of the electrolyte is a function of the molar concentration of the electrolyte solution. The equivalent resistance of the setup thus depends on \( Re \). Since the power supply was used in constant current mode, keeping the current fixed at a particular value will still result in different electric field for electrolyte of different molar concentration as \( Re \) will change. Similarly, for a particular concentration of electrolyte the applied electric field will change if different discharge currents are used. In other words the applied electric field strength, one of the key factors responsible for controlled alignment of NPs, at the substrate surface will be a function of the amplitude of AMP discharge current and the molar concentration of the electrolyte.

![Figure 7.13: Equivalent resistance circuit for AMP discharge setup.](image)

It may also be stated that the localized electric field due to the microplasma gives energetically favourable paths that help in the formation of aligned assembly. During the exposure of plasma the surface of the Pt coated silicon gains which depend upon the discharge current. In the present case, the 5mA current used may be enough to produce the floating potential need to create electric field along the surface of the
conducting platinised silicon. The direction of the alignment can be defined with the direction of the flux of the electric field of the ions and radicals during the plasma treatment of the electrolyte. It may be understood that the metal cations may have coulombic interaction with the electric field of the radicals, resulting the alignment in the nanoparticles.

It was observed during the experimentation that the NPs are formed in the electrolyte solution, indicated by the change in colour of the solution, soon after the AMP discharge is initiated. Initially the electrolyte was pale yellow and this transformed to darkish yellow on exposure to the plasma. This change in colour was observed to be enhanced with increase in the magnitude of discharge current and also with higher concentration of the ions in the electrolyte solution the change in the colour of the solution is attributed to the formation of the nanoparticles. Higher the discharge current and concentration faster is the nucleation and growth of the nanoparticles. This may result in increase in the size or clustering of the nanoparticles. Such an observation was also been reported on the synthesis of Ag nanoparticles using similar method (Chang et al. 2010). It can be hypothesized that the relative size of the NP and their rate of production depend upon the AMP current magnitude, time of AMP discharge and the concentration of anions and cations in the electrolyte solution. The bigger sized NP will be difficult to align because of their larger inertia and hence controlled alignment will not be observed. If the NP size is small then they can be aligned at suitable applied electric field strength provide the discharge duration is not too long, as seen in Figure 7.12(a). The SEM which reveals clusters for the higher concentration shown in Figure 7.12(d) clearly support this theory.

The substrates coated with the FePt nanoparticles synthesized at 2mM H₂PtCl₆ and 10mM Fe₂SO₄ for exposure at 5 mA for 5 min were annealed at 600 °C for investigating the structural and magnetic phase transformation. The SEM of the above is shown in Figure 7.14 (a,b). An increase in the particle size is observed due to Oswald ripening.
Figure 7.14: (a) SEM images of 2mM H₂PtCl₆ and 10mM Fe₂SO₄ electrolyte exposure at 5 mA for 5 min annealed at 600 °C (b) magnified image of (a).

7.6.2 Structural studies

Figure 7.15 shows the XRD patterns of as-prepared and annealed FePt nanoparticle synthesized under the above mentioned conditions. The XRD of as-prepared sample, refer Figure 7.15(a), shows the diffraction peaks corresponding to (111) and (200) planes at 2θ of 40.10° and 46.75° respectively confirming the formation of chemically disordered A1 FCC phase with a = 3.872 Å. The average crystallite size of the as prepared nanoparticles, using Scherrer’s formula, is found to be about 14 nm ±1.2 nm. Figure 7.15(b) of the annealed sample shows the superstructure peaks at 24.02° and 32.95° corresponding to (001) and (110) diffraction planes respectively which are the characteristic peaks of the chemically ordered L1₀ FCT structure. The additional peak (+) appearing at 2θ 41.40° along with the (111) of FCT shown in Figure 7.15(b) is associated with the FCC phase of FePt. The additional peak at 35.95° (shown by *) shows the presence of the iron oxide phase. The oxidation of the iron may be due to the surface oxidation during the preparation of the nanoparticles. The silicon dioxide
peaks (indicated by #) are also prominent at 44.22° and 44.80° due to the presence of SiO₂ layer on the silicon substrate. The splitting of the (200) peak is also observed confirming the structural transformation from cubic to tetragonal phase. The atomic rearrangement of Fe and Pt in the FePt alloy unit cell after heat treatment, gives rise to a lattice distortion or tetragonality. The c/a ratio, where “a” and “c” are the lattice parameters, is estimated to be about 0.96 confirming the tetragonality in the annealed sample. The ordering parameter, estimated using the intensity ratio of (001) and (111) peaks, is found to be 84% revealing substantial chemical ordering in the unit cell (Medwal et al 2012; Medwal et al 2013, Sehdev et al. 2011)). Further the average crystallite size for the annealed sample has been estimated using the Scherrer’s formula and found to be 42 nm.

Figure 7.15: X-ray pattern of (a) as synthesized (b) 600 °C annealed FePt nanoparticles.

7.6.3 Magnetic Studies

The magnetic measurement has been performed on the as prepared nanoparticles with FCC phase. It has been observed that the as prepared nanoparticles exhibit a soft ferromagnetic behaviour with coercivity ~ 100 Oe as seen in Figure 7.16(a). Also the MH loop is found to saturate in the range of the applied magnetic field studied. The
soft magnetic nature of as prepared nanoparticles is due to the disordered A1 phase with low value of magnetocrystalline anisotropy.

Figure 7.16: MH loop of (a) as synthesized (b) 600 °C annealed FePt nanoparticles.

The MH loop of the annealed samples at 600 °C shows a broadening in the loop while exhibiting no tendency to saturate. This is due to the high anisotropy for the FCT phase. A coercivity of 1.8 kOe is observed for annealed sample as shown in Figure 7.16(b). Though there is a phase transformation from FCC to FCT phase, a moderate
value of the coercivity observed may be due to the surface oxidation of the nanoparticles, in conformity with the XRD result. The partial phase transformation (84% from XRD) to the L1\(_0\) phase is the reason for the low coercivity value. The obtained coercivity is not as high as reported for the material prepared from the other techniques. However, there is an ample scope to enhance the coercivity by controlling the synthesis conditions.

### 7.7 Conclusion

The plasma treatment is very efficient for surface cleaning of 2D self organization of the nanoparticles. For the DC plasma the duration of the plasma treatments varies from 20 minutes to 60 minutes with high power. However, with the dense plasma focus under the hydrogen gas atmosphere, this can be achieved in very short time. The pulsed high energy density plasma may result in the uniform distribution of the interparticle diffusivity and grain growth over the long range positional ordering due to Ostwald ripening of the FePt nanoparticles. It is noted that as exposed sample do not show the structural and magnetic phase transformation. This can be achieved by the post annealing treatment. However, a low value of coercivity observed, may be due to the surface oxidation of uncapped nanoparticles.

The successful synthesis of FePt alloy nanoparticles with chemical reaction coupled with atmospheric microplasma is demonstrated. The controlled alignment of the FePt NPs, as observed in SEM images, was achieved at suitable combination of molar concentration of electrolyte and AMP discharge parameters. The XRD results show the structural transformation from A1 FCC phase to L1\(_0\) FCT phase with 84% ordering after annealing. This was also indicated by the magnetic measurements. The AMP assisted chemical synthesis method could be versatile and low cost technique. This technique may also be very useful for the high yield production of FePt nanoparticles. The production of NPs can be simultaneously obtained in solution as well as on substrate.
7.8 References

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