

Research Article

Ferromagnetic Resonance Characterization of Nano-FePt by Electron Spin Resonance

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Received 29 June 2012; Revised 18 October 2012; Accepted 26 October 2012

Academic Editor: Jose M. Pedrosa

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Electron spin resonance (ESR) measurements at room temperature and X-band microwave frequency were performed on highly crystalline FePt system thin films. Fairly high DC static magnetic field absorption of about 300 mT was observed in these films. We attribute the high field absorption to ferromagnetic resonance (FMR). Upon increasing iron content in FePt system, no detectable spin waves modes were identified already at room temperature. This signifies a homogeneous distribution of the magnetization across the films. We qualitatively attributed such homogeneity distribution in the films to self-assembly of these Fe-Pt system nanoparticles. The results revealed that the FePt system contains hyperfine coupling with sextet $I = 5/2$ exhibiting a phase reversal behaviour compared to FMR line. Both iron content and crystallite size increased the FMR intensity making the films good candidates for large data storage mediums and spintronics.

1. Introduction

Magnetic recording media plays a vital role in the development of nonvolatile data storage technologies. Particularly, magnetic hard disk drives are important parts in many devices such as video cameras and computers. The year 1956 marked the generation of first magnetic hard disk with recording density of 2 kB/in² that was successfully built by IBM [1]. Since then, the areal density (the number of bits/unit area on a disk surface) has successively increased [2]. Nowadays, products with an areal density of more than 700 GB/in² are commercially available [3]. The increase in the areal density needs to be continued due to the future demand for information storage that is drastically advancing. Due to advancement in information technology (IT) and computer science, areal density in a level of 1 Tb/in² or more is inevitable. Iron platinum (FePt) nanoparticles (NPs) are

actively being pursued as a potential candidate for larger storage capacities on hard-disk drives than any other materials due to its high magnetocrystalline anisotropy (MA) [4]. MA is a process when the atomic structure of a crystal of a certain material introduces preferential direction of magnetisation, and in most cases, it will be the easy axis of magnetisation [5]. This phenomenon is mostly common in ferromagnetic materials. Traditional magnetic recording materials such as Co/Cr have limitations since their magnetic direction of each recording bit would become unstable at room temperature due to thermal fluctuation [6]. FePt does not only possess higher magnetic anisotropy but also possesses better thermal stability [7]; this makes it a better candidate for magnetic recording unlike other materials.

Ferromagnetism is a phenomenon by which a material produces its own magnetic field due to the alignments of atomic magnets in a particular direction. This arrangement is

energetically preferred, hence, once they get this arrangement they do not get misaligned. This can be removed by demagnetizing field, by heating it, by striking. Substances having this property are known as ferromagnetic. Substances are classified as ferromagnetic, antiferromagnetic, nonmagnetic (diamagnetic), or paramagnetic. Paramagnetic substances are ferromagnetic under a certain temperature called Curie temperature.

When a ferromagnetic substance outwardly behaves as a nonmagnetic substance, it can be magnetized by applying a magnetizing field upon which it gets magnetized, but when the magnetising field is removed, it does not get demagnetized. However, paramagnetic materials do return to a demagnetised state. So, ferromagnetic materials would show magnetization even when the applied field is momentarily zero. This phenomenon is due to absorption in the full saturation state and is a direct signature of ferromagnetic state of a material.

An alloy of iron and platinum would show some degree of ferromagnetism from Fe and a proportion of paramagnetism from Pt. In electron spin resonance experiments presented here, FePt possesses what is known as ferromagnetic resonance (FMR) at room temperature as illustrated in Figure 1; this implies that FePt can be ferromagnetic especially when Fe content is elevated. Ferromagnetic materials have a strong attraction to applied magnetic fields and are able to retain their magnetic properties even after the field has been removed. They have a large and positive susceptibility. This phenomenon is responsible and used in data mass storage materials. Spin waves, similar to resistance in electricity, is a major drawback to spin alignment in a typical magnetization process. However, ferromagnetic films of suitable thickness have been shown to withstand spin waves across the film that has been excited by the microwave field [8–10]. These arise from collective excitations in arrays of spins and can be detected in ferromagnetic resonance experiments [8, 11]. Spin waves are propagating disturbances in the ordering of magnetic materials. These intrinsic excitations in magnetic materials are dependent mainly on the chemical composition or structure of the material [8–11]. The Hamiltonian of ESR process takes into account an electron and a nucleus interaction. This interaction can be readily observed with the ESR experiments as hyperfine structures. In this paper, we present the FMR study for potential high-density magnetic recording and thermal stability of FePt system. The analysis of increasing iron (Fe) content on FePt system and FMR intensity response together with the effect of crystallite size on the FMR intensity is presented. Moreover, the present work will show results on the hyperfine coupling with narrow width and interestingly of opposite sign to that of FMR line. We believe this phase reversal behaviour is observed for the first time in our FePt system. In addition, the study of the angular dependence of the high field absorption by FePt gives enough evidence of magnetic anisotropy present in these films.

2. Experimental Section

2.1. Material Laser Preparation. The Fe-Pt NPs were prepared using a method previously described by

Mwakik-unga et al. [12]. Precursor for this Fe-Pt system comprised a CH₃OH solution in which Fe(III) acetylacetonate [Fe(III)(C₅H₇O₂)₃, purity ≥ 99.9%], denoted by Fe(III) (acac)₃, and Pt(II) acetylacetonate [Pt(II)(C₅H₇O₂)₂, purity > 97%] solution, denoted by Pt(II) (acac)₂, were completely dissolved. All chemicals were purchased from Sigma-Aldrich and used without any purification. The concentration of Fe(III) (acac)₃ and Pt(II) (acac)₂ was 2.4 and 0.6 mM, respectively. Four samples were irradiated using different incident laser fluence settings. Soon after irradiation, black precipitates formed and were washed with hexane to remove impurities. These precipitates Fe-Pt NPs were allowed to dry on silicon (Si) (111) substrates for scanning electron microscopy (SEM), transmission electron microscope (TEM), and X-ray diffraction (XRD) analyses. Some of these results are presented elsewhere [13].

2.2. Sample Characterization. The FMR data were taken at room temperature using an electron spin resonance spectrometer (JEOL-JES-FAS 200) operating at the X-band microwave frequency, with the sample located at the centre of a standard TE₁₀₂ microwave resonant cavity and fixed to a goniometer, allowing the study of in-plane and out-of-plane angular dependence of the absorption field and linewidth. The FMR spectra were taken using standard phase-sensitive detection techniques, applying modulation fields up to 1.0 mT, modulation frequency of 100 kHz, and microwave power of up to 10 mW. The microwave resonance frequency at $\theta_H = 0^\circ$ for all the samples was 8988.9158 ± 0.8960 MHz.

3. Results and Discussion

In this paper, measurements were conducted in the usual electron spin resonance (ESR) geometry; the DC static magnetic field was parallel to the film surface, that is, $\theta_H = 0^\circ$, and the AC magnetic field was also always maintained parallel to the film. FMR was observed at fairly high DC static magnetic field of ≈ 295 mT; the FMR spectra were almost symmetric. Upon increasing the iron content in Fe-Pt system, no detectable spin waves modes were identified as evidenced in Figure 1. The FMR spectrum observed at high field by Martins et al. [8] and Jin et al. [9] includes spin waves at lower angles giving evidence that FMR can emanate together with spin waves. Our FMR spectra, however, show only the uniform mode with some six features (sextet) seen around 320 mT centre field as depicted in the inset Figure 1. We attribute these features to the interaction between electron and nuclear spin angular momenta, a phenomenon known as hyperfine structure coupling with a spacing between them of 8.482 ± 0.192 mT. These features have the same intensity as observed in FMR spectra of all other samples. These features could not be attributed to the Mn marker that is used and are calibration standard inherent in the instrument since the typical g values for these features are totally different from the g value for the Mn²⁺ spins. We have also done energy-dispersive X-ray analysis on the samples after ESR measurements to recheck any Mn trace impurities. Even at higher electron energy, no Mn element was observed.

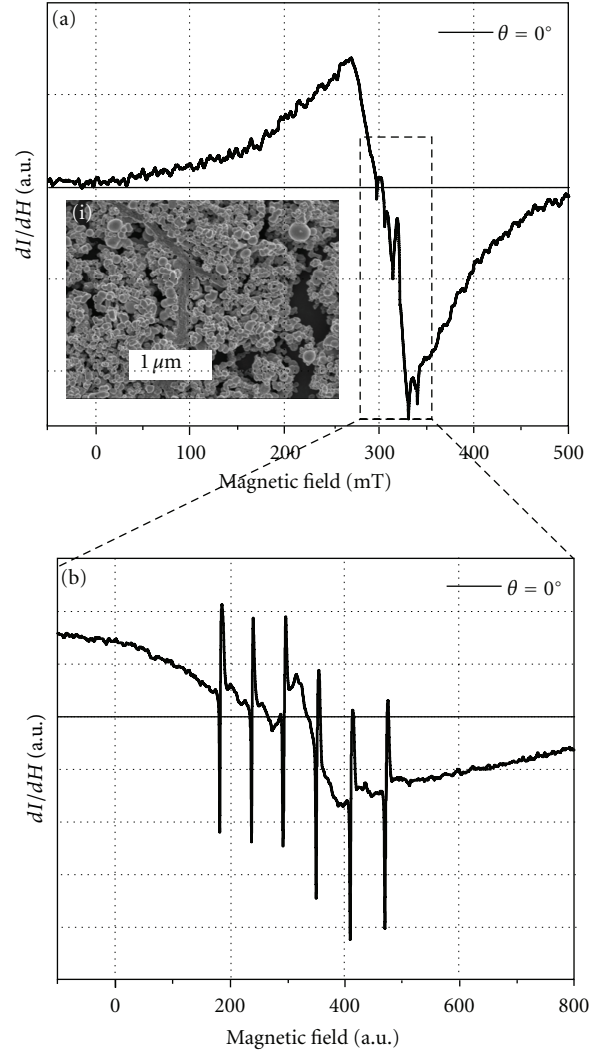


FIGURE 1: FMR spectrum of $\text{Fe}_{0.78\pm 0.2}\text{Pt}_{0.33}/\text{Si}$ given in (a). The angle θ_H gives the direction of the applied field H with respect to the normal film. The inset in (i) corresponds to the hyperfine coupling and a typical SEM image is given (b).

The low magnification SEM image in Figure 1 inset shows that these FePt nanoparticles are spherical over a large area. Interestingly, this sextet with narrow line width has phase reversal behaviour in comparison to FMR line. The possible explanation is the transition taking place between converging (or diverging) energy levels [14]. This observation was correlated to the phase reversal of the dynamic nuclear polarization (DNP) by Lambe et al. [15] and Abragam and Bleaney [16]. This DNP mechanism was first realized using the notion of the Overhauser effect [17]. This effect relies on stochastic interaction between an electron and a nucleus. While the Overhauser effect is time-dependent electron-nucleus interaction, among others it is the solid effect, cross effect, and thermal mixing which are time-independent. Thus, we would like to view this as an indication that the same DNP-solid effect mechanism is involved in this present experiment. The detailed analysis of this latter phenomenon is beyond the scope of this present work more especially of their angular dependence. However, this is visible in film

FMR spectra, wherein two main peaks at 001 that is shifting to lower angles by adding more iron content and 111 that is not shifting were observed in our XRD data reported elsewhere [13].

The absence of spin waves can also be suppressed by patterned media [6, 7, 18, 19]. This consists of a regular array of magnetic dots which have uniaxial magnetic anisotropy. This qualifies the laser solution photolysis technique as model self-assembly method for the preparation of pure materials. Self-assembly is highly regarded as an alternative solution to overcome thermal fluctuation [6, 7]. Thermal fluctuation triggers these spin waves which make magnetic films unstable at room temperature; hence, they are unlikely to be excited at lower temperatures.

It is observed that the large, the iron content the larger the spatial size of the nanoparticles (NPs) [4, 7, 20]. This behaviour occurs mostly when the NPs are spherical in nature. Figure 2 depicts the FMR intensity as plot against the iron content. FMR absorption spectra increase with the Fe

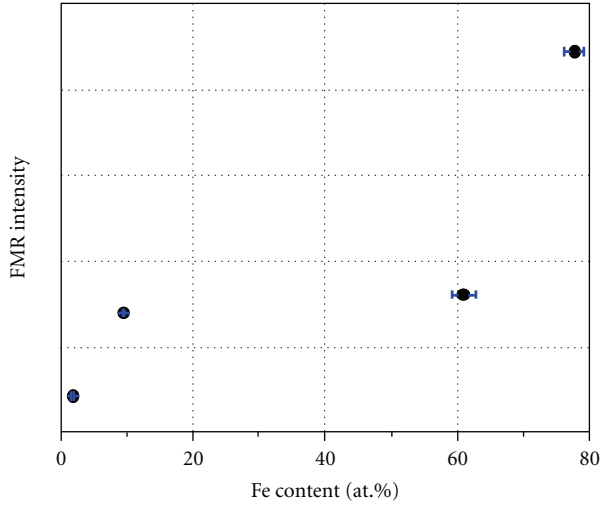


FIGURE 2: FMR intensity of the thin films as a function of iron content. These NPs embedded on Si substrate by a self-assembly are spherical.

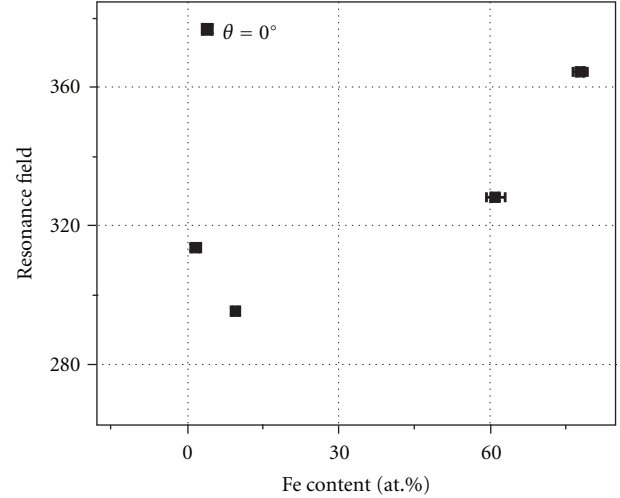


FIGURE 4: Resonance field plotted against Fe content. The plot suggests a higher resonance magnetic field as Fe content rises up as expected.

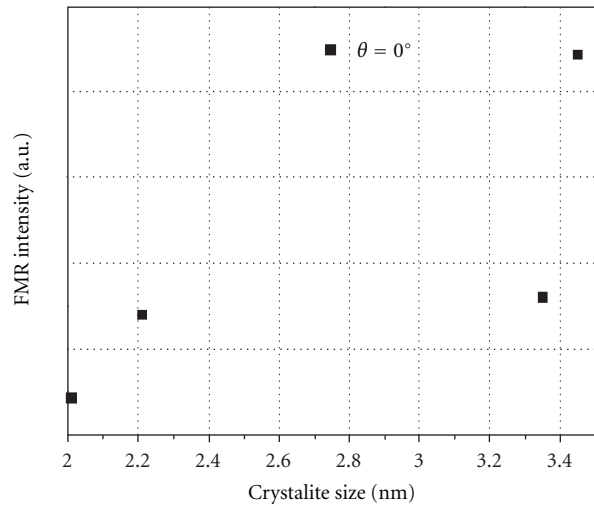


FIGURE 3: FMR intensity as a function of crystallite size of the thin films.

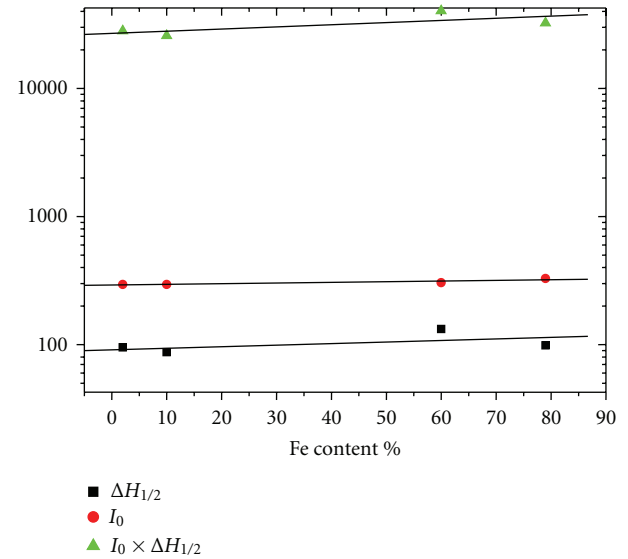


FIGURE 5

content since an increasing number of magnetic moments from the ferromagnetic Fe interact with microwave magnetic field radiation. Moreover, NPs have enhanced surface area and hence increase the chances for effective interaction. Similar FMR spectra without spin waves were also observed by Zaghbi et al. [21] at room temperature in lithium iron orthosilicate. However, the observed FMR intensity is extremely less than what we observed in our films indicating that the films are highly ferromagnetic. Moreover, Sun et al. [4] argued that iron-rich nanocrystal assemblies have the largest coercivity. This is consistent with earlier reports on vacuum-deposited FePt thin films [1, 22].

The increase in FMR intensity with crystallite size as indicated in Figure 3 is in good agreement with [23]. The authors claimed that room temperature coercive force decreased with decreasing crystallite size. Such magnetic properties have

been probed for a number of samples of circular γ - Fe_2O_3 particles of the type used in magnetic recording tapes. A similar work was reported with FePt/ Fe_3O_4 particle size [24]. Annealed at 560° for 30 minutes, 6 nm FePt NPs show a coercivity of 1.2 T, however 3 to 4 nm particles have a coercivity of only 0.5 T [24].

In addition to this present study, the usual Lorentzian distribution equation was used to analyze the resonance field with varying iron content. This equation is given as

$$I(H) = \frac{I_0}{1 + \left(\frac{H_0 - H}{\Delta H_{1/2}}\right)^2}, \quad (1)$$

TABLE 1: A summary of parameters after fitting (1) and (2) to the ESR data for all FePt samples.

Sample	$\Delta H_{1/2}$ (mT)	Resonance field (mT)	$I_0 \times \Delta H_{1/2}$
1	95.216	295.25	28112.524
2	87.306	295.25	25777.0965
3	132.201	304.83	40298.83083
4	98.704	328.20	32394.6528

where I_0 , H_0 , H , and $\Delta H_{1/2}$ represent intensity at resonance magnetic field, resonance magnetic field, varying magnetic field, and the width at half maximum of the field, respectively.

The derivative of (1), given by

$$\frac{dI}{dH} = \frac{2I_0 \left((H_0 - H) / \Delta H_{1/2} \right)}{\Delta H_{1/2} \left[1 + \left((H_0 - H) / \Delta H_{1/2} \right)^2 \right]^2} \quad (2)$$

is presented by the ESR spectrometer. In this study, either the data were integrated using a trapezium method and (1) was fitted to the resulting data or (2) was simply fitted to data plotted in Figure 1(a). The quality of fitting of either model to either dataset may be limited due to the multiple nature of the valence state especially of the Fe similar to V compound as well as W and other transition metals [25–27]. Either way, a summary of parameters obtained is given in Table 1. It is evident from Table 1 that the resonance field (centre field) decreases on the platinum rich side and shifts quite significantly to higher field on the iron-rich side most likely due to increase in iron content as shown in Figure 4. The widths at half maximum results as a function of iron content are depicted in Table 1. The $\Delta H_{1/2}$ decreases on the Pt-rich side and increases quite significantly on the iron-rich side; thereafter it decreases upon increasing more iron.

It must also be mentioned that the area under ESR traces is proportional to the number of spins available for ESR activity. The area under such traces can be estimated as $I_0 \times \Delta H_{1/2}$. In Figure 5, there is a log-normal plot of I_0 , $\Delta H_{1/2}$, and $I_0 \times \Delta H_{1/2}$. Thus, it can be concluded, as expected, that since the area under the Lorentzian trace increases as the Fe content increases, then there are more spins available for FMR activity as more Fe is introduced into the FePt alloy.

4. Conclusion

We have successfully synthesized NPs of Fe-Pt system using localized surface plasmon resonance. These NPs were allowed to organise themselves on Si (111) substrates. The higher field absorption by the films is attributed to the FMR. FMR is a signature of ferromagnetism in our films. An FMR spectrum was observed without disturbances arising from spin waves commonly triggered by thermal fluctuations. We qualitatively attribute such magnetic stability in the films to self-assembly of these Fe-Pt system NPs that are spherical. We can be tempted to conclude that such film synthesis technique is ideal for good quality magnetic thin film NPs. FMR intensity increased as a function of iron content in the Fe-Pt system making our films good candidates for large data

storage mediums and spintronics. In addition, an increase in iron content also increased the crystallite size increasing the storage capability as well.

Acknowledgments

S. S. Nkosi would like to thank the financial support received from CSIR National Laser Centre (NLC) (Project no. LHIE100) and the opportunity to conduct his research there. He also would like to thank DST/CSIR-National Centre for Nano-Structured Materials for the characterization of his samples. A special thanks again is due to Henk van Wyk of NLC for the laser setup.

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