Fabrication and surface transformation of FePt nanoparticle monolayer

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Abstract

The monolayer of FePt nanoparticles with the mean size of ~4 nm was fabricated on a glass substrate by the Langmuir—Blodgett (LB) technology. The monolayer of FePt nanoparticles has a smooth surface and a high density structure as shown by the AFM image. The array structure of FePt nanoparticles on the surface of the film is clearly with a cubic symmetry in appropriate condition. Small-angle X-ray diffraction (SXRD) measurement of multilayer structure for the FePt nanoparticles has indicated that the superlattices consist of well-defined smooth layers. The transfer of nanoparticle layers onto a solid substrate surface was quite efficient for the first few layers, exhibiting a proportional increase of optical absorption in the UV–vis range. This results potentially opens up a new approach to the long-range ordered array of FePt nanoparticles capped by organic molecules on substrate and provide a promising thin film, which may exhibit the excellent ultra-high density magnetic recording properties.

Keywords: Langmuir–Blodgett (LB); Monolayer; FePt; Nanoparticles

1. Introduction

Recently, the demands for developing future high-density magnetic recording media are increasing, since the magnetic recording density has reached nearly the maximum value for the conventional continuous media. Over the past few years, the areal density ($D_A$) of longitudinal magnetic recording media has been increasing at an annual rate of about 40–60%. Extremely high-density recording (EHDR) with $D_A$ of about 100 Gb/in.$^2$ is expected in a few years. In order to have adequate signal-to-noise ratio, media with higher $D_A$ require magnetic grains with smaller sizes and higher coercivities [1–3]. As the candidates for overcoming this limit, FePt ordered alloy nanoparticles are now attracting much interest. This alloy has the L1$_0$-type ordered structure with high magnetocrystalline anisotropy as high as $10^5$–$10^7$ J/m$^3$ after heat treatment [4].

The research of the two-dimensional (2D) ordered array of nanoparticles is becoming an important factor for the development of high-density magnetic recording media and single-electron tunneling device. Some methods, such as self-organization, electrophoretic deposition, Langmuir–Blodgett (LB) and nucleation under bacterial S-layers, etc., have been devised to prepare the 2D ordered arrangement of nanometer dimensions [5]. The LB technique has been proven a powerful and simple method to prepare the high-density nanoparticle monolayer and multilayer film with controllable layer numbers and thickness. Other technique, such as evaporation, cannot provide film with the adjustable particle layer number. The LB technique, which is based on monodisperse nanoparticles, nanowires and nanorods capped by long-chain molecules, is an important and simple method to obtain uniform ordered monolayer of nanoparticles. Of these, LB technique of Au, Ag, CdS and Fe$_2$O$_3$, etc. nanoparticles have extensively been investigated for their potential application in nano-devices [6–17]. Recently, Lieber’s group used this method to investigate the aggregates of semiconductor nanowires (NWs), and efficiently patterned by photolithography.
Furthermore, Yang’s [21,22] group reported that monolayer and multilayer of BaCrO$_4$ nanorods and Ag NWs, which also showed that smectic arrangement in a high surface pressure. These results indicated that LB could be an effective means to construct nanodevices.

Since the demonstration by Sun et al. [23], the uniform nanoscale FePt particles from chemical method have drawn great interest in the recent years. Such magnetic nanoparticles can self-assemble into ordered periodical arrays, which are promising candidates for a new generation of magnetic high-storage media [24–27]. But self-assembly technology is difficult to control a better organizational monolayer than that obtainable for the LB films. The purpose of this research is to prepare the FePt nanoparticles with narrow dispersivity, arrange 2D ordered monolayer and multilayer by LB technique and transfer to the surface of solid substrates. The array structure of FePt nanoparticles on the surface of the film is clearly with a cubic symmetry in appropriate condition. The size distribution of FePt nanoparticles was characterized by using High Performance Particle Sizer (Malvern HPPS). The microstructures and morphology of FePt monolayer are investigated by atomic force microscope (AFM). The characterization of LB nanocomposite films was carried out with UV–vis spectroscopy.

2. Experimental section

2.1. Preparation of FePt nanoparticles

The FePt nanoparticles are synthesized using Sun’s method based on decomposition of iron pentacarbonyl and reduction of platinum acetylacetone in the presence of oleic acid and oleyl amine stabilizers [3]. A typically synthetic procedure is as follows: under airless conditions, platinum acetylacetone (0.25 mmol), 1,2-hexadecanediol (0.75 mmol) and dioctylether 20 ml were mixed and heated to 100 °C. Oleic acid (0.25 mmol), oleyl amine (0.25 mmol), and Fe(CO)$_5$ (0.50 mmol) were added successively. The mixture was refluxed at 297 °C for 30 min and then naturally cooled down to room temperature under the flow of argon gas. The size-selective precipitation was carried out in air using hexane and ethanol as a solvent and non-solvent, respectively. The FePt nanoparticles can be easily redispersed in hexane.

2.2. Formation of the FePt nanoparticle monolayer and multilayer

The FePt nanoparticle colloidal suspension was spread dropwise (typically 0.5–1 ml of 0.1 mg/ml concentration) on the water surface of a LB trough (KSV 5000). The nanoparticle surface layer was monitored with a Wilhelmy plate. The KSV system was controlled by a PC-AT clone computer and KSV Film Control System Software. Isotherm compression and data collection were automatically executed through the use of computer software. The nanoparticles were compressed by moving the barriers at a speed of 1 mm/min. The surface pressure isotherm was recorded throughout the compression process. At different stages of compression, the nanoparticles at the water–air interface were transferred carefully by retracting a hydrophilic glass substrate, which was immersed vertically in the pure water in the trough before the particle suspension was spread. The retracting speed was controlled at 0.5–2 mm/min.

2.3. Sample characterization

X-ray diffraction (XRD) patterns of the FePt nanoparticles and thin films were determined by using a Rigata/max-C diffractometer with Cu-K$_\alpha$ radiation (wavelength 1.54056 Å). The ratio of Fe and Pt was determined by energy-dispersive X-ray (EDX) analysis done with an Oxford EDX spectrometer and the inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300 ICP instrument. An HPPS (Malvern HPPS) was employed to obtain the characterization of the size distribution of FePt nanoparticles. The infrared (IR) spectra of FePt nanoparticles were obtained on a Nicolet Impact 410 FTIR spectrometer of dried samples mixed with KBr. The microstructures and morphology of FePt monolayer are investigated by atomic force microscopy (AFM), using a NanoScope IIIa scanning probe microscope. The nanoparticle layers transferred onto a solid substrate surface were characterized using UV–vis spectroscopy. Transmission electron microscopy was performed using a 200 kV side entry JEOL JEM-2010 transmission electron microscope (TEM).

3. Results and discussion

3.1. Preparation of FePt nanoparticles with narrow size distributions

3.1.1. TEM

The unique properties of nanoparticles are determined by their size, shape, particle structure and surface structure, etc. Shape and size of monodisperse FePt nanoparticles, synthesized by a solution-phase chemical procedure, have been studied by transmission electron microscopy. TEM samples were prepared by depositing a droplet of the diluted FePt solution onto a carbon-coated copper grid. Fig. 1 shows a TEM image of the as-synthesized FePt nanoparticles. Fig. 1(a) is a low-magnification TEM image showing a typical morphology of the sample, where the monodisperse FePt nanoparticles with sizes of ~4 nm in diameter self-assemble to form a 2D distribution onto the supporting carbon film. The distribution of the size is very narrow distribution. The images reveal widely separated FePt nanoparticles and little aggregation. High-resolution transmission electron microscopy (HRTEM) (Fig. 1(b)) indicates that the material consists of small crystallites with good crystallinity. A selected-area electron diffraction
pattern (Fig. 1(c)) indicates that the as-synthesized FePt nanoparticles are of a face-centered cubic (FCC) lattice structure, confirming the formation of the chemically disordered A1–FePt phase, which is consistent with the expected composition [27]. The composition of the nanocrystals is determined to be Fe55Pt45 by EDX, well in agreement with the values obtained on the basis of the ICP analysis.

3.1.2. HPPS

The preparation of FePt nanoparticles with narrow and uniform size distribution is one of the most important matters in preparing the high-quality granular films and the extremely high-density recording films. Therefore, the size uniformity of the FePt nanoparticles has been studied in detail. We have prepared the FePt nanoparticles with low and uniform size distribution by altering the ratio of the organic solvent to surfactant, controlling the uplifted speed of temperature and the time. Fig. 2 illustrates the typical size distribution of FePt nanoparticles prepared by chemical synthesis. Only one peak at around 4.2 nm is observed and standard deviation in the size distribution is found to be <5%, which is consistent with that estimated from the TEM analysis. This implies that the FePt nanoparticles with monodispersity and narrow size distributions are obtained.

3.1.3. XRD

The FePt nanoparticles crystallographic orientation and degree of chemical ordering of the films were determined from XRD patterns. Fig. 3 shows XRD patterns of the 4-nm Fe55Pt45 nanoparticle film under different experimental conditions. The indexing is based on tabulated FCC and face-centered tetragonal (FCT) FePt reflections [3,23]. As shown in Fig. 3(a), XRD has shown that the as-synthesized FePt nanoparticles are of a chemically...
disordered FCC lattice structure. The diffraction peaks of the as-synthesized samples appear at 2θ of 40° and 47°, which correspond to (1 1 1) and (2 0 0) peaks, respectively. The average size of FePt nanoparticles on the film surface was estimated by measuring the width of the XRD peaks, which was used in the Scherrer equation. Their average size was found to be approximately 4 nm, which is in good agreement with that estimated from the TEM and HPPS measurements.

The FCT FePt nanoparticle could yield high coercivity based on the previous investigation, and will be a candidate for future ultra-high density magnetic recording media applications. The phase transition of FePt nanoparticles from FCC to FCT is important for achieved high coercivity, so the phase transition of FePt nanoparticles at different temperature was discussed. The XRD patterns of the FePt nanoparticles film annealed under Ar atmosphere for 20 min at temperatures of 550 and 580 °C are shown in Fig. 3(b) and (c), respectively. XRD measurements on annealed particle film show that the phase transition occurs at about 550 °C, and the Fe and Pt atoms rearrange into the long-range chemically ordered FCT structure after annealing process. This result indicate that the post-deposition annealing is necessary to obtain the chemically ordered FePt phase. Moreover, too high a temperature or too long an annealing time, will result in aggregation of nanoparticles. XRD analyses show that the optimum temperature for the phase transformation is 580 °C, which is consistent with that previous reported [23].

3.1.4. IR spectra
In order to further understand the effect of the annealing on the structure of organic molecule capped on the FePt nanoparticles, a Fourier transform infrared spectroscopy (FTIR) transmission spectra was obtained to examine the change of the organic molecule capped on the FePt nanoparticles before and after being annealed (Fig. 4). In Fig. 4(a) the IR spectra of the FePt nanoparticles capped by oleic acid and oleylamine are displayed. The spectrum is dominated by the absorptions attributable to the vibrational modes of the surfactants [28]. The band at 2853 and 2926 cm⁻¹ correspond to the vibrations of the symmetric and asymmetric CH₂ stretching modes of the oleyl group, whereas the broad band at about 3006 cm⁻¹ indicates the presence of the stretching modes of the C–H bonds adjacent to the C=–C bond [29]. The peak at 1710 cm⁻¹ is due to the stretch mode of COOH group and indicates that some fraction of the oleic acid is bonded to nanoparticles either in monodentate form or as an acid. The 1582 cm⁻¹ peak could be due to the NH₂ scissoring vibration, which suggests that oleylamine is adsorbed with the NH₂ group intact. It is shown that there are differences in spectrum between FePt nanoparticles and annealed nanoparticles at 580 °C. The annealing treatment at 580 °C for 20 min leads to the complete disappearance of the surfactant absorptions including the bands arising from the C–H vibrational modes at 2926 and 2853 cm⁻¹ (Fig. 4(b)). Obviously, the surfactant molecules are decomposed as indicated by the distinct intensity decrease of the main IR absorptions after annealing. These results indicated that annealing lead to influence on the chemical structure of the organic capping materials on the FePt nanoparticles.

3.2. Characterization of the FePt monolayer and multilayer

The FePt nanoparticles are easily dispersed into hexane. Then, the FePt nanoparticles solution is dispersed equably on the liquid surface having a large occupied surface area, and the condensed and stable monolayer is formed by extrusion. The condensed monolayer and multilayer of FePt nanoparticles can be successfully transferred vertically onto the surface of solid substrates.

3.2.1. Isotherms and LB film formation
Fig. 5 shows the π–A isotherms of FePt nanoparticle suspension with a particle concentration of 1 mg/ml in hexane. When the barrier compressed, the surface pressure increased and a densely packed monolayer of the particles tended to form. From the point of about 250 nm², the surface pressure apparently started to increase, corresponding to an average particle area of 125 nm², which is greater than the geometrical cross-sectional area of a single particle (according to the estimated area of particle is about 60 nm² by XRD and TEM). With the barrier compressed further, the rapid increase of surface pressure could be related to the formation of close packed particle structures, alike solid-state structure. We found that a surface pressure of π = 15–20 mN/m is the optimal condition for a good-quality monolayer of FePt nanoparticles. At this point, the area occupied per particle is about 60–70 nm².
3.2.2. Characterization of surface morphology and grain size by AFM

The surface morphology of the as-synthesized FePt monolayer films and organic precursor monolayer deposited onto glass were examined by AFM. AFM images were captured at the following stages of the experiment: (1) the capping organic precursor (here is oleic acid and oleyl amine with 1:1 mole ratio), which is not grafted in surface of FePt nanoparticles, deposited on hydrophilic glass substrate, (2) FePt nanoparticles with organic capping molecule deposited on hydrophilic glass substrate, (3) after post-deposition annealing of the organic precursor monolayer, and (4) after post-deposition annealing of monolayer of FePt nanoparticle with organic capping molecule. All the conditions remained the same for formation of monolayer on the hydrophilic glass substrate by LB technology at a surface pressure of 20 mN/m.

Fig. 6 shows the AFM image of the organic precursor on hydrophilic glass substrate, which is not grafted on the surface of FePt nanoparticles. The surface morphology can be identified from the bright lines, which are the organic molecules on the glass substrate. It can be seen that as-prepared monolayer film of the organic molecule with uniform network spatial distribution appears on the surface of sample. This indicates that the orientation of the organic molecule is not close packed and perpendicular on the solid substrate. The height difference between black and white corresponds to 5 nm in this figure. In the AFM micrograph, a roughness analysis of the film shows the root-mean-square (rms) roughness as $R = 0.7$ nm.

The representative AFM images of the monolayer of FePt nanoparticle with organic capping molecule transferred onto glass substrate are shown in Fig. 7. The images show that the films have a granular structure with small number of objects of $\sim 5$ nm high, which can be structural defects and three-dimensional (3D) aggregates. The films are mainly composed of small particles below 10 nm in diameter. It can be seen that the monolayer film was very uniform and the granular structure on the surface reveals the presence of the FePt nanoparticles. Since the chain length of the organic molecule (oleic acid/oleyl amine) should be about 2.2 nm [30,31], and the average size of FePt nanoparticles is found to be approximately 4 nm, so the size of the particles on the surface of the monolayer film is about $4 + 2 \times 2.2 = 8.4$ nm. This estimation is reasonable and is consistent with AFM measurement results. Here we assume that the FePt nanoparticles are closely packed and
the average thickness of the organic molecule layer is 2.2 nm in the composite films. Thus the expected spacing between FePt cores is about 4.4 nm. A roughness analysis of the film shows the rms roughness of $R = 0.4$ nm [32,33]. Obviously, the close-packing of nanoparticles reduced the roughness of film surface.

To analyze any changes in the microstructure or morphology of the monolayer during post-deposition annealing, the pure organic monolayer and FePt monolayer were annealed in an Ar atmosphere at 580 °C for 20 min. As shown in Fig. 8, the film surface of the pure organic monolayer after annealing is very uneven (rms = 3.8 nm) than that of the original organic monolayer, and an island-like structure is observed after annealing. The island-like structure which is sparse, fairly round and uneven appears on the film surface. The similar island-like structure was showed on the surface of FePt monolayer under the same annealed conditions (Fig. 9(a)). These results indicated that the aggregation of the precursor organic molecule on glass substrate relate to post-deposition annealing process.

Fig. 9 presents the AFM image of the FePt nanoparticle monolayer annealed at 580 °C for 20 min. The film surface was roughened after annealing and the island-like structure was formed (Fig. 9(a)). Moreover, there was an ordered arranged striate clearly appearing on the surface of the monolayer. To analyze the structure on the monolayer surface, the select-area monolayer was indicated on Fig. 9(b). Although some aggregated domains are observed in part, the substrate surface is covered almost completely by finely distributed, compact spheroidal particles. It should be noted that the array structure of FePt nanoparticle monolayer on the surface of the film is clearly with cubic-like packing in Fig. 9(b). These results indicated the array structure of FePt nanoparticle monolayer is influenced by the aggregation and decomposition of the precursor organic molecule in post-deposition annealing process. Previous studies on FePt nanoparticle assembly show that the symmetry relate to the length of organic capping molecule and the annealing history of the sample [3]. In this research, the decomposition and aggregation of the organic capping molecule reduce length of organic capping molecule and particle spacing under annealing condition, and high temperature increases particle mobility. It was implied that the nanoparticle mobility, the decomposition and aggregation of the precursor organic molecule and relatively weak interparticle interactions led to the nanoparticle reorganization formed cubic in the nanoparticle monolayer after annealing. Further, comparing Fig. 6 with Figs. 7–9, we find that the organic molecules wrapped around the FePt nanoparticles can prevent the particle aggregation and make the film have uniform and smooth surface. These factors are important for the appliance of the extremely high-density recording films. More detailed studies need to be done for the further understanding of this mechanism.
3.2.3. **Small-angle X-ray diffraction**

The monolayer and multilayer films of the FePt nanoparticles could be successfully transferred vertically onto the surface of the glass solid substrates. The periodic structure of the FePt nanoparticle film was calculated directly from the positions of Bragg reflections. Small-angle X-ray diffraction (SXRD) reveals a multilayer structure for the FePt nanoparticle film. Fig. 10 shows the diffraction profiles of 25 layers FePt LB film deposited on a glass slide. XRD measurements of the FePt multilayer give only one peak. These results imply the multilayer of the FePt nanoparticles has ordered and good periodic structure.

3.2.4. **UV–vis spectra of FePt films**

Fig. 11 shows the UV–vis absorption spectra of the FePt nanoparticle monolayer and multilayer. These spectrum displays a major absorption peaks at 380 nm. The curve for absorbance at 380 nm plotted against the number of layers is presented in the inset of Fig. 11. A perfectly linear relationship up to 11 layers is obtained. The good linearity indicates that the FePt nanoparticles can be successively and regularly deposited layer by layer during the whole deposition process. This demonstrates that the layer-by-layer deposition of homogeneous, multilayer films with 3D quantum superlattice and precisely controlled thickness could be successfully achieved by LB technique [34].

4. **Conclusions**

The monolayer and multilayer films of the FePt nanoparticles could be successfully transferred vertically onto the surface of solid substrates by LB technology. Nanoparticles on surface of monolayer and multilayer were directly observed by AFM. The deposition of FePt nanoparticle onto the substrate surface was quite successful in the first few layers as characterized by optical absorption measurements and small-angle X-ray diffraction. IR photoelectron spectroscopy reveals that the organic molecules on the surface of FePt nanoparticles are decomposed during post-deposition annealing process. It was found that in the nanoparticle monolayers the molecule mobility due to decomposition and aggregation of the precursor organic molecule and relatively weak interparticle interactions during annealing, led to the reorganization of the particles and a structure transformation from disordered to ordered cubic packed. The formation of ordered monolayer and multilayer of FePt nanoparticles demonstrates that under appropriate conditions FePt nanoparticles can be arrayed on the solid substrate through LB technology, and the structural features of the films can be tuned by the post-treatment conditions. These results potentially open up a new approach to the long-range ordered array of FePt nanoparticles capped by organic molecules on substrate and provide a promising thin film, which may exhibit the excellent ultra-high density magnetic recording properties.

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