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A novel method for synthesis of size-controlled $L1_0$ FePt nanoparticles

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ABSTRACT

Monodisperse FePt nanoparticles with an average particle size of 2.7 nm are synthesized by a polyol process and an etched silicon structure is also formed by an electrochemical process in HF acid. Then, the etched silicon surface as a substrate is coated with FePt nanoparticles. Chemical bonding between nanoparticles and the etched silicon surface prevents the coalescence of the particles during thermal annealing. Annealing at 600 °C for 1 h under a reducing atmosphere (90Ar% + 10H_2%) leads to realize phase transformation from fcc to fct $L1_0$ structure and the magnetic behavior changes from the superparamagnetic into the ferromagnetic one. After annealing, the coercivity reaches a maximum value of 3.3 kOe for particles coated on the etched wafer. Furthermore, the monosize nanoparticles with an average size of 15 nm are distributed uniformly on the etched silicon surface. So, after phase transition to $L1_0$, the FePt nanoparticle size limits to the average value (15 nm).

1. Introduction

Chemically ordered face-centered tetragonal FePt nanoparticles are suitable for data storage applications with Giga bite capacity. Therefore, uniform surface distribution of monosize magnetic nanoparticles with coercivity of Tesla order is required. Achieving ultra-high density magnetic recording media requires precise control of nanoparticles size, size uniformity, and their distribution on a surface. In addition, it requires materials that have revealed high magnetocrystalline anisotropy [1]. Much effort has been devoted to synthesis of magnetic FePt nanoparticles by the solution-phase method to achieve fine control on the particle size. The as-synthesized FePt nanoparticles have a chemically disordered fcc structure and are superparamagnetic at room temperature due to their small size and low anisotropy. Annealing at high temperatures is required for phase transformation from disordered fcc structure to the chemically ordered fct structure. The fct FePt phase has revealed a high magnetocrystalline anisotropy (7×10^7 erg/cm^3), because of its large coercivity value. The large magnetocrystalline anisotropy is caused by Fe and Pt interactions, originating from spin–orbit coupling and hybridization between Fe 3d and Pt 5d states. The degree of ordering depends strongly on the annealing temperatures. Furthermore, annealing induces changes in the interparticle spacing, which undesirably leads to the coalescence of nanoparticles. This is due to the start of decomposition of organic stabilizers (oleic acid and oleylamine) participating in the reaction around each particle. When the interparticle distance is reduced to the atomic scale, the magnetostatic interactions change to the exchange coupling one [2,3]. The essential problem is inducing high coercivity in small nanoparticles with fct phase that prevent their coalescence.

Several attempts have been allocated to seeking the solution of such a problem, aiming at size uniformity of nanoparticles in $L1_0$ phase and their uniform distribution on a substrate. So, in order to prevent the coalescence of FePt nanoparticles, different methods have been proposed. For example, doping with a third element such as B_2O_3 [4], Ag [5,6], and Au [7] significantly decreases the fcc–fct phase transition temperature; conversely, additive Pd, Cr, and Cu increase the ordering temperature [8]. Nevertheless, these attempts have shown moderate success to prevent the agglomeration of FePt nanoparticles. Furthermore, although dispersion of FePt nanoparticles in MgO and SiO_2 reduces magnetic interactions between particles in $L1_0$ phase, researchers have no impressive success in prevention of core particles from aggregation and the nanoparticles are not single-sized [9]. An alternative approach is to form a core–shell structure with inert sell protecting the inner FePt core during the annealing process [10–12]. Nevertheless, it is difficult to assemble particles with monolayer morphology [13] and the nanoparticles also suffer from a low coercivity [14]. The polymer-mediated approaches were proposed to obtain FePt nanoparticle films with controlled thickness [15,16]. However, the annealing results in particle aggregation of the films and the coercivity is thickness dependent. Shukla et al. performed

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a comparative study of ordered self assembled monolayers of FePt on both fluorinated carbon (a-CF_x) and silicon surfaces coated with native oxide. They showed less sintering of FePt on fluorinated carbon (a-CF_x) than films on silicon surfaces coated with native oxide [17]. Although a monolayer film has been fabricated, the distribution of nanoparticles is not completely uniform. Yu et al. [18] prepared monodispersive FePt nanoparticles on Si substrates using amino-functional silane, [3-(2-aminoethlyamino) propyl] trimethoxysilane (APTS), as a coupling layer. Stabilization of FePt nanoparticles on the APTS surface was achieved, while the coercivity value for the 800 °C-annealed films were only of the order of 10^2 Oe. Recently, Kang et al. [19] have reported the synthesis of $L1_0$ FePt nanoparticles inside ordered mesoporous aluminosilicate/carbon composites, but the results showed that the coercivity have a low value at room temperature. Coating of single size FePt nanoparticles with high coercivity on silicon substrates is appropriate for magnetic recording media. However, it is interesting to study the synthesis of respective FePt nanostructures with control over size and size distribution on an appropriate substrate for utilizing as magnetic recording media.

In the present work, monodisperse FePt nanoparticles with average size of 2.7 nm have been successfully synthesized by a polyol process using iron (III) acetylacetonate as a precursor. Then, the etched silicon substrate was fabricated electrochemically by HF acid. Hexane dispersion of FePt nanoparticles was coated on etched silicon substrates by wet chemistry. Etched Si was utilized as a suitable substrate for dispersing FePt nanoparticles to prevent their aggregation during annealing. Effect of this etched surface and the bonding of nanoparticles to the surface on size uniformity of particles and avoiding their coalescence during annealing were studied by XRD, XPS, and SEM analysis.

2. Experimental

2.1. Synthesis of FePt nanoparticles

The FePt nanoparticles were prepared via the Polyol method [20,21]. Synthesis of these nanoparticles involves the reduction of iron (III) acetylacetonates (0.5 mmol) and platinum (II) acetylacetonates (0.5 mmol) using 1,2-hexadecanediol (5 mmol) as the reducing agent in phenyl ether solvent (25 ml) in the presence of oleic acid (0.75 mmol) and oleyamine (0.75 mmol) ligands. The mixture was stirred for 10 min at room temperature under a flow of N_2 atmosphere (5 cc/s). Then, the solution was heated to 247 °C at a rate of approximately 7 °C/min, followed by refluxing at 247 °C for 30 min before cooling down to room temperature. Afterwards, purification of nanoparticles was accomplished by cyclic precipitation and redispersion with ethanol and hexane, respectively. During this process, the impurities were separated and removed by centrifugation (8000 rpm, 10 min). Finally, the particles were dispersed in hexane in the presence of renewed surfactants (36 μl of each one) and any undissolved material was removed by the final stage of centrifugation.

2.2. Synthesis of etched silicon substrate

To achieve uniform surface distribution of the FePt nanoparticles, an etched silicon as a substrate was fabricated electrochemically in HF acid. The (1 0 0)-oriented boron doped single crystal P Si wafers with 0.005 Ω cm resistivity and thickness of about 525 μm were utilized. Before anodization, the wafers were cleaned with ethyl alcohol and deionized water. An electrical contact for electrochemical etching was achieved by evaporation of Al film onto backside of the wafer in 10^{-5} mbar vacuum. Then, it was annealed at 400 °C for 30 min to impenetrate ohmic layer with 2 μm thickness. Following attachment of a 0.7 mm Cu wire to Al layer with Ag paste, the backside of samples was coated with an acid-proof wax to avoid the contact of electrolyte with Al layer. A constant current density of 50 mA/cm^2 was applied to the system for 4 min and the electrochemical etching was performed in a lateral Teflon cell. The electrolyte solution was the mixture of HF (48%):dionized water:C_2H_5OH (2:2:1). After anodization process, each sample was rinsed with dionized water and air-dried. Immediately, the acid-proof wax was detached and the substrate was prepared for FePt dispersion coating.

2.3. Coating

The etched silicon surface puts in contact with FePt nanoparticle dispersion with concentration of about 2 mg/mL. To produce a uniform surface, the rate of hexane evaporation was controlled. It was fixed at 0.67 cc/h. The samples were annealed at 600 °C for 1 h under the reducing atmosphere (90Ar% + 10H_2%). Thermal increasing rate was 5 °C/min.

2.4. Characterization

The Fe and Pt elemental analysis of samples was performed by EDS at 17 kV using Philips XL30. The specification of size and shape of the nanoparticles was carried out by TEM analysis using a LEO system, model 9120AB operating at 120 kV. To determine the structure of nanoparticles, we performed the X-ray diffraction (XRD) measurement using an X'Pert MPD Philips system with Cu Kα radiation (λ = 1.54 Å). The magnetization of FePt samples

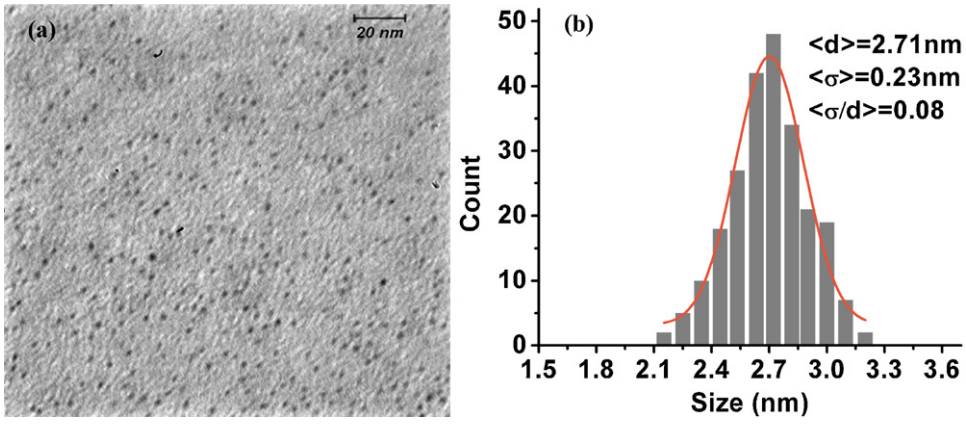

Fig. 1. TEM image of the as-synthesized FePt nanoparticles (a). The particles are monodispersed with a 2.71 nm diameter and standard deviation of 0.23 nm. (b) Curve fitting is based on the assumption of a log-normal distribution.