Controlled arrangement of FePt nanoparticles on Si substrate

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Abstract. We describe a simple and easy method of fixation of FePt nanoparticles on Au patterns formed on Si substrates by using 1,10-decanedithiol, which is expected to act as a binder between the FePt nanoparticles and the Au patterns on the Si substrates. Atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) measurements revealed that the FePt nanoparticles were selectively fixed on the Au patterns. It indicates that an array of the FePt nanoparticles is successfully formed on the Si substrate by simply immersing the Au patterned Si substrate in the FePt nanoparticle solution containing 1,10-decanedithiol.

1. Introduction

Ferromagnetic FePt alloy with the ordered L₁₀ structure possesses large uniaxial crystal magnetic anisotropy energy (Ku, ca. 6 x 10⁶ J/m³) [1-3]. Since the strong anisotropy energy is about an order of magnitude larger than that of the currently used CoCr-based alloys, the superparamagnetic limit at room temperature decreases to particle size of about 3 nm [4]. Therefore FePt nanoparticle with the L₁₀ structure is expected as one of promising candidates for the magnetic recording media with ultrahigh densities beyond 1 Tbit/inch² in the near future [5]. Especially, L₁₀-FePt nanoparticles synthesized by chemical solution based methods attract much attention from the viewpoint of practical use because of their well-defined morphology and easiness of handling for the fabrication of arrays on substrates through being dispersible in solvents [6, 7]. Since the key issue for application of the ferromagnetic nanoparticles synthesized by the chemical solution based methods is formation and fixation of desirable arrays on a substrate, it is significantly important to establish a technique for fixation of FePt nanoparticles on Si substrates [8-10].

In this paper, we developed a simple and easy method of fixation of FePt nanoparticles on Au patterns formed on Si substrates by using a dithiol compound. Since the thiol group is known to have an ability to form a covalent bond both with Au and Pt atoms, dithiol compounds having thiol group at both chain ends are expected to act as a binder between the FePt nanoparticles and the Au patterns [11 12]. Here we employed the FePt nanoparticles with the chemically disordered face-centered cubic (fcc) structure and 1,10-decanedithiol as a dithiol compound. It is natural that the fcc-FePt nanoparticles have similar reactivity against thiol group as those of the chemically ordered L₁₀-FePt nanoparticles since the surfaces of both nanoparticles are composed of Fe and Pt atoms. Therefore the method developed in this work is expected to be applied to...
fabrication of ordered arrays of the L1₀-FePt nanoparticles, which have potential applications as ultrahigh density magnetic recording medias. AFM, SEM and EDX measurements revealed that the dithiol-modified FePt nanoparticles were selectively fixed on the Au patterns formed on Si substrates.

2. Experiments
We fabricated patterns of Ti/Au layers on Si substrate by the lift-off method in combination with e-beam lithography. The Ti layer was deposited as a binder between Au layer and Si substrate in order to form a flat surface of Au layer. The Ti/Au patterns on Si substrate possess a thickness of 20 nm. Schematic illustrations of the sample were shown in the Fig. 1. Relatively large sizes of the patterns are employed for easy detection of fixation of nanoparticles on the Au parts. The fcc-FePt nanoparticles were synthesized by basically the same way as in the initial work of Sun et al [6]. Fig. 2 shows a typical transmission electron microscopy (TEM) image of the fcc-FePt nanoparticles modified with oleic acid and oleylamine. The TEM image indicates that the nanoparticles are well dispersed without aggregations. The average particle diameter and the standard deviation were estimated to be 6.1 nm and 1.4 nm, respectively. Fixation of the FePt nanoparticles on the Au-patterned Si substrates was performed as follows: First, 10 µl of 1,10-decanedithiol was added to 1.0 ml of chloroform solution of the FePt nanoparticles and the solution was left overnight. The procedure was performed so as to replace oleic acid and oleylamine on the nanoparticles to 1,10-decanedithiol. Then, the Au-patterned substrates were immersed in the solution and left overnight. Finally the substrates were cleaned with butanone in an ultrasonic bath in order to remove physisorbed nanoparticles and then dried in ambient condition.

TEM observations were performed using JEOL JEM-1010D. SEM observations and EDX measurements were performed using JEOL JED 2140. AFM images were observed by using SII SPA300HV.

3. Results and discussion
Fig. 3 (a) and (b) show the 2D AFM images of the Au-patterned Si substrate before fixation of the nanoparticles. The AFM images confirm that successful fabrication of the desired Ti/Au patterns as schematically illustrated in Fig. 1. The surface of Au and Si parts possesses relatively good flatness. Standard deviation of the surface roughness of Au and Si parts are 0.72 nm and 0.14 nm, respectively. Fig. 3 (c) shows the 3D plots of the image shown in Fig. 3 (b). It indicates that the Ti/Au layer possesses a thickness of about 20 nm, further confirming successful fabrication of the desired Ti/Au patterns. Fig. 2 (d) and (e) show the 2D AFM images of the Au-patterned Si substrate after fixation of the nanoparticle. We can observe a lot of attachments.
Figure 3. 2D ((a) and (b)) and 3D ((c)) AFM images of the Au-patterned Si substrate before fixation of the nanoparticles. Corresponding AFM images after fixation of the nanoparticles are shown in (d), (e) and (f).

on the Au parts of the Si substrate in comparison with the corresponding images before fixation (Fig. 3 (a) and (b)), while the Si part remains almost intact. Standard deviation of the surface roughness of Au and Si parts are 1.88 nm and 0.16 nm, respectively. It is worth noting that the AFM images were collected after cleaning by means of an ultrasonic. It indicates that the attachments form a strong bond with Au atoms. Fig. 3 (f) shows the 3D plots of the image shown in Fig. 3 (e). It clearly demonstrates that the attachments are selectively fixed to the Au parts. The thickness of the attachment layer is estimated to be 14.4 nm on average.

We performed EDX measurements so as to confirm that the attachments on the Au parts were the FePt nanoparticles. Fig. 4 (a) shows the SEM image of the Au-patterned Si substrate after fixation of the nanoparticle. Fig. 4 (b) shows results of EDX analysis of the Si part ("Area X" in Fig. 4 (a)). Only Si was observed in the "Area X". Fig. 4 (c) shows results of EDX analysis of the Au part ("Area Y" in Fig. 4 (a)). In comparison with the result shown in Fig. 4

Figure 4. (a) SEM image of the Au-patterned Si substrate after fixation of the nanoparticle. EDX analysis of (b) Si part ("Area X" in (a)) and (c) Au part ("Area Y" in (a)).
(b), we can observe existence of the additional elements such as Au, Ti, Fe and Pt. It is evident from the structure of the sample that the elements of Au and Ti are originated from Ti/Au patterns. Existence of Fe and Pt elements strongly indicates that the attachments observed in Fig. 3 (a) are the FePt nanoparticles fixed to the Au parts on Si substrate.

These experimental results strongly indicate that 1,10-decanedithiol acts as a binder between the FePt nanoparticles and Au patterns as described in our strategy, and that an array of the FePt nanoparticles is successfully formed on the Si substrate. However, the attachments observed in Fig. 3 (d) and (e) possess an average size of about 19 nm. By considering the fact that the average diameter of the FePt nanoparticles is about 6 nm, the attachments are aggregates of the FePt nanoparticles rather than isolated FePt nanoparticles. Average thickness of the attachments is estimated to be 14.4 nm, further supporting this view. We infer that the FePt nanoparticles form aggregated states in the solution since the 1,10-decanedithiol also can act as a binder between the FePt nanoparticles themselves.

4. Conclusion
We developed a simple and easy method of fixation of the FePt nanoparticles on the Au patterns formed on Si substrates by using 1,10-decanedithiol. Experimental results strongly indicate that dithiol compounds, which are functionalized at both chain ends, can act as a binder between the FePt nanoparticles and Au thin film. It was revealed that an array of the FePt nanoparticles is successfully formed on the Si substrate by using AFM, SEM and EDX measurements. Recently, we have succeeded in preparing FePt nanoparticles with L1_0 structure by developing a new synthetic strategy named “SiO_2-nanoreactor” method [13-16]. Since the L1_0-FePt nanoparticles are expected to have similar reactivity against thiol group as those of the fcc-FePt nanoparticles used in this work, the present method should also be applicable to the L1_0-FePt nanoparticles. Together with the successfully synthesis of the L1_0-FePt nanoparticles, this work will open a way to realization of a prototype of nanoparticle-patterned media.

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