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MAGNETIC NANOSTRUCTURES : FABRICATION AND APPLICATIONS FROM MEMORY DEVICES TO BIOSENSOR (REVIEW)

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ABSTRACT

MAGNETIC NANOSTRUCTURES : FABRICATION AND APPLICATIONS FROM MEMORY DEVICES TO BIOSENSOR. For magnetic storage application, we successfully fabricated nanodots and nanopattern using electron-beam lithography (EBL) technique followed by ion irradiation. Perpendicularly magnetized squared-bits with the sizes of 100 to 500 nm were clearly observed using magnetic force microscopy (MFM) images. MFM images showed that the most of the patterned squared-bits with size of 100 nm have either uniformly bright or dark magnetic contrasts. Magnetization curves of patterned films were strongly influenced by the bit size and spacing between bits and indicated the existence of exchange coupling between the bits via irradiated spacing. On the other hand, for biosensor application, we recently develop Surface Plasmon Resonance (SPR)-based biosensor for biomolecules detection device. Magnetic nanoparticles such as magnetite (Fe_3O_4) and $CoFe_2O_4$ were purposed as candidate for active materials to increase accumulation of target biomolecules on sensing surface of SPR-based biosensor. Fe_3O_4 and $CoFe_2O_4$ nanoparticles with different sizes of 8 to 17 nm have been successfully synthesized chemically by co-precipitation method. The surface of nanoparticles had been modified using polyethylene glycol (PEG)-4000 to increase the crystallinity, decrease agglomeration and control the shape to more spherical. However, modification using PEG-4000 decreased the saturation magnetization which is due to the existence of α-FeO(OH) and γ-FeO(OH) phases from bonds at interface of $CoFe_2O_4$.

Keywords: Magnetic Nanostructures, Memory, Biosensor, Magnetite, Nanodots, Surface Plasmon Resonance

ABSTRAK

NANOSTRUKTUR MAGNETIK : FABRIKASI DAN APLIKASI DARI MEDIA PENYIMPANAN HINGGA BIOSENSOR. Telah dipabrikasi *nanodots* dan *nanopattern* dengan menggunakan teknik *Electron-Beam Lithography* (*EBL*) yang dipadu dengan iradiasi ion untuk aplikasi media penyimpan data. *Nanodots* berbasis pada material magnetik dengan arah magnetisasi tegak lurus substrat telah dipabrikasi dengan ukuran yang bervariasi yaitu 100 nm hingga 500 nm. Citra *Magnetic Force Microscopy* (*MFM*) secara jelas menampilkan magnetik domain dengan pola gelap terang yang menunjukkan arah dari magnetisasi, dan *nanodots* mempunyai domain magnetik tunggal pada ukuran 100 nm. Selain itu, nanopartikel magnetik berbasis ferrite telah dipabrikasi dengan menggunakan metode sintesis kimia, untuk aplikasi sebagai bahan aktif biosensor berbasis *Surface Plasmon Resonance* (*SPR*). Nanopartikel Fe_3O_4 dan $CoFe_2O_4$ telah dipabrikasi dengan ukuran bervariasi yaitu 8 nm hingga 17 nm. Enkapsulasi dengan PEG-4000 juga telah berhasil dilakukan untuk mencegah proses penggumpalan pada nanopartikel saat sintesis tengah berlangsung. Beberapa fase selain ferrite juga muncul pada sampel setelah dilakukan proses enkapsulasi, seperti α-FeO(OH) dan γ-FeO(OH).

Kata kunci: Nanostruktur magnetik, *Memory*, Biosensor, Magnetit, *Nanodots*, *Surface Plasmon Resonance*

INTRODUCTION

Magnetic nanostructures have become controllable on the nanometer scale. Such fine structures exhibit a wide range of fascinating phenomena, such as low dimensional magnetism, induced magnetization in noble metals, electron interference patterns, oscillatory magnetic coupling and giant magnetoresistance. Some techniques can produce patterns with nanoscale details on surfaces, which have a central role in the development of new electronic, optical, and magnetic devices and systems, as well as biosensor application.

In recent years, there have been intensively studied in the patterned media to realize thermal stable magnetic recording media using a number of techniques, including electron beam (EB) lithography, holographic lithography, and others [1-3]. However, lithography technique has drawbacks such as poor planarity. Planarization is one off crucial issue in magnetic recording media. Ion irradiation is one of an excellent tool to modify magnetic properties without modification of the sample topography [4]. Using Ga ion irradiation to alter the properties of magnetic films and multilayers has attracted increasing interest, since basic magnetic properties such as coercive field and magnetic anisotropy field can be locally and controllably changed to engineer the behavior of sub-micrometer scale magnetic devices. Ion irradiation also decrease the Curie temperature, so that it can define regions which are non magnetic at room temperature [4,5].

Magnetic nanoparticles (MNPs) have become interesting subject of research because of their unique physical and chemical properties compared to bulk particle. Various methods have been developed to fabricate magnetic nanoparticles, such as coprecipitation method, thermal decomposition, microemulsion and hydrothermal [6]. There are also a polyolmethod [7], sonochemical [8] and other methods. Between these methods, coprecipitation method is the most effective method and relatively simple compared to other methods. This method produces a grain size distribution with relatively small size and performed at room temperature [7].

One of the unique characteristics of the MNPs is their superparamagnetic phenomenon. Material with superparamagnetic properties holds a high magnetization value under the influence of external magnetic field, but when there is no external magnetic field the average value of the magnetization is zero. The nature of the superparamagnetic generally emerges from small size ferromagnetic material (in nanometer order) [9]. It is therefore required to carry some research studies related to the control of the size distribution of nanoparticles and their magnetic properties. By controlling the size distribution, it is expected to obtain the effectiveness of the functionalization of nanoparticles synthesis [10]. One of the widely studied materials is cobalt ferrite ($CoFe_2O_4$) MNPs. In addition to its potential of having superparamagnetic properties, another special property that distinguishes $CoFe_2O_4$ nanoparticles with Fe_3O_4 is $CoFe_2O_4$ anisotropy constant value which is higher than Fe_3O_4 and γ-Fe_2O_3 [11]. However, $CoFe_2O_4$ nanoparticles are more difficult to react in coprecipitation method than Fe_3O_4 because of its origin from the salt with different kinds of metal ions. Ahn et al [12] found that the paramagnetic intensity of $CoFe_2O_4$ is visible along with the small size of the particles while the Curie temperature increased linearly with the increase in particle size**.** The objective of this paper is to review the fabrication process of magnetic nanodots structures and nanoparticles, and their application for memory devices and biosensors.

EXPERIMENTAL METHODS

This paper reviews our recently work on fabrication of magnetic nanostructures and their application for magnetic storage and material active of biosensor. To fabricate the smaller size ion-irradiation-patterned media may be limited by resolution of mask. Previously, patterning Co/Pd perpendicular magnetic multilayers without significant modifications of the surface roughness using e-beam lithography technique followed by focused ion beam (FIB) have been investigated, as one of a new approach to realize thermal stable magnetic storage based on ion-irradiation-patterned perpendicular magnetic storage media [13,14]. Planar-patterned $CrPt_3$ nanodot with various pitch (bit & space) sizes is fabricated by 30 keV Kr+ ion irradiation. Fabrication of planar-irradiated BPM with various bits/space sizes have been previously studied [15]. Magnetite (Fe_3O_4) and $CoFe_2O_4$ nanoparticles grain size dependence on temperature variation in more detail and determination of the grain size dependence on the variation of the concentration of coprecipitan, have been successfully investigated. Relation between magnetization properties and microstructure of the samples will also be studied. Therefore, this research is to be expected to add an information in the attempt of controlling the size of $CoFe_2O_4$ nanoparticles to obtain the effective character for the application as active material in surface plasmon resonance (SPR).

RESULT AND DISCUSSION

The phase of nanoparticles is investigated by X-Ray Diffraction (XRD). XRD patterns of the sample as shown in Figure 1. The XRD results showed the well crystallized nanoparticles have some peaks which identify the character of $CoFe_2O_4$ phase. From the obtained XRD patterns, the average grain size of $CoFe_2O_4$ nanoparticles was determined from the full width at half maximum (FWHM) of the x-ray diffraction peak using Scherrer's equation [16]

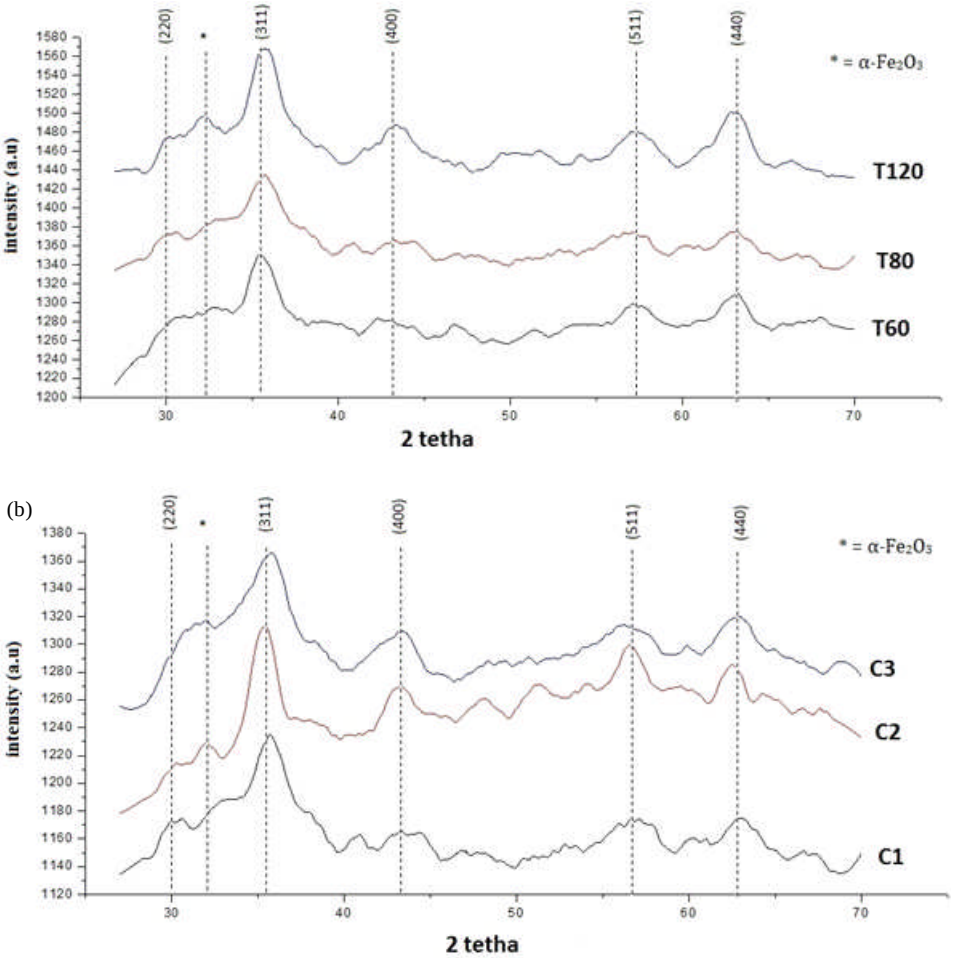

Figure 1. XRD patterns of the sample with (a) variations in temperature synthesis and (b) variation of the concentration of NaOH [17].

Tabel 1. Synthesis parameter of $CoFe_2O_4$ nanoparticles with temperature variations

No	Name of Sample	Mass of $CoCl_2.6H_2O$ (g)	Mass of $FeCl_3.6H_2O$ (g)	Volume of HCl (37%) (mL)	NaOH Concentration (M)	Stirring Duration (minute)	Temperature Synthesis (°C)
1	T60	1.188	2.703	3.5	1.5	120	60
2	T80	1.188	2.703	3.5	1.5	120	80
3	T120	1.188	2.703	3.5	1.5	120	120
4	C1	1.188	2.703	3.5	1.5	120	80
5	C2	1.188	2.703	3.5	5.0	120	80
6	C3	1.188	2.703	3.5	15	120	80

$$D = 0.9\lambda/(B\cos\theta) \quad \text{.....} \quad (1)$$

where:

D = The particle diameter,
λ = The x-ray wavelength,
B = The FWHM of a diffraction peak,
θ = The diffraction angle.

Samples have been synthesized by varying the temperature and NaOH concentration, as shown in Table 1 [17]. The XRD results showed that the peaks were identified as characteristic of $CoFe_2O_4$ with the main peaks in the three samples at approximately 2θ=35.2° region which is the top main peak (311) of the cubic-shaped $CoFe_2O_4$ cubic spinel. This analysis is confirmed by the appearance of other peaks are also characteristic of the peak areas of $CoFe_2O_4$ (220), (400), (511) and (440). Lattice parameter values obtained by profile refinement of XRD data for the samples varied in 60°C temperature synthesis (T60), 80°C (T80) and 120°C (T120) is 8.379; 8.371 and 8.353 Å, respectively. Lattice parameter value is close to the value of the lattice parameter of bulk $CoFe_2O_4$ size reference is 8.395 Å [18].

In addition, there are other peaks seen in the results of XRD patterns, indicated as the phase α-Fe_2O_3. Scherrer equation calculation with values obtained crystal grain size is 8.8; 8.9 and 9.7 nm for sample T60, T80 and T120, respectively. This indicates that the

particle size increases with increase of temperature synthesis. It can be concluded that the temperature parameter plays a role in determining the grain size of nanoparticles. Furthermore, the nanoparticles were synthesized by varying the concentration of NaOH also showed peaks in the same region with samples synthesized by varying the temperature. This indicates that the sample was synthesized with NaOH concentration variations have also crystallize well. From this sample lattice parameter values obtained 8.371, 8.401 and 8.383 Å respectively for the samples synthesized with 1.5 M NaOH concentration (C1), 5 M (C2) and 15 M (C3). If these results are compared with the reference is 8.395 Å [18] showed that the three samples crystallize well with the value of the lattice parameter approaching with $CoFe_2O_4$ bulk size. The main peak of the sample C2 is higher than that of the other two samples. Similarly, the sample with variation of concentration of NaOH also appeared α-Fe_2O_3 phase. The crystal grain size is 8.9, 8.6 and 7.7 nm for C1, C2, C3 respectively. These results indicate that the crystalline grain size of nanoparticles decreased with increasing concentrations of NaOH. It can be concluded that the concentration of coprecipitant (NaOH) also plays a role in determining the grain size of nanoparticles. Figure 2(a) is TEM images of nanoparticles for $CoFe_2O_4$ and PEG-4000 coated $CoFe_2O_4$. After surface modification of $CoFe_2O_4$ using PEG-4000, grain size increased to 42.4 nm, as shown in Figure 2(b).

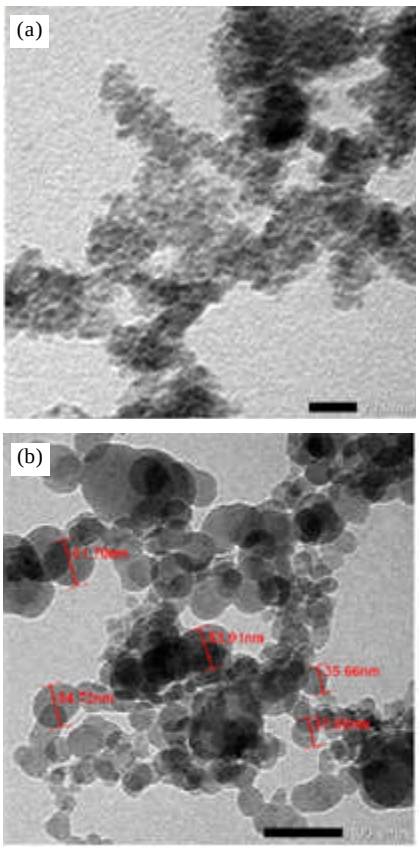

Figure 2. TEM images of nanoparticles (a) $CoFe_2O_4$; (b) $CoFe_2O_4$+PEG-4000 [17].

Ion-Irradiation-Patterned Co/Pd Films

AFM images of ion-irradiation patterned Co/Pd multilayer films at ion dose of 5×10^{15} ions/cm^2 with squares size of 500, 400, and 200 nm are shown in Figure 3(a), (b), and (c), respectively. The ion irradiation patterned Co/Pd film at various AFM images was smooth. The surface roughness of ion irradiation patterned film becomes important properties. Three-dimensional AFM images of patterned media give further insight into modification at the surfaces, as shown in Figure 3. For all samples, the height of square bits was about 6 nm, since the etching depth of irradiated region is about 6 nm. Since the thickness of Pd capping layer is 10 nm, only Pd capping layer is etched by the ion irradiation and Co/Pd multilayers will not be oxidized or etched. It can be clearly seen that e-beam lithography technique can be used for creating a residual mask into several hundreds nanometer and fabricating patterned Co/Pd multilayer film without significant change in surface roughness.

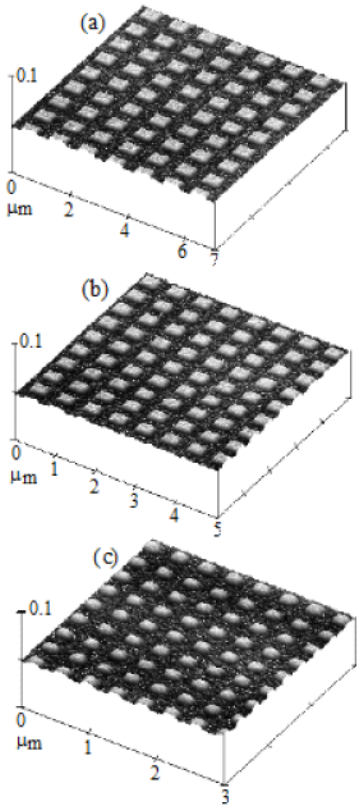

Figure 3. Bird-view AFM images of magnetic squares with size of (a) 500, (b) 400, and (c) 200 nm [19]

Figure 4 shows *M-H* loops and MFM image of as-grown Co/Pd multilayer films. The MFM tip was magnetized in the z direction (perpendicular to the plane of the sample) prior to the measurement. Images were

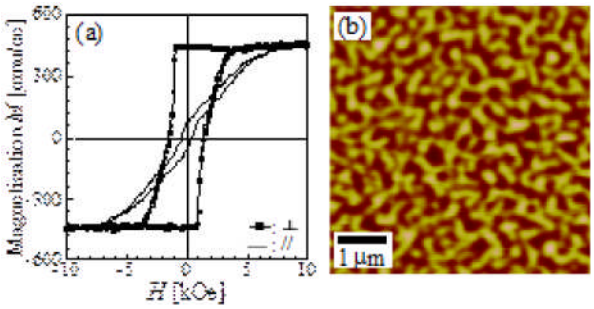

Figure 4. M-H loop (a) and MFM image (b) of as-grown Co/Pd multilayer film [19]

taken without any external magnetic field applied after the sample deposition. Here, lift scan height during measurement was 50 nm. As-grown film shows perfect perpendicular hysteresis loop, as shown in Figure 4(a). The *M-H* loop measured perpendicular to the film plane shows that coercivity is about 1.5 kOe and remanence ratio was about 1. It has been reported that Ga ion irradiation at ion dose of 5×10^{15} ions/cm^2 and energy of 22 keV modified magnetization direction of Co/Pd multilayers, which corresponds to the magnetic anisotropy changes from perpendicular to in-plane direction and the etching depth of irradiated region was about 6 nm [19]. The result was reasonable since the effective magnetic anisotropy energy, K_{eff}, decreases by ion irradiation from 1.2×10^6 erg/cc for as grown film to -0.3×10^6 erg/cc for irradiated film at 5×10^{15} ions/cm^2 [18]. It was assumed that the ion beam induced atomic disordering of the interface and the inter-diffusion of Co and Pd atoms during ion irradiation is thought to be responsible for the change of magnetic anisotropy of Co/Pd multilayer films [19]. The typical perpendicular maze domain structure with a stripe domain structure is clearly seen in the MFM image of as-grown film, as shown in Figure 4(b). The stripe domain width is about 220 nm.

Figure 5 shows MFM images of patterned Co/Pd nanodot with various bit size of 500 nm and 200 nm, as shown in Figure 5(a) and 5(b), respectevely. Significant difference in magnetic contrast between un-irradiated and irradiated area can be clearly seen at patterned films, where a multi-domain structure still observed. The MFM image indicates that each un-irradiated square consists of localized perpendicular magnetic domain structures.

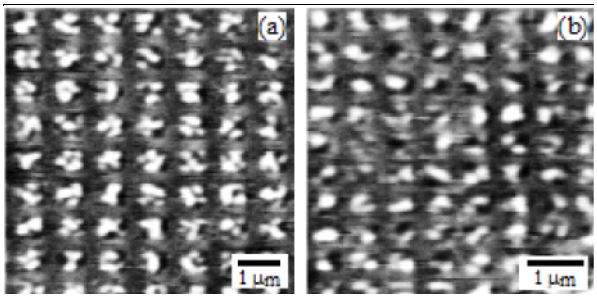

Figure 5. MFM images of patterned sample with square bits size of 500 (a) and 400 nm (b) [19]

The absence of magnetic contrast in irradiated area is due to the change of the magnetization direction from perpendicular to in-plane.

CONCLUSION

$CoFe_2O_4$ nanoparticles have been synthesized by coprecipitation method. Synthesis has been performed by varying the synthesis parameters, such as temperature and concentration of coprecipitant. The results showed that microstructures of $CoFe_2O_4$ could be controlled by synthesis parameters. We have demonstrated that ion irradiation modified the magnetic properties and the microstructures of magnetic thin films. Ion irradiation had a significant influence on the regularity of the periodic structure in Co/Pd multilayer films because of the interdiffusion between atoms at the interface. The modifications of magnetic properties by ion irradiations were associated with the decrease of the interfacial magnetic anisotropy. The MFM image of the irradiated films showed that the domain width gradually decreased with increasing ion dose. The significant difference of magnetic contrast and domain structure between irradiated and un-irradiated regions was observed in the patterned films. Sharp boundary between perpendicular and in-plane region was also observed, which indicate that localized patterns can be engineered by ion irradiation.

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