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RESEARCH ARTICLE

FePt Nanoparticles Fabricated by Pulsed Laser Ablation

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Two unique laser processes of 'PLA in low vacuum (PLALV)' and 'PLA in liquid (PLAL)' have been examined to fabricate FePt nanoparticles and the magnetic and structural properties were investigated. The particles as prepared by PLALV showed a superparamagnetic behavior with an fcc structure. The annealing temperature dependence of the transformation from fcc to fct structure was studied by the structural and magnetic properties. A large coercivity of 3.6 kOe at 300 K was obtained by the low temperature (500 C) annealing. Composition deviation due to Fe dissolution in PLAL process was successfully suppressed by Ar bubbling.

Keywords: PLA, FePt Nanoparticle, Annealing.

1. INTRODUCTION

Pulsed laser ablation (PLA) technique has been developed as a high energy film preparation method. Recently, some unique PLA methods have attracted much attention as a nanoparticle fabrication process. We have tried two unique PLA processes to prepare FePt nanoparticles in this study. The mean free path of the ablated particles decreases inversely proportional to the atmospheric pressure and the plume is significantly confined around kPa range. Since the effective particle formation occurs within the small and high density plume, a high energy nanoparticle fabrication is expected by the PLA in low vacuum (PLALV).[1,2] The other laser process of PLA in liquid (PLAL) is a novel and simple method to prepare nanoparticle solution. The plume in the liquid is well confined and the high energy particle formation is expected also in this process.[3,4]

Since the ferromagnetism is maintained even for nanometer size due to the large magnetic anisotropic energy, FePt alloy particles are promising for a high density recording material.[5] The hard magnetism appears only for $L1_0$ ordered alloy with a face centered tetragonal (fct) structure. Post annealing treatments are necessary since most preparation methods give disordered alloy with a face centered cubic (fcc) structure.[6,7] Though laser ablation methods are effective process for the high energy particle formation as described above, no PLA study has reported for FePt nanoparticle fabrication. We have examined two unique PLA processes for the FePt nanoparticle fabrication for the first time and investigated the structural and magnetic properties in this study.

2. EXPERIMENTAL DETAILS

The PLALV chamber was first evacuated to 10^{-4} Pa by turbo-molecular pump to reduce the residual gas contamination before the Ar gas was introduced. The third harmonic Nd:YAG laser light (352 nm) with 100 mJ/pulse power and 10 Hz frequency was focused onto the rotating disk shaped FePt target. Substrates were placed at side positions as illustrated in Figure 1(a). Polyimide film and quartz glass plate have been used as substrates and little substrate dependence was confirmed. The detailed experimental conditions are reported in elsewhere.[8]

The instrumental setup of PLAL is very simple as shown in Figure 1(b). The target FePt plate placed at the bottom of the glass bottle filled with 30 mL solvent was ablated by the focused laser light. The second harmonic 532 nm wavelength was employed to reduce the absorption by the solvent. The laser power conditions were the same as the PLALV. Deionized water with and without Ar bubbling and hexane were examined as solvents. The degassed pretreatment of 3 hours Ar bubbling is to degas the solvents. More detailed experimental conditions are described in Ref. [9].

For both PLALV and PLAL samples, the structural properties were investigated by X-ray diffractometry (XRD) and the morphology was observed using transmission electron microscope (TEM) and field emission scanning microscope (FE-SEM). The magnetization curves

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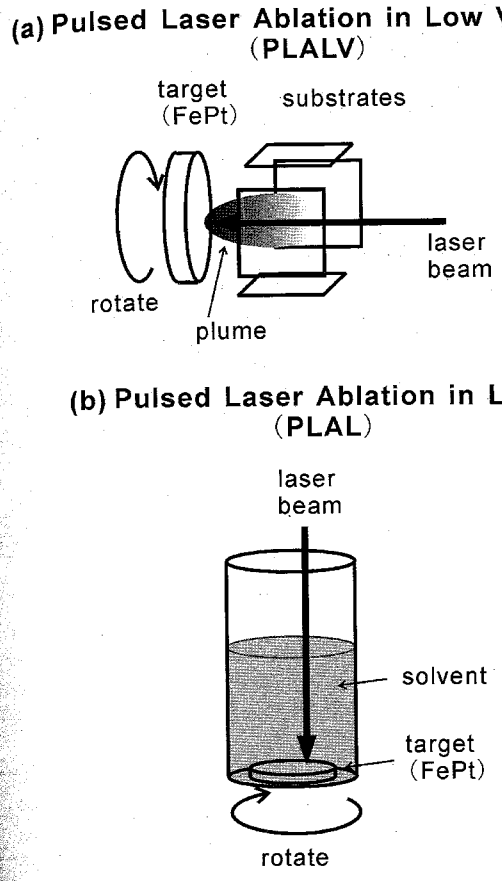

Fig. 1. The schematic diagram of (a) PLAV and (b) PLAL methods.

were measured by a superconducting quantum interference device (SQUID) magnetometer. Composition analysis was also performed for some samples using energy dispersive X-ray spectrometer (EDS) attached to FE-SEM.

3. RESULTS AND DISCUSSION

The plasma area composed of ablated particles is called 'plume' for PLA process. The plum size generally decreases and the particle density becomes higher with increasing Ar pressure as mentioned above. In our PLALV chamber, the visible plume size actually decreased from 15 mm (0.1 kPa) to 3 mm (10 kPa). Average particle sizes obtained from TEM images as a function of Ar pressure are listed in Table I. Continuous film structure was observed for the samples deposited lower than 0.1 kPa. The particle growth within the plume is considered dominant. The smaller particle size at higher pressure is explained by the shorter growing time due to the smaller plume area and the quench effect by the higher collision probability. Since the plume confinement effect seems saturated above 5 kPa. judged from these results, the samples discussed below were prepared at 5 kPa.

The annealing temperature dependence was investigated by XRD analysis as shown in Figure 2. The nanoparticles deposited on the polyimide films were wrapped with

Table I. Particle size as a function of Ar pressures.

Pressure (kPa)	0.1	1	5	10
Average diameter (nm)	film	5.5	3.5	3.8

tantalum foil and heated in high vacuum of $\sim 5 \times 10^{-4}$ Pa for one hour. Since the annealing temperature was measured by the thermocouple attached to the heater side tantalum foil surface, actual temperature will be a little lower. The notation of (lmn) is common indexing to both fcc and fct structures and *(lmn) is only for fct in the figure. The broad reflections indicated by triangles between 20 and 30 degrees are derived from polyimide substrate. No specific fct reflection for nanoparticles as prepared and annealed lower than 400 C means a disordered fcc structure. Significant change between 400 and 450 C indicates the starting of ordered structure formation. Little structural ordering proceeds above 500 C judged from small difference between 500 and 550 C XRD profiles in the figure.

Nanoparticles as prepared and annealed at 300 K show almost the same coercivities at 300 K (zero) and 5 K (~1 kOe) in Figure 3 and consistent to the XRD results described above. The coercivities increase monotonously for 400 and 450 C annealed samples. This magnetic behavior suggests that the local atomic ordering starts at 400 C and the magnetic properties are more sensitive to the

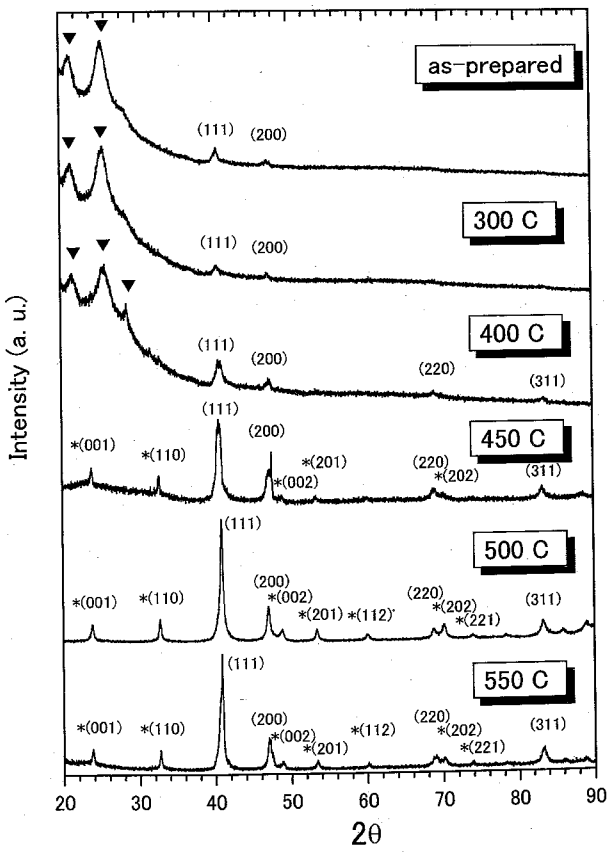

Fig. 2. XRD measurements of annealed particles prepared by PLALV.

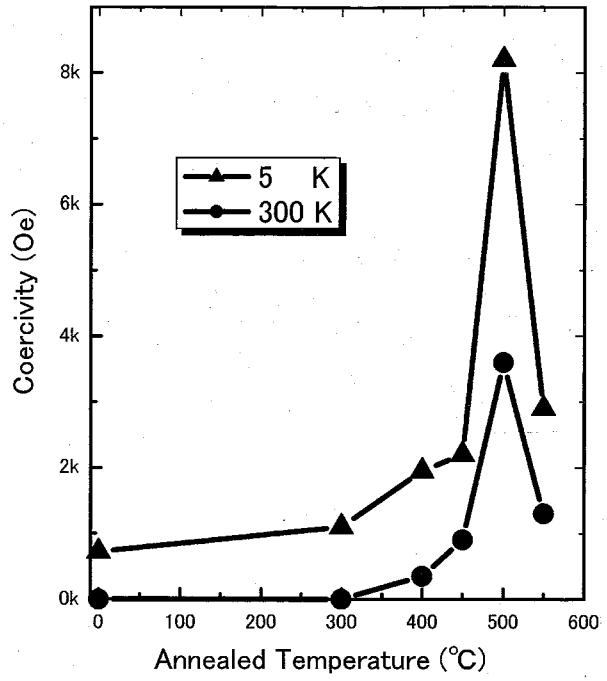

Fig. 3. Coercivities as a function of annealed temperature measured at 5 and 300 K.

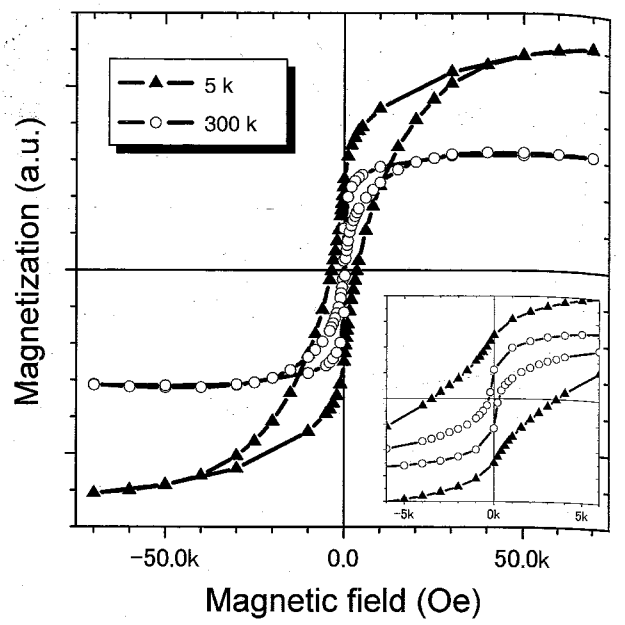

Fig. 4. Magnetization curves of the nanoparticles prepared by PLAL. The nanoparticles fabricated in degassed hexane. Post annealing was performed at 600 C for 30 min. The inset is a magnification around coercivity fields.

local structural change than XRD. Maximum coercivities of 8.2 kOe (5 K) and 3.6 kOe (300 K) were obtained for 500 C annealing and then they drop at 550 C. The fcc–fct transformation of FePt nanoparticles have been observed for the annealing at 600 C or above.[6] This fairly low transformation temperature in this study is considered due to some small structural difference for the initial nanocrystals. Actually, the difference in the distance between substrate and plume changed the annealing effect clearly in spite of no change detectable by XRD or TEM observation.[8] These results suggest that the local atomic ordering in the FePt nanoparticles depends on the initial crystal growth conditions. We have no reasonable explanation about the drop. There might be some structural difference for the starting nanoparticles before annealing.

Though the detailed particle formation process in PLAL has not been understood well, strong solvent dependences have been observed. Three kinds of solvents, deionized water, degassed deionized water and degassed hexane, have been examined in this study. Nanoparticles produced from $Fe_{50}Pt_{50}$ source target change the composition dependent on the solvents as listed in Table II. Since the mixture image of sphere like particles and irregular shaped plate was obtained for water solvents by FE-SEM, composition analysis was performed for both a few 10 μm square area (average) and point area (<10 nm in diameter) at sphere shaped particles (particle). The results of water show significant decrease in Fe composition for particle and little deviation from the source for average. It means that a large part of ablated Fe atoms are ionized and dissolved into the water and Pt rich particles are produced. The pre-treatment of Ar bubbling suppress the Fe dissolution effectively as shown for degassed water. In the case of hexane, only the particle shaped images were observed. Little composition difference between degassed water and hexane particles indicates the main reason of the Fe dissolution air contamination in the solvent. A typical magnetization curves for FePt nanoparticles prepared in hexane is illustrated in Figure 4. Only a small coercivity of 300 Oe at 300 K was observed by 600 C annealing. The small coercivity is considered due to the insufficient composition control. Further developments will be necessary for PLAL process.

Table II. Fe atomic composition by EDS.

Solvent	Water	Water (degassed)	Hexane (degassed)
Fe composition (%)	44 (average)	49 (average)	35
	13 (particle)	35 (particle)	

4. CONCLUSION

Two unique laser processes of PLALV and PLAL were examined to fabricate FePt nanoparticles. Low temperature annealing of 500 C could transform the nanoparticles prepared by PLALV from disordered fcc to ordered fct structure and a large coercivity of 3.6 kOe at 300 K was obtained. Composition deviation due to Fe dissolution in PLAL process was successfully suppressed by Ar bubbling and ferromagnetic behavior showing 300 Oe coercivity at 300 K was observed.

References and Notes

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