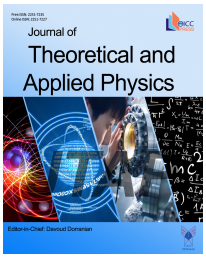

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Effect of annealing on the magnetic prperties of $FePt_3$ and $CoPt_3$ nanoparticles

Fereshteh Javani[1], Seyed Ali Sebt[1], Ana Khajehnezhad[1,*], Azadeh Aezami[2]

[1]*Plasma Physics Research Center, Science and Research Branch, Islamic Azad University, Tehran, Iran.*
[2]*Departments of Physics, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran.*

[*]**Corresponding author:** akhajehnezhad@gmail.com

Original Research

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Abstract:

$FePt_3$ and $CoPt_3$ compound nanoparticles were studied, magnetically and structurally. Compound ordering in crystal structure of these nanoparticles is formed at 600º C. Meanwhile, the shape and size of grains are prominent to be controlled. In this work, layers of $FePt_3$ and $CoPt_3$ nanoparticles with thicknesses of respectively 20 nm and 10 nm were fabricated on Si wafer, in $L1_2$ compound ordered phase. In these layers the size of nanoparticles were less than 10 nm according to Field Emission Scanning Electron Microscopy (FE-SEM) analyses. Direct synthesis method using sputtering system was applied. In order to orient nanoparticles, they were annealed, at 350º C and then cooled, in magnetic field of 30 mT. X-ray Diffraction (XRD) and Vibrating Sample Magnetometer (VSM) analyses showed crystalline, compound and directional ordering of these nanoparticles, respectively.

Keywords: Magnetic nanoparticles; $FePt_3$; $CoPt_3$; Directional ordering; Sputtering

1. Introduction

Both as prepared Fe_xPt_{1-x} and Co_xPt_{1-x} bimetallic compounds, have fcc crystal structure and after a phase transition through annealing process [1] they have $L1_0$ or $L1_2$ compound ordering for $x = 0.5$ and $x = 0.7$, respectively [2]. In $L1_0$, c lattice constant is smaller than a and fcc structure is converted to fct [3]. Crystal and compound ordering can be investigated from x-ray diffraction peaks. The appearance of (001) and (011) weak peaks in this structure is the sign for compound ordering [4, 5] and partial separation of (002) and (200) peaks from each other is the sign for the difference between a and c lattice constants, which is the evidence for conversion of fcc to fct [5].
The effect of the presence of magnetic field while grains grow or during annealing and cooling is the formation of third ordering. That is, crystal directions of grains are the same, with respect to each other. This effect leads to increase in (001) peak intensity [6] and if the direction of magnetic field is perpendicular to the surface of the sample, (001) direction of grains is also perpendicular to this surface. In such conditions, magnetically, grains coalescence to some extent and exchange interaction results in ferromagnetic effect [7, 8]. This changes the curve of magnetization (M) versus applied magnetic field (H), and causes magnetization to reach to saturation in lower magnetic field. $L1_0$ compound ordering has high magnetic coercivity [9] and therefore is used in magnetic memories [10]. Consequently, many works have been done on FePt [11, 12].
In order to form compound ordered phase, the sample needs to be annealed at 600º C. This gives rise to metallic nanoparticles coalescence and change in their shape and size. There are different methods suggested to overcome this problem [13, 14]. The growth of nanoparticles at high temperature means that in direct synthesis method, compound ordered phase can directly be formed at lower temperatures, so that the shape and size of nanoparticles remain unchanged.
In this work, focus is on fabrication of $FePt_3$ and $CoPt_3$ nanometric granular layers and making them directional. In order to keep the shape and size of the nanoparticles, the temperature was not raised higher than 350º C. Effects of the presence of 30 mT magnetic field during anneal-

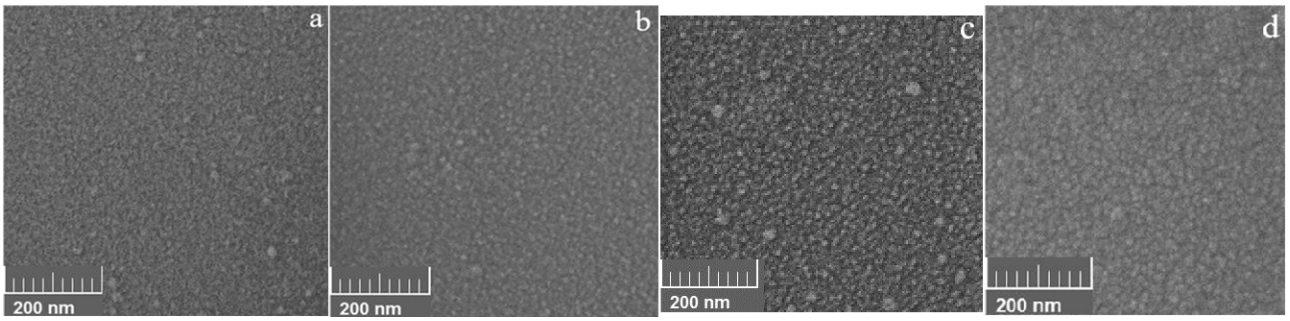

Figure 1. FE-SEM results of nanometric granular layers fabricated by sputtering method; a) sample 1, b) sample 2, c) sample 5, d) sample 6.

ing on FE-SEM, XRD and VSM results were investigated, which shows that the size of nanoparticles remains nearly unchanged and they are crystally and magnetically directional.

2. Experimental details

Nanometric granular layers of Iron-Platinum and Cobalt-Platinum compound were deposited on Si wafer using sputtering system. The synthesis conditions were as follows: Co-sputtering, base vacuum of $10-5$ Torr, deposition rate of 0.3 Å/S and 0.6 Å/S for Co-Pt_3 and Fe-Pt_3 layers, respectively. Argon pressure of $10-2$ Torr and the temperatures of two series of substrates were respectively at room temperature for $CoPt_3$ and 360º C for $FePt_3$.
In first step, $CoPt_3$ layer of 10 nm thickness was deposited on Si wafer using rf power supply and two targets of Co and Pt, by Co-sputtering method. Then, 20 nm Fe-Pt layer was deposited on two series of substrates which were Si wafer and $CoPt_3$/Si layer, using dc power supply and two targets of Fe and Pt, by the same method. Therefore, three series of samples were obtained on Si substrates: $CoPt_3$ single layer, $FePt_3$ single layer and $FePt_3$/$CoPt_3$ bilayer.
After that, some samples were placed in vacuum media of 350º C perpendicular to 30 mT magnetic field of a permanent magnet for 30 min. Also, they were cooled in such magnetic field up to room temperature. It lasted 1 hour for temperature to reaches to 100º C.
XRD analysis was done in order to determine crystal structure of the samples.

For determination of the shape, size and distribution of grains on the substrate, FE-SEM analysis was performed and magnetic properties of the samples were studied via VSM analysis.
The steps of samples fabrication are respectively as follows:

a) $CoPt_3$ layer:

1- 6×4 mm wafers were cut and washed in ultrasonic system using acetone and were put in sputtering chamber on anode's place.

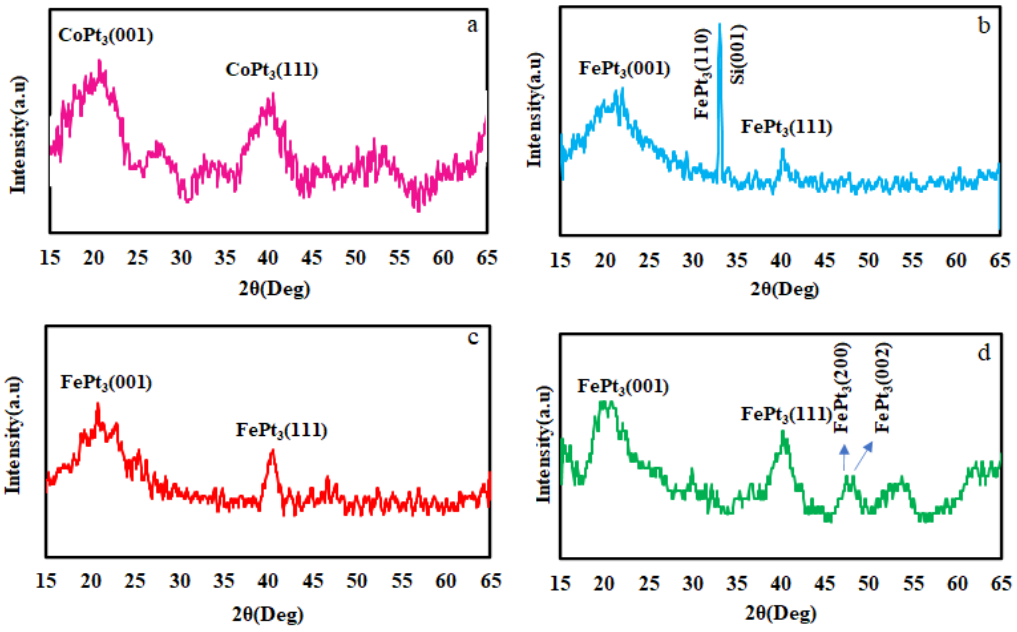

Figure 2. XRD patterns of samples; a) $CoPt_3$, b) $FePt_3$, annealed and cooled in magnetic field of 30 mT, c) as prepared $FePt_3$/$CoPt_3$ and d) $FePt_3$/$CoPt_3$ annealed and cooled in magnetic field of 30 mT.

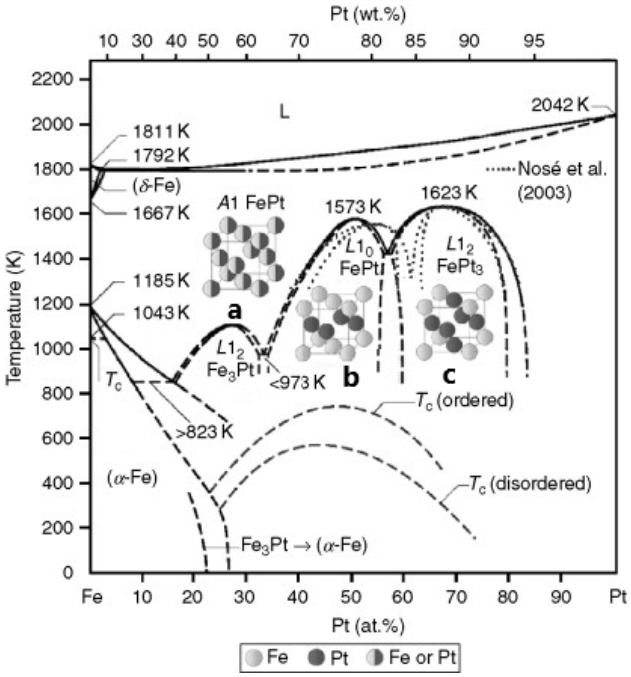

Figure 3. Schematic of crystal structure of three different phases. The difference is in compound orderings of compounds [15].

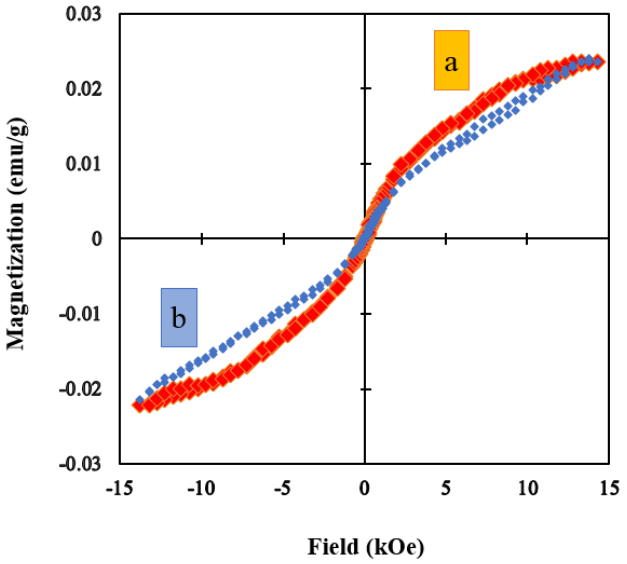

Figure 4. VSM analyses of bilayer samples of $FePt_3/CoPt_3$, a) annealed and cooled in magnetic field, and b) as prepared.

2- Cobalt and Platinum compound target were put on cathode's place that was connected to rf power supply to be turned on after reaching to deposition step.
3- The vacuum pressure reached to the order of Torr (1 mmHg) using rotary pump.
4- The vacuum pressure reached to the order of $10-5$ Torr using Turbo pump that its rotational speed reached up to 80000 rpm, gradually. Then, in order to flow Ar gas, the rotational speed of turbo pump decreased to 45000 rpm.
5- The flow rate of Ar gas made the pressure of the chamber $10-2$ Torr.
6- In this pressure and when the samples were covered by a shutter, rf power supply was turned on and the power was increased in order the plasma to be formed.
7- By changing the pressure of Ar gas and the power of power supply, the deposition rate was controlled at 0.3 Å/s.
8- By opening the shutter, the thickness and time increased gradually up to final thickness of 100 Å where power supply turned off according to system's data.
9- The samples were kept under vacuum until the next deposition.

b) $FePt_3$ layer:

1- Some previous prepared samples and new clean raw wafers were put on the anode of the sputtering system.
2- Platinum and Iron compound target was put on cathode which was connected to dc power supply.
3- The steps of 3 to 5 of part (a) were repeated.
4- The temperature of the anode's heater was set at 360º C.
5- The dc power supply was turned on and the voltage was increased in order the plasma to be formed.
6- By making gradual changes in the voltage and changing the pressure of Ar gas, while samples have been covered by shutter, deposition rate was adjusted to 0.6 Å/s.
7- By opening the shutter, deposition started according to the data and it continued until reaching to the final thickness of 200 Å and then power supply was turned off.
8- Samples were kept under vacuum.

c) Annealing in magnetic field

1- A place was prepared for permanent magnet on top of the anode with 1 cm distance and parallel to that.
2- Three samples of first series, four samples of second series (prepared compound bilayers explained in respectively (a) and (b) parts), and four samples of single layers of b series were put on horizontal surface of anode with 1 cm distance to magnet's pole, where the magnetic field is 30 mT. This magnetic field was measured using tesla meter.
3- In $10-2$ Torr, while the rotational speed of Turbo pump was on %20, the heater was turned on in order the surface of the anode and samples to be heated. The rate of increase in temperature was 1º C/s and the final temperature reached to 350º C.
4- When annealing started, the rotational speed of Turbo pump was adjusted to %50 and consequently the pressure decreased to $10-4$ Torr.
5- Samples were kept in this vacuum at 350º C, in 30 mT magnetic field for 30 min.
6- The heater was turned off, while the vacuum and magnetic field remained unchanged. The temperature reached to 100º C exponentially, during 1 h.
7- The vacuum and magnetic field remained unchanged until the temperature reached to the room temperature.
The number of samples were as follows:
1) As prepared $CoPt_3$
2) As prepared $FePt_3$
3) Annealed and cooled $CoPt_3$ in magnetic field
4) Annealed and cooled $FePt_3$ in magnetic field

5) As prepared $FePt_3/CoPt_3$
6) Annealed and cooled $FePt_3/CoPt_3$ in magnetic field

3. Results and discussion

Figure 1 shows FE-SEM results of metallic nanoparticles layers fabricated using sputtering method. $CoPt_3$ layer with thicknesses of 10 nm and $FePt_3$ layer with thicknesses of 20 nm, both deposited on Si substrate, are shown in Figures 1(a) and (b), respectively. Figure 1(c) shows as prepared $FePt_3/CoPt_3$ bilayer and Figure 1(d) shows the bilayer after annealing and cooling in magnetic field. All four samples have spherical grains, with the size of smaller than 10 nm distributed on the surface of the layer, uniformly. The size of nanoparticles did not increase during annealing at 350º C, due to the presence of magnetic field. The EDS determined the percentage of Pt and Fe in FePt sample: %26 Fe, %74 Pt.

X-ray diffraction (XRD) pattern of samples is shown in Figure 2 according to JCPDS cards number 29-0499 for Figure 2(a) and 29-0716 for 2(b), 2(c) and 2(d) Figures. Pt that has fcc structure, does not show (001) and (011) peaks, due to zero structure factor, but in $Copt_3$ (Figure 2a) and $FePt_3$ (Figure 2b) compound ordered phases containing two types of atoms these two peaks are formed. Figure 3 shows crystal structure of compounds of two Fe and Pt atoms in three different phases [15]. According to Figure 3(a), these two atoms, in as prepared compound, at room temperature, are distributed randomly in atomic positions of fcc structure. When there is the same ratio of two atoms in the compound, due to high temperature, $L1_0$ compound ordering in fct crystal lattice is formed (Figure 3b). $FePt_3$ compound [16], at high temperature, according to Figure 3(c), has $L1_2$ compound ordering with fcc crystal structure, which occurs in the synthesized samples of this work.

Due to the difference in atomic shape factor of these two atoms, structure factors of $L1_0$ and $L1_2$ are not zero but weak, and it is expected that (001) and (011) peaks appear weakly. However, high intensity of (001) peak, the absence of (011) peak and lower intensity of (111) peak are the signs showing that samples which were annealed and cooled in the presence of magnetic field were directed in $L1_2$ structure. Therefore, most nanoparticles were grown in (001) crystal direction which is perpendicular to the surface of the layer.

Figures 2(c) and 2(d) show $FePt_3/CoPt_3$ bilayer samples respectively before and after annealing and cooling in presence of magnetic field of 30 mT. Appearance of (111) peak in $2\theta = 41°$, and partial separation of (002) and (200) peaks from each other respectively in $2\theta = 47.2°$ and $2\theta = 48°$ are the evidence for the partial formation of fct structure [17] with its a = 3.9856 Å and c = 3.9201 Å lattice constants, so that $c/a = 0.98$.

In XRD results, for small angles, the slope of the graph is positive, which is due to low thickness of the samples (10 nm, 20 nm, and 30 nm) and passage of part of X-ray photons from sample without diffracting that leads to the formation of background radiation in small angles with higher intensity. Lower slope of background, in XRD pattern for $FePt_3/CoPt_3$ bilayer, is for larger thickness of this sample (30 nm) with respect to other samples.

Figure 4 shows magnetization (M) versus magnetic field intensity (H), measured by VSM analysis. As prepared $FePt_3/CoPt_3$ sample has been compared to annealed and cooled in magnetic field $FePt_3/CoPt_3$ sample. Annealing at 350º C and cooling in magnetic field of 30 mT leads to alignment of nanometric single domain grains that are nearly joined to each other and strengthen the effect of exchange interaction in sample [7]. As a result, M(H) reaches to its saturation limit in lower applied magnetic field. Figure 4(a) in comparison to 4(b) shows this result. That is, saturation field (H_s) of the sample decreases because of cooling in magnetic field, and the behavior of the magnetization of the nanoparticles (Fig. 4a), in comparison to as prepared sample (Fig. 4b) is more similar to ferromagnetic nanoparticles.

4. Conclusion

Three types of directional, compound and crystalline ordering were formed in $FePt_3$, $CoPt_3$ and $FePt_3/CoPt_3$ granular nanolayers. Direct synthesis method in deposition by sputtering system results in growth of nanoparticles with the size of smaller than 10 nm. Although 600º C is required for phase transition from fcc to fct structure with $L1_2$ compound ordering, this phase was also formed in 350º C through direct synthesis method. The appearance of (001) peak, in XRD pattern, is the evidence for the presence of this phase. Moreover, the perpendicular magnetic field to the surface of the layer resulted in ordered orientation of these nanoparticles so that their (001) crystal direction is perpendicular to the surface of the layer which can be investigated through high intensity of this peak.

Ethical approval
This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval is not applicable.

Authors Contributions
All the authors have participated sufficiently in the intellectual content, conception and design of this work or the analysis and interpretation of the data (when applicable), as well as the writing of the manuscript.

Availability of data and materials
Data presented in the manuscript are available via request.

Conflict of Interests
The author declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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