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# Magnetic properties of CoPt–$SiN_x$/Ag nanocomposite films

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ABSTRACT

When the thickness of Ag under layer is 25 nm, the CoPt/Ag film has maximum out-of-plane squareness ($S_\perp$), minimum in-plane squareness ($S_\parallel$), and the largest out-of-plane coercivity ($H_{c\perp}$), they are 0.95, 0.35, and 15 kOe, respectively. Different volume percent of $SiN_x$ ceramic materials were co-sputtered with $Co_{50}Pt_{50}$ films on the Ag under layer to reduce the grain size of the CoPt film. Comparing the X-ray diffraction pattern of CoPt-$SiN_x$/Ag films without annealing with that of the films which annealed at 600 and 700 °C, it is found that the intensities of CoPt (0 0 1) and CoPt (0 0 2) superlattice lines were reduced after annealing. As the $SiN_x$ content is raised to 50 vol%, the particle size of CoPt is reduced to be about 9 nm.



## 1. Introduction

Recently, CoPt alloy has been investigated for ultra-high magnetic media application due to its high magnetocrystalline anisotropy and high thermal stability [1–4]. The as-deposited CoPt films possess face-centered-cubic (FCC) phase, which could be transferred to face-centered-tetragonal (FCT) phase by introducing the proper under layer beneath the CoPt films [5–7]. Xu et al. [8] had shown that high perpendicular anisotropy CoPt film could be obtained by adding the Ag layer beneath the CoPt film. On the other hand, the growth rate of recording area density has been increased and expected to exceed 1 Tbit/in$^2$ within few years [9–11]. For high-density recording medium, it was required that a bit dimension is only hundreds of atomic diameters. Therefore, the grain size should be decreased to be smaller than 10 nm as the bit sizes decreased. Moreover, the exchange-coupling effect should be minimized in order to lower the transition noise. Several researchers had controlled the grain size of the magnetic film by adding nanomagnetic materials ($SiO_2$ [12], $Al_2O_3$ [13], etc.). In our previous study [14], we had added the $SiN_x$ into the FePt films and examined the magnetic properties of $(FePt)_{1-y}$–$(SiN_x)_y$ films. It was found that the average grain sizes and the in-plane coercivity ($H_{c\parallel}$) of $(FePt)_{70}$–$(SiN_x)_{30}$ film which annealed at 750 °C for 30 min are 40 nm and 8 kOe, respectively. However, there is less paper to discuss on the $SiN_x$ ceramic material inserted to the CoPt film, which has many good properties such as oxidation resistance, corrosion resistance, and wear resistance. In this work, we introduced different thicknesses of Ag under layers beneath the CoPt films to achieve a transformation of CoPt films from FCC to FCT structure and to obtain high perpendicular anisotropy of the CoPt film first. Then we added the $SiN_x$ ceramic material with different volume percents to the CoPt films and postannealing in an attempt to reduce the grain sizes of CoPt films to be smaller than 10 nm.

## 2. Experiments

First, the Ag under layers were deposited on naturally oxidized Si (1 0 0) wafer and glass substrates with different thicknesses at room temperature. Then different volume percent of $SiN_x$ ceramic material and 20 nm $Co_{50}Pt_{50}$ films were co-sputtered on the Ag films at room temperature. Finally, the films CoPt-$SiN_x$/Ag were annealed at different temperatures for 30 min. The composition and thickness of the film were determined by an energy-dispersive X-ray spectrometer and an atomic force microscope, respectively. Magnetic properties of the films were measured by using a vibrating sample magnetometer with a maximum applied field of 15 kOe and a superconducting quantum interference device. The film structure was examined by an X-ray diffractometer and a field emission gun high-resolution transmission electron microscope (FEG-TEM).

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## 3. Results and discussions

### 3.1. CoPt (20 nm)/Ag (x nm) films

According to the past researches [8,15,16], it has been reported that the Ag under layer has 5.7% misfit larger than CoPt and result in expanding the CoPt [0 1 0] and [1 0 0] axes. This in-plane expansion cause the shrinkage of the CoPt [0 0 1] axis, which is perpendicular to the film plane. It is implied that the distortion of the CoPt unit cell may enhance the CoPt $L1_0$ ordering and aiding the formation of the $L1_0$ CoPt (0 0 1) variant with the easy-axis perpendicular to the film plane. Therefore, we introduce the Ag films as the under layer first, and expect that the perpendicular anisotropy CoPt film can be obtained.

From analyzing the $I_{001}$ and $I_{111}$ ratio of CoPt/Ag films with different annealing temperatures (where $I_{001}$ and $I_{111}$ are the related integrated intensity of the (0 0 1) and (1 1 1) peaks), it is found that the maximum $I_{001}/I_{111}$ ratio occurs at about 25 nm Ag under layer when the annealing temperatures is 700 °C.

Fig. 1 shows the X-ray diffraction patterns of the CoPt/Ag (x nm) films annealed at 700 °C for 30 min. One regularity feature of Fig. 1 is the increase in the superlattice (0 0 1) intensity with the thinner Ag under layer; this indicates that the ordering process is efficiently promoted by decreasing the Ag-layer thickness. The Ag (0 0 2) orientation may suppress the Ag (1 1 1) preferred orientation and broke up the epitaxy of CoPt (0 0 1) on the Ag (1 1 1) plane. In future work, the high-resolution cross-section FEG-TEM images of the CoPt/Ag (x nm) films annealed at 700 °C for 30 min will be examined to clarify this epitaxial mechanism. We can calculate the lattice parameter of Ag under layers and CoPt films, and investigate the epitaxy between the Ag and CoPt films. Moreover, the ordering parameter (Sorder) of CoPt/Ag (x nm) films were calculated, it is found that the Sorder value of the CoPt/Ag films with different Ag thicknesses are all higher than 0.9 and indicate that the CoPt/Ag films have been ordered.

Fig. 2 is the M–H loop of the CoPt (20 nm)/Ag (25 nm) films annealed at 700 °C for 30 min. It shows that the magnetic CoPt (0 0 1) film exhibits perpendicular magnetic anisotropy with an out-of-plane squareness ($S_\perp$) and in-plane squareness ($S_\parallel$) of about 0.9 and 0.55, respectively. The saturated magnetization ($M_s$) and out-of-plane coercivity ($H_{c\perp}$) values are about 420 emu/cm$^3$ and 14 kOe, respectively. Therefore, the 25 nm Ag film is chosen to be the under layer due to the fact that it will enhance large perpendicular magnetic anisotropy of the CoPt/Ag films.

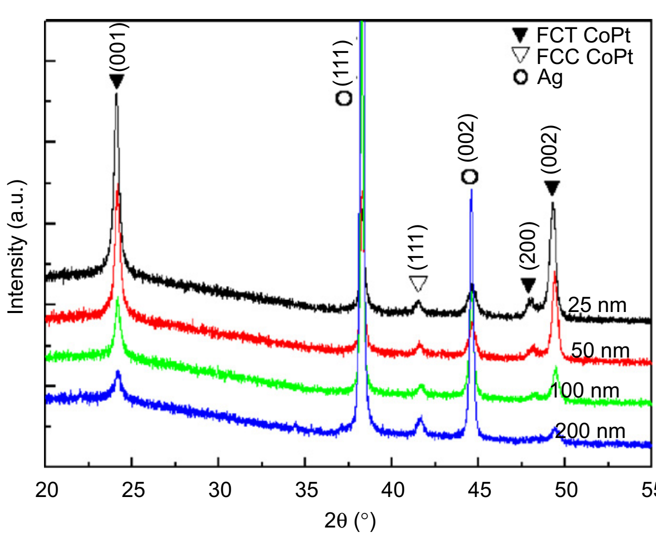


**Fig. 1.** X-ray diffraction patterns of the CoPt/Ag films annealed at 700 °C for 30 min.

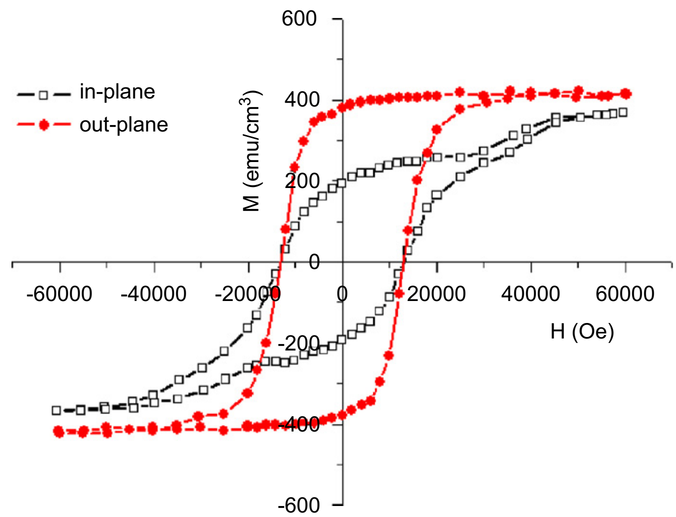


**Fig. 2.** M–H loop of the CoPt (20 nm)/Ag (25 nm) film annealed at 700 °C for 30 min.

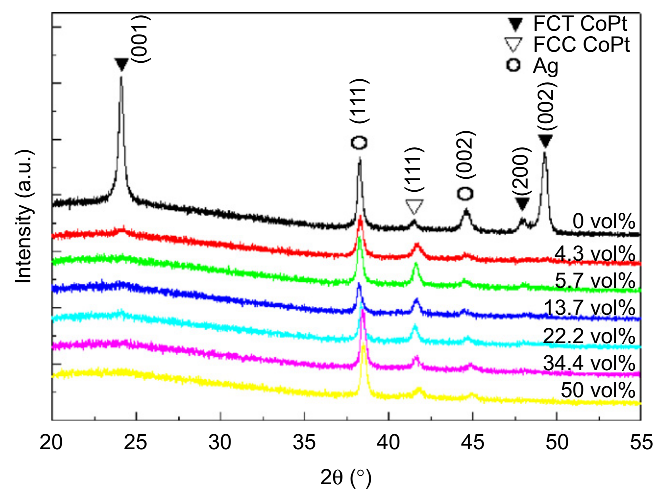


**Fig. 3.** X-ray diffraction patterns of the $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films annealed at 600 °C for 30 min.

### 3.2. $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films

There are no CoPt (0 0 1) and (0 0 2) superlattice peaks in the X-ray diffraction pattern of the as-deposited $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films. After the $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films are annealed at 600 °C for 30 min, it is found that the ordering phase of (0 0 1) superlattice peak only appears in the CoP/Ag film without adding $SiN_x$, as shown in Fig. 3. It implies that the $SiN_x$ will break up the epitaxy between CoPt (0 0 1) and Ag (1 1 1) and lower the perpendicular magnetic anisotropy of the film. After the $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films are annealed at 700 °C for 30 min, the CoPt (0 0 1) and (0 0 2) superlattice peaks of the $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films appear when the $SiN_x$ contents are low, as shown in Fig. 4. This is because partial γ-CoPt disordered phases transformed to $\gamma_1$-CoPt ordered phase at this annealing temperature. This indicated that the addition of $SiN_x$ would impede the transformation of γ-CoPt to $\gamma_1$-CoPt phase.

Fig. 5 is the effect of $SiN_x$ volume percent on the $H_c$ of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films annealed at 600 and 700 °C for 30 min. We can see that the increase of $SiN_x$ contents in the films will increase the annealing temperature required for phase

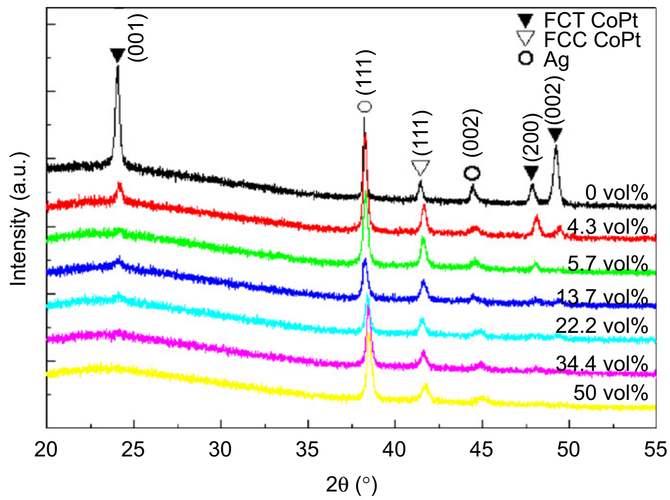


**Fig. 4.** X-ray diffraction patterns of the $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films annealed at 700 °C for 30 min.

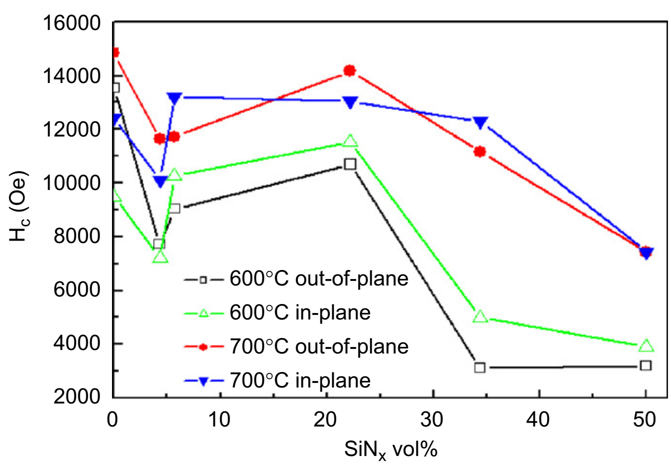


**Fig. 5.** Effect of $SiN_x$ volume percent on the $H_c$ values of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films annealed at 600 and 700 °C for 30 min.

transformation. To obtain the coercivity which is larger than 3 kOe, the pure $Co_{50}Pt_{50}$ film must be annealed at temperature which is higher than 550 °C. This means that the phase transformation temperature of pure $Co_{50}Pt_{50}$ is about 550 °C. However, it will raise the phase transformation temperature to be higher than 700 °C as the $SiN_x$ is added to the $Co_{50}Pt_{50}$ film. When the amount of the magnetic phase is fixed, not only the magnetic grain sizes but also the intergranular distances are increased with the increase in annealing temperature. Moreover, as the $SiN_x$ content is 4.3 vol%, the CoPt particles are isolated partially and the particle sizes are not uniform. It is suggested that some CoPt particles below the single domain diameter (Ds) cause a decrease of $H_{c\perp}$ and $H_{c\parallel}$ values of $(CoPt)_{95.7}$–$(SiN_x)_{4.3}$/Ag film. As the $SiN_x$ content increase from 4.3 to 22.2 vol%, the particle-size distributions of CoPt become broader. From the FEG-TEM images of $(CoPt)_{77.8}$–$(SiN_x)_{22.2}$/Ag film (not shown here), we found that partial CoPt grains are isolated. Therefore, the magnetization of $(CoPt)_{77.8}$–$(SiN_x)_{22.2}$/Ag film may be the domain rotation [17] and it will lead to higher $H_{c\perp}$ and $H_{c\parallel}$ values of $(CoPt)_{94.3}$–$(SiN_x)_{5.7}$/Ag film than those of the $(CoPt)_{95.7}$–$(SiN_x)_{4.3}$/Ag film. As the $SiN_x$ content is higher than 22.2 vol%, the $H_{c\perp}$ and $H_{c\parallel}$ of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films decrease rapidly when the $SiN_x$ content is increased. From the FEG-TEM image of the $(CoPt)_{50}$–$(SiN_x)_{50}$/Ag film, it shows that the particle-size distributions of CoPt seems more uniform than that of the

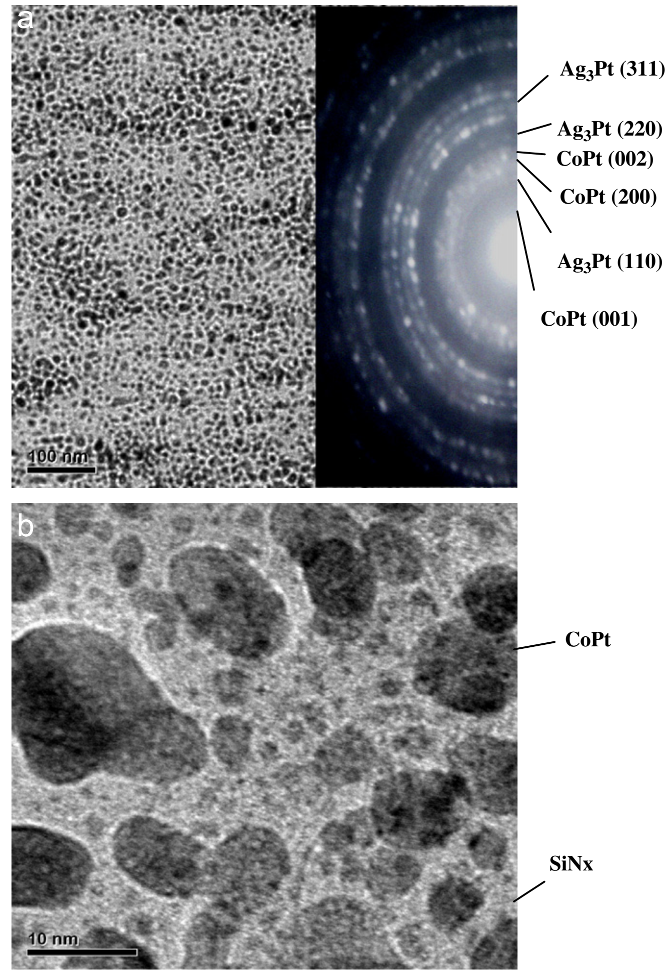


**Fig. 6.** FEG-TEM images of $(CoPt)_{50}$–$(SiN_x)_{50}$/Ag films annealed at 700 °C for 30 min. (a) Low magnification and (b) high magnification.

$(CoPt)_{77.8}$–$(SiN_x)_{22.2}$/Ag film, as shown in Fig. 6(a). From the enlargement of FEG-TEM image of the $(CoPt)_{50}$–$(SiN_x)_{50}$/Ag film (as shown in Fig. 6(b)), it is found that some particles are smaller than 8 nm (Fig. 6(b)). By calculating the $D_p$ (minimal stable particle diameter) with anisotropy energy density ($Ku = 3.6 \times 10^6$ erg/cm$^3$) and anisotropy field ($H_k = 30$ kOe) of CoPt [18], we obtained that the $D_p$ is about 8.8 nm. As the particle size is smaller than 8.8 nm, the thermal-agitation effect will cause the $H_{c\perp}$ and $H_{c\parallel}$ of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films decrease drastically.

On the other hand, as the $SiN_x$ content is higher than 22.2 vol%, the $H_{c\perp}$ and $H_{c\parallel}$ of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films which annealed at 700 °C for 30 min are higher than 7 kOe. According to Xu et al. [8], the Ag may diffuse into the CoPt films as the Ag (111) peaks shift slightly to a high angle. This phenomenon could induce vacancies, as well as increase the mobility of Co and Pt atoms. This also results in enhancing the kinetics for transformation and promoting the CoPt ordering. From the diffraction patterns of our film (see Fig. 6(a)), it can be found that the $Ag_3Pt$ diffraction rings are formed. This implies that the Ag has diffused into the CoPt films and promoted CoPt ordering.

## 4. Conclusion

We have investigated the magnetic properties of co-sputtered nano-composited $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films over the varieties of annealing temperatures and $SiN_x$ contents. On adding 25 nm Ag under layer to the CoPt (20 nm) film, a maximum perpendicular magnetic anisotropy CoPt/Ag film would be obtained. The $S_{\perp}$, $H_{c\perp}$, and $M_s$ values of the CoPt(20 nm)/Ag (25 nm) films which annealed at 700 °C are about 0.95, 15 kOe, and 420 emu/cm$^3$, respectively. Granular structure of CoPt–$SiN_x$ films with average grain size about 9 nm could be obtained by annealing the $(CoPt)_{50}$–$(SiN_x)_{50}$/Ag films at 700 °C.

However, this annealing temperature is little high, the further important research is to reduce the ordering temperature of CoPt/Ag film and $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films. Therefore, the experiments about adding the Cu into the $(CoPt)_{1-y}$–$(SiN_x)_y$ film are going on in our laboratory. We expect that the (0 0 1) texture of $(CoPt)_{1-y}$–$(SiN_x)_y$/Ag films can be maintained and the ordering temperature can be lowered. Moreover, in order to realize perpendicular films with the easy-axis of magnetization of all grains perpendicular to the film plane, the MgO (2 0 0) under-layer can be inserted to the CoPt/Ag films to enhance the CoPt fct (0 0 2) orientation.

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