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Perpendicular coercivity enhancement of CoPt/TiN films by nitrogen incorporation during deposition

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The effect of N incorporation on the structure and magnetic properties of CoPt thin films deposited on glass substrates with TiN seed layers has been investigated. During the deposition of CoPt, introducing 20% N_2 into Ar atmosphere promotes the (001) texture and enhances the perpendicular coercivity of CoPt film compared with the film deposited in pure Ar and post-annealed under the same conditions. From the *in situ* x-ray diffraction results, it is confirmed that N incorporation expands the lattice parameter of CoPt, which favors the epitaxial growth of CoPt on TiN. During the post-annealing process, N releases from CoPt film and promotes the $L1_0$ ordering transformation of CoPt. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4936365]

I. INTRODUCTION

Bit patterned magnetic recording media (BPMR), where each bit is defined by one dot in the patterned dot arrays, is considered to be a promising ultra high density recording technology for the future.[1–4] In bit patterned media, in order to maximize the signal-to-noise ratio,[5] a continuous magnetic film with perpendicular magnetic anisotropy is patterned into an ordered array to record the data.[6–9] Another effective way to further increase the signal-to-noise ratio is to increase the aspect ratio (the ratio between the height and the diameter) of each dot. Large aspect ratios can lower the demagnetization energy and keep sufficient grain volume to maintain the thermal stability.[10] In order to increase the aspect ratio, the thickness of the continuous magnetic films needs to be increased initially. However, for $L1_0$ FePt or CoPt thin films deposited on amorphous substrates with seed layers, which are the most promising materials that have a practical fabrication method for fabricating BPMR at low cost, increasing the film thickness will generate large c-axis distribution and promote the formation of in-plane variants.[11,12] For instance, in Perumal's study of FePt films deposited on oxidized Si substrates with a MgO seed layer, by increasing the thickness of FePt from 4 nm to 10 nm, magnetocrystalline anisotropy decreased from 3.9×10^7 erg/cc to 1.8×10^7 erg/cc.[11] Therefore, it is desirable to increase the thickness of the films without sacrificing the magnetocrystalline anisotropy. It has been reported that by depositing FePt films in Ar and N_2 atmosphere, $L1_0$ phase transformation was promoted and in-plane coercivity was enhanced after annealing due to the rapid release of N.[13] Another study by You *et al*. reported that by introducing N_2 during deposition, $L1_0$ ordering degree and in-plane coercivity were enhanced for only the FePt films with Fe-rich composition (i.e., $Fe_{56}Pt_{44}$).[14] Although the effect of N_2 was not clearly revealed and only in-plane coercivity was increased in both studies, they provided a possible way to promote $L1_0$ phase transformation. If the addition of N_2 during deposition can enhance the perpendicular coercivity in FePt or CoPt thin films, it will be helpful for fabricating continuous magnetic films applied in BPMR with higher magnetocrystalline anisotropy.

In this work, we investigate the structure and magnetic properties of CoPt thin films with thicknesses of 10 nm by N_2 addition during deposition. We show that $L1_0$ ordering transformation and perpendicular coercivity are enhanced with N_2 addition. The mechanism of the N_2 effect is revealed by conducting *in situ* x-ray diffraction (XRD) measurement by changing the measuring temperature.

II. EXPERIMENTAL

10 nm thick CoPt films were deposited on fused quartz substrates with 30 nm thick TiN seed layers at 400 °C by dc magnetron sputtering. The base pressure in the chamber before deposition was better than 3.75×10^{-7} Torr, and the deposition pressure was 1.5×10^{-3} Torr. $Co_{0.44}Pt_{0.56}$ (composition confirmed by inductively coupled plasma-optical emission spectrometer) film was deposited from a 2 in. composite Co-Pt target. For TiN deposition, the flow rate ratio between N_2 and (N_2 + Ar) was fixed as 10%. For the subsequent CoPt deposition, the flow rate ratio was changed by 0% and 20%, respectively. After deposition, samples were annealed at 700 °C for 1 h in vacuum (better than 1.9×10^{-6} Torr). The thickness of each layer was controlled by deposition time with a pre-calibrated deposition rate.

Magnetic properties were measured using a vibrating sample magnetometer (Riken Denshi BHV-50 V) with a maximum magnetic field of 15 kOe. To investigate the structure of the films, XRD profiles were taken using a Bruker D8 Discover diffractometer by applying Cu Kα radiation.

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Atomic force microscope (AFM) and transmission electron microscopy (TEM) were utilized to observe the surface morphology of the films. Element distribution in the depth direction was measured by time of flight secondary ion mass spectrometry (TOF-SIMS: 5-100-AD).

III. RESULTS AND DISCUSSION

Figure 1 shows the surface AFM images of the samples with different N_2 flow rate ratios during the deposition of CoPt (N_2 flow rate ratio was fixed at 10% for TiN deposition). CoPt layers exhibit continuous morphology in all samples. The films deposited with 20% N_2 show larger surface roughnesses compared to those deposited without N_2. In Fig. 1(d), after annealing at 700 °C, island-like shapes with brighter contrast appear on the surface of CoPt layer, which may be due to the surface diffusion of the CoPt layer after annealing at high temperature. However, no such phenomenon occurred in Fig. 1(b), implying that during the annealing process, N may release from the CoPt layer and promote the surface diffusion of the CoPt layer. The effect of N will be investigated later by using TOF-SIMS and in situ XRD.

To further investigate the structure of CoPt film, TEM images of the sample with 20% N_2 annealed at 700 °C were taken as shown in Fig. 2. As shown in Fig. 2(a), a sharp transition interface can be clearly identified between the CoPt and TiN layers. The thickness of the TiN layer was estimated and the CoPt layer remains continuous even after annealing at 700 °C. From the HR-TEM image in Fig. 2(b), one can see that due to the annealing effect, larger grains with in-plane grain size of ∼20 nm are formed. The FFT result (the inset of Fig. 2(b)) shows that the CoPt layer is (001) oriented in the perpendicular direction and the (001) reflection can be seen clearly, indicating the formation of $L1_0$ phase. The plan-view TEM in Fig. 2(c) shows that the CoPt layer has polycrystalline structure in the in-plane direction with no preferred orientation. Consistent with the FFT result, a (110) CoPt electron diffraction pattern can be observed in Fig. 2(d), indicating that (001) oriented $L1_0$ CoPt structure was formed after annealing at 700 °C.

The corresponding XRD profiles are shown in Fig. 3. Before annealing, the film with 20% N_2 flow rate ratio exhibits an obviously stronger CoPt (200) peak than the film with 0% N_2 flow rate ratio (Fig. 3(a)). As shown in Fig. 3(c), after

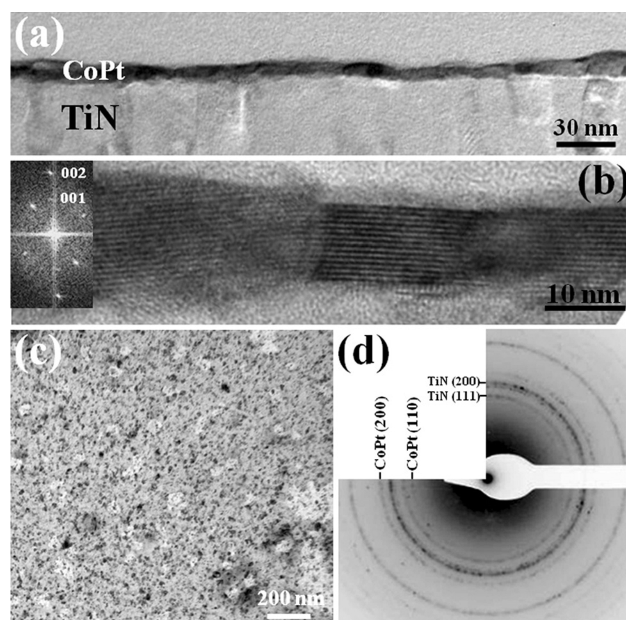

FIG. 2. TEM images of TiN/CoPt films with N_2 addition after annealing at 700 °C: (a) cross-sectional TEM image, (b) HR-TEM image, the inset is the FFT result of CoPt, (c) plan-view TEM image, and (d) electron diffraction pattern.

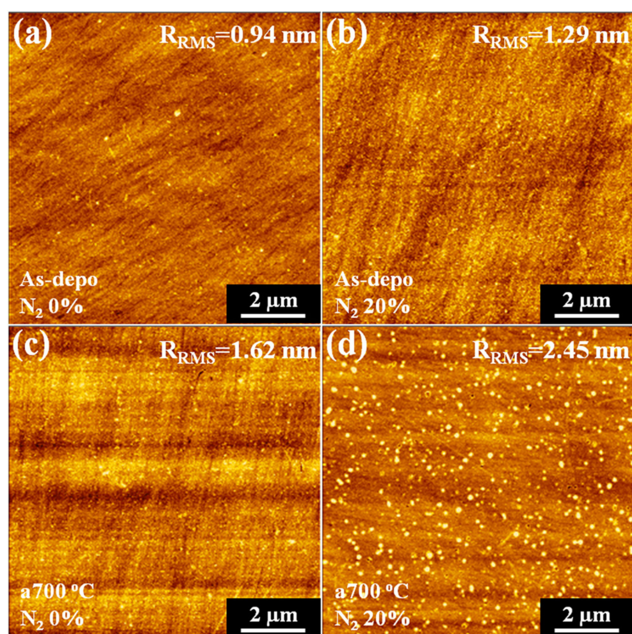

FIG. 1. AFM images of TiN(30 nm)/CoPt(10 nm) films with different N_2 flow rate ratios during the deposition of CoPt: (a) 0%, before annealing; (b) 20%, before annealing; (c) 0%, annealed at 700 °C; and (d) 20%, annealed at 700 °C.

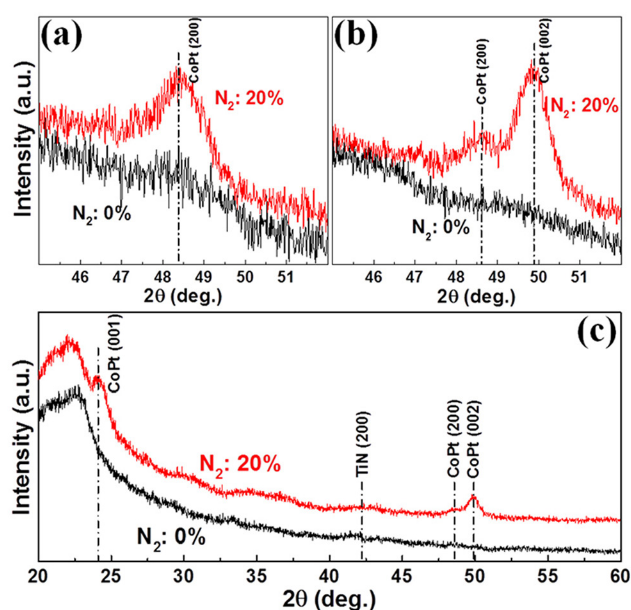

FIG. 3. XRD profiles of TiN(30 nm)/CoPt(10 nm) films with different N_2 flow rate ratios during the deposition of CoPt: (a) before annealing, (b) after annealing at 700 °C, and (c) XRD profiles with a larger range for the samples after annealing at 700 °C.

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annealing at 700 °C, the film with 20% N_2 flow rate ratio shows stronger CoPt (001) and (002) peaks compared with the film deposited with 0% N_2 flow rate ratio (comparisons of the enlarged (002) peak are shown in Fig. 3(b)). The $L1_0$ ordering parameter is calculated to be about 0.73 for the film with N_2 deposition after annealing at 700 °C.[15] While for the film deposited without N_2, no obvious (001) CoPt peak is detected after annealing, which makes it difficult to calculate the $L1_0$ ordering parameter. The above phenomenon indicates that introducing N_2 during the deposition of CoPt promotes the (100) orientation of the CoPt layer, which also promotes the $L1_0$ ordering transformation of CoPt after annealing.

Figure 4 shows the corresponding *M-H* curves of TiN(30 nm)/CoPt(10 nm) films after annealing at 700 °C. Without introducing N_2 during the deposition of CoPt, the sample shows similar magnetization behavior in the in-plane and perpendicular directions with a perpendicular coercivity of 3.7 kOe. By introducing 20% N_2, perpendicular magnetic anisotropy is obtained and the perpendicular coercivity increases to 9.5 kOe. The perpendicular coercivity enhancement with N_2 addition during the deposition of CoPt is consistent with the XRD results and further confirms that N_2 addition can promote the $L1_0$ ordering transformation of CoPt.

The above study shows that by introducing N_2 into Ar atmosphere during the deposition of CoPt, CoPt (100) preferred orientation is promoted, and after annealing, $L1_0$ ordering transformation is also promoted, leading to an enhancement of perpendicular magnetic anisotropy. However, the mechanism of the N_2 effect is still not clear. One possible mechanism is that during the annealing process, N atoms release from the CoPt layer, which promotes the diffusion mobility of Co and Pt atoms, favoring the $L1_0$ ordering transformation of CoPt. In order to understand how the N incorporation affects the structure and magnetic properties of CoPt films, we focused on N content changes in the CoPt layer before and after annealing. As shown in the elemental depth profiles in Fig. 5, before annealing, N-involving components show high intensities within the CoPt layer, as denoted by CoN^-, PtN^-, and $CoPtN^-$. However, after annealing, N-involving components drastically decreased (highlighted by red squares). Obvious changes cannot be observed for other elements before and after annealing. This phenomenon indicates that N effused out from the CoPt layer after the post-annealing process.

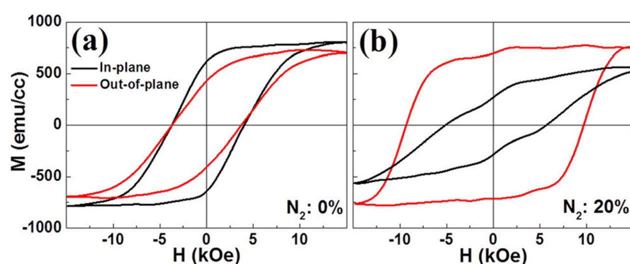

FIG. 4. *M-H* curves of TiN(30 nm)/CoPt(10 nm) films with different N_2 flow rate ratio during the deposition of CoPt: (a) 0% and (b) 20%. Both samples were annealed at 700 °C.

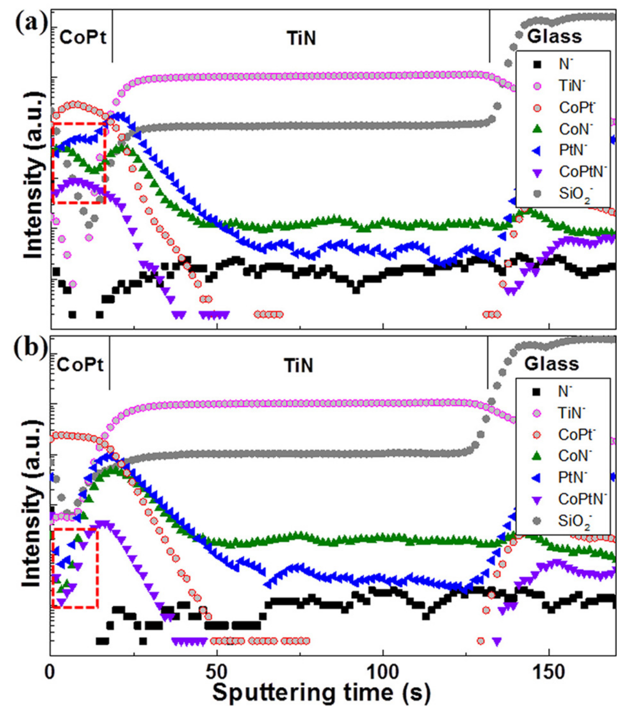

FIG. 5. TOF-SIMS depth profiles of TiN(30 nm)/CoPt(10 nm) with N_2 flow rate ratio of 20% during the deposition of CoPt: (a) before annealing and (b) after annealing at 700 °C. Red squares indicate N-involving components change before and after annealing.

As is well known, when depositing CoPt on the TiN seed layer, local epitaxial growth between CoPt and TiN occurs,[15] and with a mismatch of 10.4% between CoPt (∼0.38 nm) and TiN (∼0.424 nm), large in-plane tensile stress will be generated in the CoPt layer. It is considered that during the deposition of CoPt, the incorporated N in CoPt can increase the lattice parameter of CoPt and benefit the epitaxial growth of CoPt on TiN. On the other hand, during the annealing process, N effuses out from the CoPt layer, which can promote the diffusion mobility of Co and Pt atoms leading to the enhancement of $L1_0$ ordering transformation. To verify the above interpretation, *in situ* XRD was taken by changing the measuring temperature for the sample deposited with N_2. As shown in Fig. 6, the temperature of the sample was increased and then decreased twice to observe the CoPt (200) peak position shift. As indicated by the dashed line in Fig. 6(a), by increasing the temperature up to 500 °C, the peak shifts to a lower angle, which indicates the thermal expansion of the lattice parameter. However, above 500 °C, despite the thermal expansion, the peak begins to shift to a higher angle, indicating the shrinkage of the lattice parameter. Two possible reasons may be responsible for this phenomenon, $L1_0$ ordering transformation (lattice parameter c is smaller than a in the $L1_0$ structure) and N release. However, since the peak starts to shift to a higher angle around 500 °C, which is much lower than the $L1_0$ ordering transformation temperature (above 600 °C),[15] $L1_0$ ordering transformation can be excluded. Furthermore, by examining the measurements in the temperature decrease of the first cycle and the subsequent increase-decrease of temperatures, the peak only shifts by following the effect of the thermal expansion.

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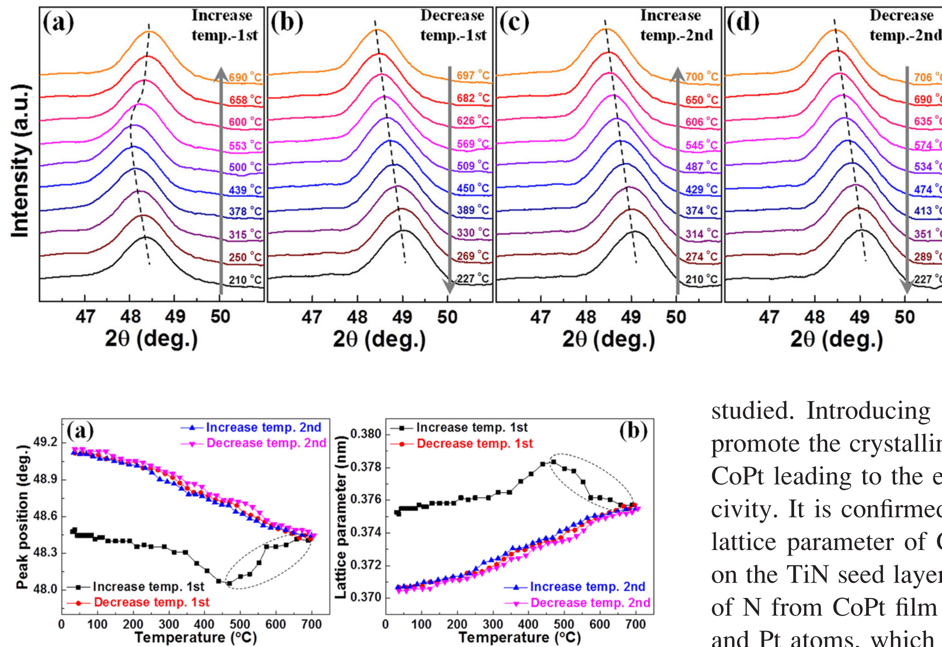

FIG. 6. *In situ* XRD profiles of TiN(30 nm)/CoPt(10 nm) with N_2 flow rate ratio of 20% during the deposition of CoPt: (a) Increasing temperature in the first cycle, (b) decreasing temperature in the first cycle, (c) increasing temperature in the second cycle, and (d) decreasing temperature in the second cycle. The peak is CoPt (200) peak, and all XRD profiles are smoothed without changing the shapes and the peak positions.

FIG. 7. (a) CoPt (200) peak position dependence on *in situ* XRD temperatures, (b) CoPt perpendicular lattice parameter dependence on *in situ* XRD temperatures. Dashed circle indicates the drastic change due to N release.

Therefore, the peak shift to a higher angle in Fig. 6(a) is caused by N release.

The dependence of the CoPt (200) peak position and calculated CoPt lattice parameter on measuring temperatures is summarized and plotted in Fig. 7. As shown in Fig. 7(a), the measurement of increasing temperature in the first cycle has a large deviation from the subsequent measurements. This indicates that N released during the temperature increase process in the first cycle and thermal expansion is responsible for the peak position changes in the subsequent measurements. As shown in Fig. 7(b), the CoPt lattice parameter increases with measuring temperature up to 470 °C due to thermal expansion. Above 470 °C, the lattice parameter drastically decreases with the further increase of the measuring temperature due to N release. By comparing the lattice parameter measured at room temperature before (~0.3753 nm) and after N release (~0.3707 nm), it is found that the CoPt lattice parameter is 1.24% larger in the as-deposited status. The above *in situ* XRD results are consistent with our interpretation. N incorporation can expand the lattice parameter of CoPt and benefit the epitaxial growth between CoPt and TiN. Through the post-annealing process, the release of N can promote the mobility of Co and Pt atoms and favor the $L1_0$ ordering transformation of CoPt.

IV. CONCLUSIONS

In conclusion, the effect of N incorporation on the structure and magnetic properties of CoPt/TiN thin films has been studied. Introducing N_2 during the deposition of CoPt can promote the crystallinity and $L1_0$ ordering transformation of CoPt leading to the enhancement of the perpendicular coercivity. It is confirmed that N incorporation can increase the lattice parameter of CoPt, and promote its epitaxial growth on the TiN seed layer. During the annealing process, release of N from CoPt film promotes the diffusion mobility of Co and Pt atoms, which enhances the $L1_0$ ordering transformation of CoPt.

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