Transactions of the Materials Research Society of Japan 29[4] 1565-1568 (2004)

Effect of Hydrogen on the Preparation of Fe/Pt Multilayer

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Effect of atmosphere during annealing of Fe/Pt bilayers was investigated. Coercivity of Fe/Pt bilayers annealed in hydrogen and vacuum atmosphere increased to several kOe at annealing temperature above 400℃. However, specimens annealed in nitrogen and argon atmosphere didn't reveal Fe-Pt ordered phase. X-ray photoelectron spectroscopy study clarified that the oxygen incorporated with Fe forms Fe_2O_3 during the annealing in nitrogen or argon atmosphere. Fe-O stable bonds in Fe_2O_3 made inter-diffusion between Fe and Pt layer difficult. Suppression of inter-diffusion caused degeneration of ordered Fe-Pt alloy. Annealing in hydrogen atmosphere was effective to remove the oxygen during the annealing. Furthermore samples annealed in high pressure hydrogen atmosphere showed higher in-plane coercivity than that of one annealed in low pressure. Also, high pressure annealing lowered order/disorder transformation temperature from 400℃ to 350℃.

Key words: Fe-Pt films, hydrogen, Fe/Pt double layer, interdiffusion, Fe_2O_3, ordered alloy

1. INTRODUCTION

Fe-Pt ordered alloy is an attractive material because of its high crystalline anisotropy K_u of 7.0×10^7 erg/cc[1]. Its K_u corresponds to thirty or forty times of that of conventional recording layers, such as CoCr based films. So that, the much attention has been paid to Fe-Pt ordered alloy for the application of the high density magnetic recording media. However ordering temperature of Fe-Pt single layer was around 600℃. Such a high temperature may cause the degradation of the media originated from expansion of grain size, inter-diffusion between recording layer and underlayer and restriction of substrates. Recently, several studies have been done in order to lower the order/disorder transformation temperature. For example, multilayering[2,3], ion irradiation[4], introduction of underlayers or interlayers[5,6], the addition of third elements[7,8], mono atomic layer control[9] and so on. In this study, much attention for atmosphere during film deposition and annealing processes have been paid to improve the ordering mechanism since the oxygen included in ambient background might contaminate the Fe-Pt thin films during the processes. It was found that the annealing in hydrogen atmosphere was so effective to obtain Fe-Pt ordered phase at lower annealing temperature. Deoxidation ability and the effect to enhance diffusion process in materials based on its smallness and lightness of hydrogen seemed play an important role[10,11] to obtain Fe-Pt ordered phase. In this study, annealing of Fe/Pt bilayers in hydrogen atmosphere were performed to confirm the effect of hydrogen during the annealing process. Annealing in hydrogen at high gas pressure was also attempted to reduce the ordering temperature of Fe/Pt thin films.

2. EXPERIMENTAL

Facing targets sputtering method was used to prepare Fe/Pt bilayers. Pt bottom layer and Fe top layer with their thicknesses of 8.5nm and 6.5nm, respectively, were deposited on crystallized glass substrates at room temperature. Sputtering Ar gas pressure was set at 2mTorr. The vacuum pumps of sputtering apparatus were a turbo molecular pump and a rotary pump. After the deposition, films were annealed for 30 minutes in a furnace at the different atmosphere conditions, such as hydrogen (1atm), vacuum (8.0×10^{-6}Torr), nitrogen (1atm) and argon (1atm) atmosphere. The vacuum pumps of furnace were a diffusion pump and a rotary pump.

Table 1 summarizes the preparation condition of the specimens. Crystallographic characteristics were measured by XRD (X-ray diffraction). Atomic composition and chemical shift of Fe and Pt atoms were evaluated by XPS (X-ray photoelectron spectroscopy). Magnetic properties were measured by VSM (vibrating sample magnetometer) at maximum applied field of 20 kOe.

Table. I Preparation condition of specimens.

Sputtering condition	
Background	2.0×10^{-6} Torr
Temperature	Room temperature
power	30～40W
Sputtering gas	Ar(2mTorr)
Substrate	Crystallized glass
Annealing condition	
Annealing atmosphere	1. Vacuum (8.0×10^{-6} Torr) 2. Hydrogen (1 atm) 3. Nitrogen (1 atm) 4. Argon (1 atm)
Temperature	200～600℃
Time	30min

3. RESULTS AND DISCUSION

3.1 Annealing in various atmospheres

Figure 1 shows the change of in-plane coercivity H_c of Fe/Pt bilayers as a function of annealing temperature T_A for various annealing atmosphere conditions. H_c of Fe/Pt bilayer annealed at 400℃ in hydrogen atmosphere increased drastically from 0.4 kOe to 5.0 kOe. Similarly, H_c of Fe/Pt bilayer annealed in vacuum increased to 2.4 kOe at T_A above 400℃. On the other hand, specimens annealed in nitrogen or argon atmosphere didn't show the increase of H_c even though the higher T_A conditions. XRD diagrams of the Fe/Pt bilayers didn't show Fe-Pt ordered phase when they were annealed in nitrogen or argon atmosphere. It seemed that the oxygen reduction conditions caused by the hydrogen atmosphere or vacuum atmosphere played an important role to improve the ordering phase transition.

Figure 2 shows the depth profiles of the atomic composition of the Fe/Pt bilayers annealed in various atmospheres observed by the XPS measurement. Each composition was calculated by integrating photoelectric peak and it was compensated with each sensitivity factor. (a) shows the depth profile of as-deposited Fe/Pt bilayer. Although a gradual change of compositions at the Fe/Pt interface might be observed, such signal change would be caused by the streaky sputter-etching rate or surface roughness during the XPS measurement. Actual interface between Fe layer and Pt layer is expected to be very steep. Depth profiles of compositions of the specimens annealed in hydrogen or vacuum atmosphere are shown in (b) and (c), respectively. Both graphs have uniform compositional gradient caused by the inter-diffusion. On the other hand, the composition profile of the specimens annealed in nitrogen (d) and argon (e) atmosphere was similar to the composition profile of (a) as-deposited one. It was also found that the oxygen was incorporated in the bilayers of (d) and (e). The oxygen seemed to locate in the Fe layers. These results indicate that inter-diffusion between Fe and Pt layers didn't occur in case oxygen was included in the bilayered films.

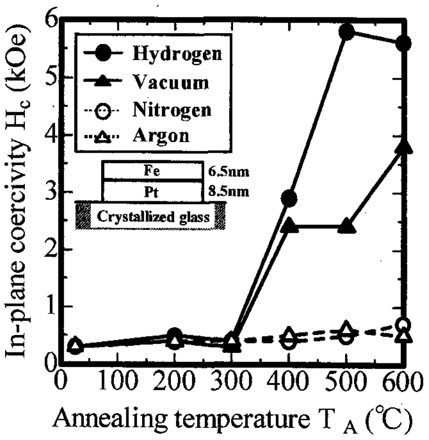
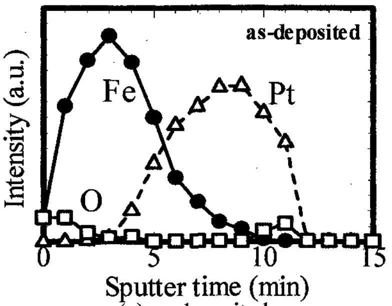
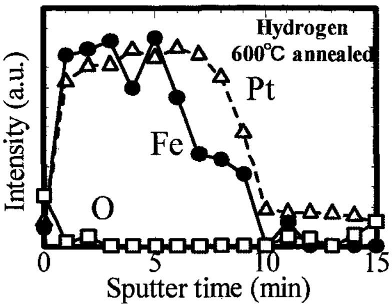


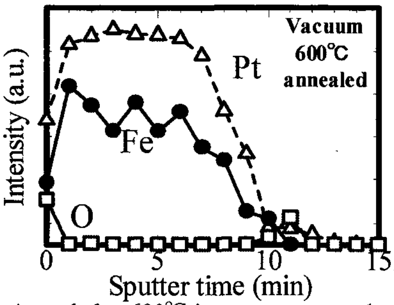
Fig.1 Annealing temperature T_A dependence of in-plane coercivity H_c in various atmospheres.



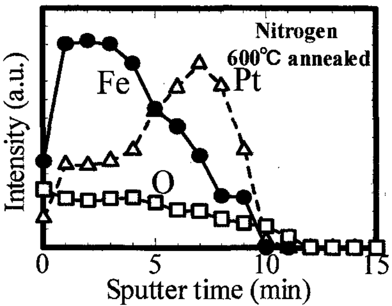
(a) as-deposited



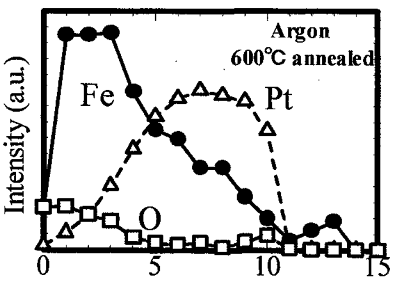
(b) Annealed at 600℃ in hydrogen atmosphere.



(c) Annealed at 600℃ in vacuum atmosphere.



(d) Annealed at 600℃ in nitrogen atmosphere.



(e)Annealed at 600℃ in argon atmosphere.

Fig.2 Depth profiles of compositions in Fe/Pt films annealed in various atmosphere.

In order to survey the bonding state of atoms more precisely, chemical shift of Fe atoms was investigated. Figure 3 shows the depth profile of chemical shift of Fe atoms for Fe region in Fe/Pt bilayers annealed in various atmosphere conditions. Fe in as-deposited sample showed energy level of pure Fe except the surface region of the film. Specimens annealed in hydrogen and vacuum atmosphere showed energy level of Fe-Pt bond. But for nitrogen and argon atmosphere, chemical shift of Fe atoms were observed which indicates the energy level of Fe_2O_3. It is considered that the formation of Fe_2O_3 suppress an inter-diffusion between Fe and Pt layer because of the stable bonding of Fe and O. So that, the formation of Fe-Pt ordered alloy was suppressed in the specimens annealed in the argon and nitrogen. Although depth profiles of the films annealed in hydrogen and vacuum atmosphere had little difference in terms of atomic compositions and chemical bonding state, photoelectric peak profiles corresponding to oxygen was slightly different. Figure 4 shows the photoelectric peak profiles of oxygen of the specimen annealed in hydrogen and vacuum. It was found that the film annealed in vacuum revealed oxygen peak, which indicates the existence of small amount of oxygen in the film. The film annealed in the hydrogen did not exhibited oxygen peak. Such a small amount of oxygen included in films influenced badly to the magnetic properties of the films, and it seemed to cause the difference of in-plane coercivity between the film annealed in hydrogen (5.0 kOe) and one annealed in vacuum (2.4 kOe).

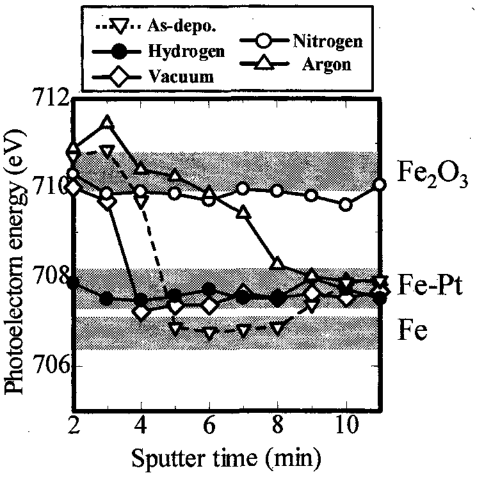


Fig.3 Chemical shift of Fe atoms after annealing in various atmospheres.

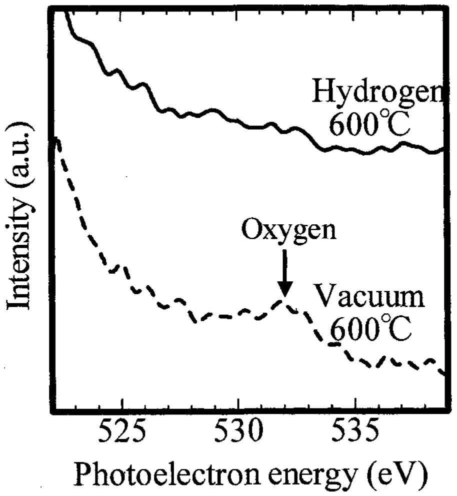


Fig. 4 Photoelectric peak of oxygen.

3.2 Effect of hydrogen in annealing process

Table. Ⅱ shows the in-plane coercivity H_c of the Fe/Pt bilayered films annealed in (a) pure nitrogen (N_2:100%), (b) a mixture gas of nitrogen(70%) and hydrogen (30%) atmosphere (H_2:30%, N_2:70%) and (c) pure hydrogen (H_2:100%). Although the film annealed in pure N_2 atmosphere didn't exhibited high H_c because of the incorporation of oxygen in the film, small amount of an adition of hydrogen (30%) into annealing atmosphere played an important role to attain high H_c of about 3.7 kOe. Incorporation of oxygen might be occurred during sputtering or annealing provided from background, flowing gas, or absorbed O_2 and/or H_2O on the film surface when films were exposed in ambient atmosphere. Such oxygen seems to diffuse into the films and make Fe_2O_3 which interrupts inter-diffusion between Fe and Pt layer. Since annealing in hydrogen atmosphere can remove the oxygen effectively, annealing in hydrogen atmosphere is very effective method to generate Fe-Pt ordered alloy thin films.

In order to observe crystallographic transition in the films by annealing process in hydrogen, slightly thick films were prepared. Figure 5 shows the annealing temperature dependence of in-plane coercivity H_c of the specimens with slightly thick layer thickness of 14 nm

Table. Ⅱ Increase of coercivity by annealing in nitrogen mixed with hydrogen atmosphere.

Annealing atmosphere	N_2 : 100 %	H_2 : 30 % N_2 : 70 %	H_2 : 100 %
In-plane coercivity H_c (Oe)	500	3700	5000

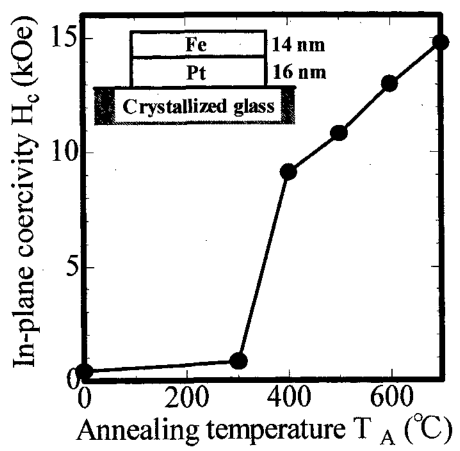


Fig.5 Annealing temperature dependence of in-plane coercivity of the specimens that had thick of 30nm in hydrogen atmosphere.

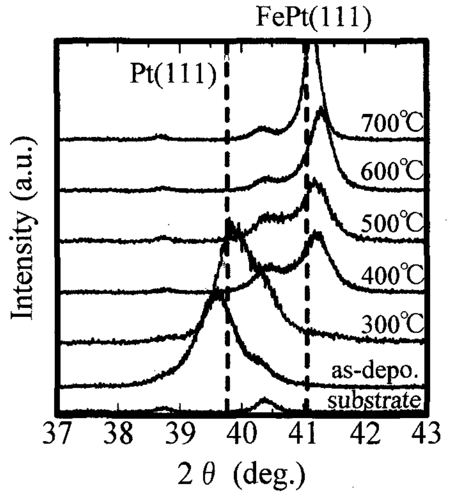


Fig. 6 X-ray diffraction diagrams of specimens annealed on various temperature in hydrogen atmosphere.

for Fe layer and 16nm for Pt layer. Intensive increase of in-plane coercivity was also observed at 400℃ as shown in Fig. 5. X-ray diffraction diagrams of the slightly thick films were also shown in Fig. 6. Although Pt(111) peak was only observed in Fe/Pt bilayers annealed below 300℃, Fe-Pt(111) peak appeared in the films annealed at above 400℃. Increase of coercivity and appearance of Fe-Pt(111) peak observed at the same temperature insist on that Fe-Pt ordered phase was directly formed without transformation through the disordered phase at the Fe/Pt interface.

3.3 Annealing in high-pressure hydrogen atmosphere

It is expected that the formation of Fe-Pt ordered phase is promoted as a result of inter-diffusion. Annealing in high-pressure hydrogen atmosphere is one of the methods to promote the inter-diffusion of a matrix material by acceleration of drift mobility of atoms caused by increasing frequency of confliction[12,13].

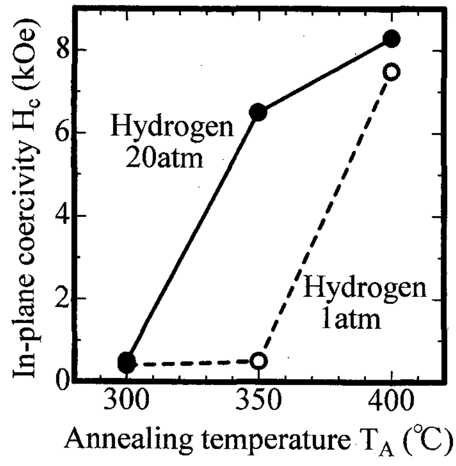


Fig. 7 Change of coercivity as a function of annealing temperature for films in different pressure of hydrogen atmosphere.

Figure 7 shows annealing temperature dependence of in-plane coercivity of the [Fe(1.0nm)/Pt(1.0nm)]$_{10}$ multilayered film annealed in 1 atm and 20 atm of hydrogen atmosphere. Although the multilayer annealed at 350℃ in 1 atm exhibited low coercivity revealing inexistence of ordered phase, the film annealed at 350℃ in 20 atm of hydrogen atmosphere revealed large coercivity of above 6 kOe. Order/disorder transformation temperature was lowered from 400℃ to 350℃ in case using high pressure hydrogen atmosphere. More increase of coercivity and lowering of order/disorder transformation temperature were expected by annealing in higher pressure hydrogen atmosphere.

4. CONCLUSION

Fe/Pt bilayers annealed in nitrogen or argon atmosphere didn't show increase of coercivity. The formation of Fe_2O_3 caused by contaminated oxygen seems to interrupt an inter-diffusion between Fe and Pt resulting the suppression of formation of Fe-Pt ordered phase. Annealing in hydrogen atmosphere was found to be very effective to obtain ordered Fe-Pt alloy alloy phase at relatively low annealing temperature around 400℃. Annealing in high-pressure hydrogen atmosphere was also effective to lower the order/disorder transformation temperature from 400℃ to 350℃. [Fe(1.0nm)/Pt(1.0nm)]$_{10}$ multilayers annealed at 350℃ in 20 atm hydrogen atmosphere revealed in-plane coercivity of 6.5 kOe.

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(Received October 8, 2003; Accepted January 28, 2004)